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PROJECT SQUID

SEMI-ANNUAL PROGRESS REPORT

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SEMI-ANNUAL PROGRESS REPORT

PROJECT SQUID

A COOPERATIVE PROGRAM
OF FUNDAMENTAL RESEARCH
AS RELATED TO JET PROPULSION
FOR THE
OFFICE OF NAVAL RESEARCH, DEPARTMENT OF THE NAVY



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Semi-Annual Progress Report

April 1, 1958

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Cornell

Fluid Mechanics

FUNDAMENTAL INVESTIGATION OF NONSTEADY FLOW

Cornell Aeronautical Laboratory, Inc. - Phase 1

G. Rudinger, Phase Leader
L. M. Somers

Introduction

This study is concerned with the extension of theoretical and experimental methods for the analysis of nonsteady-flow problems. Theoretical investigations of such problems are frequently carried out by means of wave diagrams based on the method of characteristics, and experimental work is based on shock tube techniques. Various cases of boundary conditions in nonsteady flow have been studied. The effect of pressure waves on small regions where the density differs from that in the surrounding gas is also being investigated.

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Discussion

Boundary Conditions in Nonsteady Flow. Problems of nonsteady flow in a duct are usually attacked by means of the method of characteristics. The construction of the resulting wave diagrams (1) requires a knowledge of the conditions that govern the reflection of pressure waves from various flow boundaries. The steady-flow boundary conditions, after being disturbed by an incident pressure wave, require a finite time to readjust themselves to their new steady-flow level and since this adjustment process is continually modified by further incident waves, the instantaneous boundary conditions become also a function of the flow history. The customary technique to avoid this difficulty is to neglect the effects of the finite adjustment time and to apply the steady-flow boundary conditions. Improved boundary conditions are now sought that should enable one to determine the errors introduced by the conventional procedure and that may be used when a high accuracy is required in a wave diagram.

The investigation of the boundary conditions for open ends was started with an analysis of the reflection of shock waves (2). The results of this investigation was later extended to incident waves of arbitrary wave form, and a paper on this study was published (3).

Another study dealt with the reflection of shock waves from orifice plates. The technical work on this problem was completed during the previous reporting period (4). A paper on this material was presented at a meeting of the American Physical Society and is also awaiting publication (5).

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An attempt is being made to extract effective boundary conditions for shock reflection at a flame front from experimental observations such as those previously obtained under Phase II of this contract (6). Only some preliminary work has been done so far on this problem. A review of the present knowledge on shock wave and flame front interactions was prepared for presentation at the Third Colloquium of the AGARD Combustion and Propulsion Panel. Although this paper was not prepared as part of Project SQUID, it is based to a large extent on work carried out under this contract and has, therefore, been given advance distribution under this project (7).

Effect of Pressure Waves on the Motion of Small Regions of Different Gas Density. It had previously been reported (4) that small gas "bubbles" the density of which is different from that of the surrounding gas do not follow an accelerated motion of the latter, such as that produced by pressure waves. The described effect can be qualitatively explained by the buoyancy of the "bubble" in the gravitational field that produces the same acceleration as the pressure waves. A relation for the ratio of the velocity of the bubble and that of the surrounding gas was derived which involved the density ratio as the main parameter. When the data for helium and sulphurhexafluoride "bubbles" in air were substituted, the results differed from the previously obtained experimental values by a factor of about 2. The reason for this discrepancy seems to be that the derived formula strictly applies only to solid particles. The energy acquired by the particle differs from that required for it to stay at rest with respect to the surrounding gas. This energy difference can then only appear as kinetic energy of the relative

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motion. In the case of a gas bubble, only part of the energy goes into the translational motion while the rest is used up in the generation of vorticity. To obtain agreement with the experimental observation, one would have to assume that about one-quarter of the energy goes into translation and three-quarters into vorticity generation. An attempt will be made to find a theoretical reasoning to derive this energy ratio independently.

A paper on the experimental part of this study was presented at a meeting of the Fluid Dynamics Division of the American Physical Society (8) and the material will be written up for publication.

Notes and References

1. G. Rudinger, Wave Diagrams for Nonsteady Flow in Ducts. D. Van Nostrand Company, Inc., Princeton, 1955
2. G. Rudinger, On the Reflection of Shock Waves from an Open End of a Duct. Journal of Applied Physics, 26, 981-993 (1955)
3. G. Rudinger, The Reflection of Pressure Waves of Finite Amplitude from an Open End of a Duct. Journal of Fluid Mechanics 3,48-66 (1957)
4. Project SQUID, Semi-Annual Progress Report. 1 October 1957, pp. 1-6
5. G. Rudinger, The Reflection of Shock Waves from an Orifice at the End of a Duct. Paper presented at the New York City meeting of the American Physical Society, January 29-February 1, 1958. (Submitted to Zeitschrift für angewandte Mathematik and Physik for publication)

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6. G. Markstein, A Shock Tube Study of Flame Front-Pressure Wave Interaction. Sixth Symposium (International) on Combustion, Reinhold, New York, 1957, pp.387-398
7. G. Rudinger, Shock Wave and Flame Interactions. Paper prepared for presentation at the Third AGARD Combustion and Propulsion Panel Colloquium, Palermo, Sicily, March 17-21, 1958. (Proceedings of the meeting to be published) Preliminary issue on microcard as Project SQUID Report No. CAL-74-P, December 1957, ASTIA AD-147699
8. G. Rudinger, The Effect of Pressure Waves in a Gas on the Motion of Small Regions of Different Density. Paper presented at the meeting of the Fluid Dynamics Division of the American Physical Society, Bethlehem, Pa., November 1957

Johns Hopkins

Fluid Mechanics

INVESTIGATION OF TURBULENCE

The Johns Hopkins University - Phase I

Leslie S. G. Kovaszny

Introduction

The research program of the Department of Aeronautics reported here is jointly sponsored by Project SQUID Nonr 1858(25) and by the Navy Bureau of Ordnance under contract Nord 15872.

During the period several problems were investigated.

Discussion

(a) Transistorized hot-wire anemometer. The major result obtained in the report period is the successful development of a simple rugged transistorized hot-wire anemometer.

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The hot-wire anemometer in general is a rather delicate and expensive complex of instruments so that the use of more than a few channels appears to be prohibitive. As soon as transistors of reasonable reliability became available, it occurred to us that their use for hot-wire anemometers may radically change this outlook.

The hot-wire anemometer is a low impedance (5 - 50 ohms), low voltage (.5 - 1.5 volt) device requiring relatively high currents (20 - 100 mA). Constant temperature operation attained with negative feedback has its attractions but it is rather involved when high impedance vacuum tubes are used as active elements. Impedance matching with transformers have their own difficulties, consequently the constant temperature (feedback) system in most cases did not compete with the constant current system employing electronic compensation of thermal lag.

We found that the transistors being low impedance devices are naturally matched to the hot-wires and we succeeded in developing a constant temperature negative feedback hot-wire set that fits into a 2 1/2" x 1 1/2" x 1" box containing seven transistors, two wire-wound potentiometers and about eleven fixed carbon resistors. Twelve volt d.c. power is required. The performance of the instrument is as follows: Using a .0001" Platinum wire we obtained a frequency response corresponding to a damped RCL resonance circuit with a resonance frequency of 17 kC, the damping can be varied but critical damping was found to be the most convenient. Square wave rise time was found, 30 - 37 microseconds. Feedback ratio (suppression of temperature fluctuations) is 200 - 300. Noise level is equivalent to a

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turbulence level of .01 - .02%. The output of such a system is a signal of the order of 1 - 3 volts at a very low impedance (about 50 ohms). By the use of two cascaded squaring circuits it is possible to attain a strictly linear velocity-voltage-output relationship. We are continuing to work on a transistorized linearizing circuit that would permit the use of hot-wire equipment as a linear velocity pick-up. Even before attaining that goal we have used the two units with commercially available squaring circuits and attained full linearity by direct calibrations.

(b) Orifice hot-wire pressure probe. During the period covered only little progress was made because the research worker (graduate student) was on leave of absence to complete certain academic requirements. The device has been in a sufficiently advanced stage so experimental work will be resumed about April 1.

(c) Spinning wake. An experiment was attempted to produce an axisymmetrical wake with a superimposed swirl in a supersonic flow. The chief interest is the exploration of temperature effects. A cruciform wing model with a cylindrical central body was fabricated and mounted in the Department of Aeronautics supersonic wind tunnel. The angle of attack of the four wings was controlled by hydraulic means. The preliminary tests at a Mach number 1.75 and atmospheric stagnation conditions have indicated that aeroelastic flutter occurred and after only a minute run the structure was permanently strained. The entire approach to the problem might need revision.

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(d) Laminar to turbulent transition. A new experimental program is planned to investigate the transition from laminar flow to turbulent flow. The specially interesting phase is the breaking down of regular periodic instability waves into "turbulent spots". Preliminary reports from other laboratories (principally, National Bureau of Standards) indicate that these are essentially three-dimensional phenomena. Our new approach involves the use of a larger number of hot-wire probes (up to 15 - 20) that was previously prohibitive but became possible with the development of the new simple transistorized hot-wire channels. A simultaneous record of the velocity (on a linear scale!) give us a strong hope to reconstruct the model of turbulent spot generation.

(e) Publications during the period. Reporting results obtained under present contract.

- (1) Betchov, R.: On the Fine Structure of Turbulent Flows, Journal of Fluid Mechanics, Vol. 3, Part 2, p. 205, Nov. 1957.
- (2) Kovaszny, Leslie S. G. & Arman, Ali: Optical Autocorrelation of Two-Dimensional Random Patterns, Rev. Sci. Instr., Vol. 28, No. 10, p. 793, October 1957.
- (3) Chu, B. T. & Kovaszny, Leslie S. G.: Nonlinear Interaction in a Viscous Heat-Conducting Compressible Gas, Jour. of Fluid Mechanics, Vol. 3, Part 5, p. 494, February 1958.

Michigan

Fluid Mechanics

STRUCTURE OF A DETONATION WAVE

University of Michigan - Phase II

T. C. Adamson - Phase Leader
R. Gealer, R. Ong, D. WilcoxIntroduction

This phase of Project Squid is divided into three tasks.

- a) Structure of a Detonation Wave
- b) Gaseous Detonations at High Pressure
- c) Interaction of Discontinuities

The first subject is a theoretical investigation, while the last two cover both theoretical and experimental work.

Discussion

The purpose of this investigation is to use techniques evolved in the study of deflagration waves in the study of detonation waves in an attempt to

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relate the dynamic parameters to the chemical parameters. The wave is assumed to be a shock followed by combustion and attention is focused on the combustion process.

The simple system described in the previous progress report (April, 1957) is still being considered. The temperature and velocity have been expanded around their values at the hot boundary, in terms of the concentration of the combustible. Second order expansions must be used since the temperature, for example, goes through a maximum if the final Mach number is greater than a critical Mach number, defined in terms of the ratio of specific heats, the molecular weight change, and the heat added. The expansions indicate that a singularity exists in the limiting Chapman-Jouguet case, so that the results would be inconclusive in this case. For this reason, expansions of the necessary variables around the point of maximum temperature rather than the point of final temperature, are being considered. These functions can be found, but they add considerable complexity to the integral involved in the final solution. Hence, a careful order of magnitude analysis of the terms in the integrand is being made so that unnecessary terms may be eliminated. A memorandum covering the work done has been written and will be available soon.

Gaseous Detonations at High Pressure

This phase has been finished, and a report has been written. This work is being submitted as a thesis for the Ph. D. by Mr. Gealer, and will be available in report form after its publication as a thesis. The results show good agreement between calculated and measured detonation wave velocities in hydrogen-oxygen mixtures in a range of initial pressures from 14.4 Psi to 1000 Psi, and initial hydrogen concentrations of 40% to 80% by volume. Cal-

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culated wave velocities were found by assuming chemical equilibrium to exist behind the wave. Since gas properties at the higher pressures were not known accurately, an analysis of possible errors in wave velocity due to given errors in these properties was made. This analysis indicated that to first order, no appreciable errors were introduced by the assumed properties.

Interaction of Discontinuities

This phase has been completed and a report is being written. The experimental work on a shock - contact discontinuity interaction has been completed and shows fair agreement with theoretically predicted results.

Princeton

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EXHAUST NOZZLE IMPEDANCE TO HIGH-FREQUENCY
LONGITUDINAL GAS FLOW OSCILLATIONS

Princeton University - Phase 9

L. Crocco, Phase Leader
J. Grey, R. Monti

Introduction

This investigation was initiated in order to study the effects of sustained longitudinal oscillations on the boundary condition represented by the exhaust nozzle of a combustion chamber. The primary purpose of the study was to correlate existing theories (1, 2, 3) with experimental measurements of the important nozzle flow parameters in the absence of combustion. The significant parameter which best describes the nozzle boundary condition has been called the nozzle admittance (reciprocal impedance), defined in (2) as the ratio of instantaneous fractional oscillations of gas velocity and density at the nozzle entrance.

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As described in the previous report, non-availability of satisfactory hot-wire equipment for instantaneous velocity measurements necessitated an indirect evaluation procedure. The results of these indirect experiments were highly satisfactory, indicating excellent correlation with theoretical predictions on a number of different nozzles for all system variables tested. The only significant departure from theory was caused by viscous and inertial damping, not considered in the analytical treatment, which produced experimental amplitudes several times smaller than predicted.

Discussion

Having completed an indirect evaluation of the analytical method, efforts to provide the direct velocity-density measurement required for nozzle admittance were continued. Some time was spent in moving the apparatus to a safer and more advantageous location in a protected test area, and a commercially available constant-current hot-wire amplifier and probes were purchased from the Flow Corporation.

Initial testing to determine the required probe configuration with respect to sensitivity, strength, and frequency response was completed. It was found on these tests that the turbulence level in the duct was excessive, and its amplification (proportional to frequency for the constant-current amplifier) was greater than that of the signal level. Application of electronic filtering was only partly successful, and consequently a

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combination of turbulence-elimination techniques, including duct polishing, turbulence screens, bell-mouthed inlets, and stagnation-tank packing are now being evaluated.

Data on several linear nozzles with different entrance Mach numbers, admittance ratios, and area ratios, as well as at least one conical nozzle and several orifice configurations, will be collected upon achievement of satisfactory turbulence-level characteristics. The effect of viscous damping is also being introduced into the theoretical analysis in order to provide better correlation with the experimental results.

References

1. Tsien, H. S., "The Transfer Functions of Rocket Nozzles," Journal of the American Rocket Society 22, 1952, p. 139.
2. Crocco, L., "Supercritical Gaseous Discharge with High Frequency Oscillations," Aerotecnica 33, 1953, p. 46.
3. Crocco, L., and Cheng, S. I., "Theory of Combustion Instability in Liquid Propellant Rocket Motors," AGARDograph No. 8, Butterworths Publications Ltd., London, 1956, Appendix B.

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Transport and Transfer Processes

THERMAL CONDUCTIVITY AND THE VISCOSITY
OF AMMONIA AND HYDRAZINE

California Institute of Technology - Phase 2

B. H. Sage, Phase Leader

Introduction

Experimental measurements of the viscosity of ammonia in the gas and liquid phases are under way. Measurements have been obtained for the gas phase at pressures from atmospheric to vapor pressure and at temperatures between 100° and 250° F. Work is in progress at the present time to determine the viscosity of the gas phase at higher temperatures. The measurements are being made with a rotating-cylinder viscometer made available to this project by the California Institute of Technology.

As a preliminary study, the viscosity of n-pentane in the liquid phase was determined at pressures up to 5000 pounds per square inch and at temperatures between 100° and 340° F. No difficulty was experienced in carrying out these investigations and evaluation of the results indicates

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that the data are in good agreement with earlier measurements upon the viscosity of n-pentane.

Revision of the thermal conductivity equipment, in order to eliminate direct contact of the thermocouples with the fluid under investigation, is under way, and it is expected that the revised equipment will be in operation by May 1958.

A manuscript describing results obtained during Phase I of this program upon the thermal conductivity of nitrogen dioxide has been published (1). A second manuscript describing the thermal conductivity of nitric oxide has been submitted to the editor of Industrial and Engineering Chemistry as a contribution to the Data Series of that journal. From the favorable comments of the reviewers, it is expected that the paper will be accepted. A third manuscript which describes the results obtained upon the thermal conductivity of nitrous oxide has been prepared and is being transmitted to Project SQUID for publication as a report of a portion of the activities of this project in the field of thermal conductivity.

Discussion

In connection with the evaluation of the thermal conductivity of the oxides of nitrogen, difficulty has been experienced for several years from the use of thermocouples in direct contact with the fluid undergoing measurement. For this reason, it was decided to revise the equipment, and plans were made to accomplish the revision in the early fall of 1957.

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However, during the move of the Chemical Engineering Laboratory to permanent quarters in the Eudora H. Spalding Engineering Laboratory, a large lathe provided with special attachments for the machining of spherical parts was severely damaged, and a delay of approximately three months in the revision of the thermal conductivity equipment resulted. Therefore primary emphasis during the past semiannual period has been upon viscosity measurements.

The rotating-cylinder viscometer has been found to be a very satisfactory instrument for the determination of the viscosity of fluids at elevated pressures. From the dimensions of the instrument and the elastic properties of the suspension for the stator, it was possible to determine upon an absolute basis the viscosity of air and of n-pentane with a maximum deviation from established values of 0.4 per cent. Since the total clearance between the rotor and stator is approximately 0.020 inches, this deviation involved an absolute uncertainty in the clearance of less than 0.0001 inch. The rotating-cylinder viscometer is a much more satisfactory instrument than the rolling-ball viscometer which has been employed heretofore in this laboratory for measurement of the viscosity of gases and liquids.

A supply of hydrazine has been obtained so that studies of the viscosity of hydrazine can be undertaken as soon as the work upon ammonia is completed. It is probable that the maximum temperature at which hydrazine can be investigated will be limited by the thermal rearrangement of this compound at elevated temperatures. In the early stages of the program, it may be necessary to limit the maximum temperature to 160° F. in order to avoid

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significant probabilities of serious damage to the equipment which could result from the rapid thermal rearrangement of the hydrazine.

Notes and References

1. G. N. Richter and B. H. Sage, Chemical & Engineering Data Series, 2, 61-66 (1957).

M.I.T.

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THERMAL CONDUCTIVITY OF GASES AND LIQUIDS
OVER A RANGE OF TEMPERATURES AND PRESSURES

Massachusetts Institute of Technology - Phase 2

Frederick G. Keyes, Phase Leader

Introduction

The low temperature equipment is still not completely assembled. However, the new jigs were completed and are an important aid in the difficult cell assembly. The -10 to 400°C installation has been developed to where it is efficient and dependable in use, and the accuracy attainable is two tenths of one percent. The completion of the carbon-dioxide measurements clears the way to a program of measurements on a variety of substances. The new high temperature cell is not yet in operation.

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Discussion

The functioning of the intermediate temperature cell installation (-10° to 400°C) continues to be highly satisfactory and investigation of the thermal conduction behavior of carbon dioxide in the critical region: 31.04°C plus and minus 30°, a density range from essentially zero to the critical density, 0.474 to 0.93 g/cm³, greatest pressure 195 atms., is completed.

In the course of the carbon dioxide investigation many interesting observations were made of conditions under which turbulence can be induced:

1. As the critical point was approached, turbulent convection in the cell was encountered for very low temperature rises, and thus the temperature rise permissible was very limited.
 2. When measurements were made at high enough pressures to liquefy the CO₂ in the lead lines at room temperature, and the cell was above room temperature, turbulence around the electrical leads caused excessive fluctuation of the thermocouple voltages.
- Additional equipment has been developed to overcome the second phenomenon, and exceptional accuracy in thermocouple thermometry has been achieved.

Without the new automatic pressure regulation and measurement, reliable results would have been all but impossible of attainment. The extremely high compressibility of a fluid in the critical region necessitates exceptional control of the pressure, to be able to specify the density with reliability. Valid measurements cannot be made with any large fluctuation of pressure.

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These extensive improvements in equipment have permitted conduction measurements within 1°C of the critical temperature at the critical pressure and this is the nearest approach to the critical point that has ever been achieved. Measurements at exactly critical temperature appear to be impossible because the fluid is unstable.

The complete interpretation of the thermal conductivity measurements obtained for carbon dioxide by others is greatly obstructed through the lack of pressure-volume-temperature data in the critical region. There is a possibility that an interested member of the physical chemistry staff may undertake to carry out the required detailed p-v-T measurements on carbon dioxide in the critical region. It may be worth remarking that detailed p-v-T data do not exist for any substance sufficient for interpreting critical region thermal conductivity data taken at random. The temperatures selected for the present research correspond to the isotherms of Michels and Michels, or of Michels, Blaisse and Michels, and thereby the uncertainty as to density is greatly reduced.

The correlation attempts employed for the data for carbon dioxide indicate unmistakably that the effect of pressure increase or the excess conductivity over the "zero" pressure value, is a function of density only or the density quotient with Kelvin temperature. This fact is also of considerable importance for extrapolation purposes. Papers are in preparation giving full information on the cell design, its theory and calibration, along with a full account of the new carbon dioxide data including the correlations.

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The following series of substances will now be investigated using the intermediate temperature equipment: argon, helium, nitrogen, mixtures of nitrogen and helium, hydrogen, carbon monoxide, methane and ammonia. All these gases will be measured for thermal conductivity over a range of pressure and from -10° to 400°C .

Northwestern

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ATOMIZATION, VAPORIZATION, AND COMBUSTION OF MULTICOMPONENT
FUEL DROPLETS

Northwestern Technological Institute - Phase 1

W. F. Stevens, Phase Leader
S. Bernsen, J. S. Chinn, M. Engel, G. G. Lamb, and P. A. Nelson

Introduction

This study concerns the atomization, vaporization, and combustion of multicomponent fuel sprays under conditions approaching those existing in the combustor of a turbo-jet engine. In particular, an understanding of the mechanism of pre-flame atomization and vaporization of sprays from pressure nozzles is being sought, with the hope that this knowledge will enable future prediction of the combustion behavior of such a spray.

Discussion

Extensive experimentation has been carried out to determine drop-size

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distributions resulting from a wide variety of spraying conditions with a substantial number of different liquids. The modified liquid nitrogen technique, as described in previous progress reports, has been employed, and the data obtained have been successfully correlated. At present, a paper is being prepared for publication, reporting the results in detail.

The nozzles used in this work were Spraying Systems Co., Type SL, a grooved-core type with interchangeable orifice inserts and core-pieces. Careful choice of components used resulted in a wide variation of nozzle parameters. The orifice diameter ranged from 0.0135 to 0.081 inches and the cone angle varied from 52° to 91°, resulting in capacities ranging from 4.0 to 112 gal/hour, when spraying water at 1000 psi. Seven different liquids were sprayed, chosen on the basis of their physical properties, as follows: cyclohexane, carbon tetrachloride, n-octyl alcohol, nitrobenzene, water, aniline, and 1,1,2,2-tetrabromoethane. The densities of these materials range from 0.774 to 2.95 gm/cc, their viscosities range from 0.879 to 8.29 cp., and their surface tensions range from 24.5 to 72.0 dynes/cm. These ranges include practically all fuels presently being sprayed with pressure nozzles.

For all of the materials and nozzle combinations investigated, the data appear to fit the square-root normal distribution. This was determined by plotting the cumulative mass versus the square-root of the sieve size on normal probability paper. In all cases, a straight line was obtained. The square-root normal standard deviation was determined from the resulting straight line, by subtracting the square-root normal mean from the drop-size

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at one standard deviation above the mean, corresponding to 84.13 mass percent.

By trial and error plotting of the data, it has been found that the mean drop diameters obtained from runs involving the six organic liquids with nineteen different nozzle orifice and core insert combinations, over a pressure range from 100 to 1500 psi, could be correlated according to the following relation:

$$Y = 0.0811 Z^2 + 0.124 Z - 0.186$$

$$\text{where } Y = \log_{10} \bar{X}/D$$

$$Z = \log_{10} \left[\text{Re} \left(\frac{\mu_0^2}{\mu} \right)^{0.55} \left(\frac{V_0}{V} \right)^{1.2} \right]$$

(refer to nomenclature at end of report)

The average deviation of the experimental mean diameters from this curve was 8.25%.

The mean drop-size data for water do not agree with that for the organic liquids, being from thirty to fifty percent larger than predicted by the relation given above. The reason for this deviation is not known, although it is probably related to the fact that water does not wet the nozzle well. However, the data for water appear to be reliable, since they agree well with available data of other investigators. By trial and error plotting, as before, the data for water obtained in this investigation (plus that of others) have been correlated according to an equation much like the one used for the organic liquids. In this case, the average deviation of the data from the

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curve of best fit was only 6.7%.

The square-root normal standard deviation data have also been successfully correlated, to give a similar curve of best fit. The average deviation of the data from this curve is 13.0%. The greater scatter of the standard deviation data is to be expected, since this parameter can be greatly affected by slight inaccuracies in the sampling or measuring technique. The fact that the standard deviation could be correlated as well as it was for such widely different liquid properties and nozzle parameters is indeed gratifying. It substantiates not only the method of drop-size measurement, but also the choice of variables for the correlation.

The correlations developed as a result of the research described above should make it possible for the combustion engineer to predict accurately the drop-size distribution which will result when a particular fuel is sprayed from a nozzle of given properties. Conversely, he should be able to specify the nozzle dimensions required to give a desired drop-size. Future work will attempt to determine the generality of the correlations, by operating other types of nozzles and determining whether the drop-size distributions resulting are consistent with the data already obtained.

Nomenclature

D_o - nozzle orifice diameter, microns
 Re - Reynolds No. (dimensionless)

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V_a - axial fluid velocity, cm/sec.
 V_t - tangential fluid velocity, cm/sec.
 We - Weber No. (dimensionless)
 \bar{X} - mean drop diameter, microns

Penn State

Transport and Transfer Processes

DYNAMIC CONDITIONS IN A SPRAY ZONE

The Pennsylvania State University, Phase No. 2

William E. Rans
Hikmet Binark

Introduction

As a basis for understanding the detailed processes of heat and mass transfer in the combustion of a fuel spray, this research concerns a study of the dynamic conditions in a spray zone and the reasons why these conditions exist. Quantities to be studied include dispersion of liquid flux around a geometrically fixed plane or center line of flow, liquid velocities, spray liquid densities, and air path-lines and air velocities throughout the spray region beyond the nozzle orifice. An understanding of the nature of the momentum transfer process between primary liquid flow and induced air flow and the nature of the air-liquid mixing process is also an objective of the project.

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Discussion

In the penetration zone of a hollow cone spray, air is induced to enter the spray sheet at right angles to the sheet, pass through the spray while changing direction, and take a final direction parallel to the nozzle axis. The magnitude of the air flow velocity is greatest at the zone of breakup and decreases as the distance from the nozzle orifice increases. The air velocity inside the spray is a maximum on the nozzle axis and decreases to a value at the inside of the spray sheet which is set by the velocity at which air is being induced from outside the sheet and by the spray cone angle. Velocity differences above the minimum value show a normal type distribution, the result of larger velocities nearer the orifice and axis. The air flow is laminar in a scale larger than the size of individual drops.

Air flow induced through a unit area of the spray sheet at a given distance from the nozzle orifice can be attributed to a momentum interchange between the air and drops moving relative to the air at the point in question. A momentum balance can be considered to hold between 1) the total drag force on all of the drops passing through a particular area of the spray sheet at any instance and 2) the component in the spray direction of air momentum leaving that area.

Drops, at the moment of their formation, are projected through the air in average directions which generate a spray cone. Because induced air crosses their paths at nearly right angles, drops travel as part of the

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spray sheet only so far as their penetration distance in still air, after which they move inside the cone and travel parallel to the nozzle axis joining the induced air flow. The inward bending of drop trajectories, caused by the air flow, is also the cause of decreased spray cone angle at increased distance from the orifice.

The velocity of air entering the spray at a given distance from the orifice is directly proportional to the velocity of liquid issuing from the orifice. The magnitude of this velocity is of the order of one-tenth that of liquid velocity, for example, an air velocity of one-tenth the liquid issue velocity was measured at two inches from the orifice of a small oil burner nozzle. For small fuel nozzles (up to 30 gallons per hour) the magnitude of this velocity is insensitive to variations in spray cone angle and changes in capacity resulting from changes in orifice diameter. The velocity of air at any point outside the spray sheet is set by the velocity of air entering the sheet and the geometrical requirements of continuity. The velocity of air inside the spray is equal to the velocity outside the spray divided by the sine of half the spray cone angle. A negative static gauge pressure is also detected inside the spray.

Mist and air fluxes inside a hollow cone spray are such that the air-liquid-ratio is a minimum on the spray axis and increases in a parabolic fashion to the spray sheet. In fuel sprays the air and fuel mist moving along the axis can be a rich mixture. Stoichiometric ratios occur at distances of the order of one inch from the axis.

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In solid cone sprays air is also induced into the spray at right angles to the spray direction. Inside the spray it turns in the direction of the nozzle axis which, in this case, is also the direction of the spray. Air and liquid velocities, fluxes of air and liquid, and momentum flux, in a spray cross section are distributed in a somewhat normal fashion across the spray axis. A momentum balance exists between the liquid issuing from the orifice and the two-phase flow at any cross section along the spray axis.

A series of experiments, which demonstrate these qualitative and quantitative aspects of the induced air flow in hollow and solid cone sprays, have been performed.

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STATISTICAL PROPERTIES OF TWO-PHASE FLOW

Princeton University, Phase 11

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Introduction

Turbulent flow processes involving the suspension of solid particles in an air stream was studied to further the understanding of turbulent transport phenomena involving two phases. Devices involving two-phase flow are solid propellant rockets and combustion chambers for solid and liquid fuels. In the combustion of liquid droplets, one is interested not only in high evaporation rate, but also in large particle diffusivity, since the smallest droplet size does not provide the best distribution. (1) In the case of a solid propellant rocket, the contribution of specific heat and mass flow of solid particles is obviously held back by the turbulent dissipation between phases; studies to date have not accounted for the latter (2, 3).

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Many studies were made on the dynamics of particle motion in a fluid. The study of oscillatory motion of a solid sphere in a viscous fluid was made by Stokes (4). The motion of a pendulum in a turbulent fluid was made by Lin (5). The general equation governing particle motion in a turbulent medium was derived by Tchen (6) and its details were recently re-considered by Lumley (7,8). Solution of the equation of motion in the Eulerian system of coordinates was attempted by Davies (9). In all studies Stokes law for drag of sphere was assumed, thus limiting the solution to small particles in a stream of relatively low turbulent intensity.

Based on such premises, study based on statistical distribution was made as published in Ref. (10), neglecting relative acceleration (4,6) and probability of space coordinate and approximating the distribution of stream turbulence as:

$$f(n) = \frac{2\sqrt{\pi}\lambda}{\sqrt{u^2}} e^{-\pi^2 \lambda^2 n^2 / u^2} \quad [1]$$

the following distribution function of turbulent motion of solid particles was obtained:

$$f_p(n) = 2\sqrt{\pi}\lambda e^{-\pi^2 \lambda^2 n^2 / u^2} / \left[\sqrt{u^2} \left(1 + \frac{4\pi^2 n^2}{F^2 \lambda^2} \right) \left(1 - \frac{1}{2} \frac{4\pi^2 n^2}{F^2 \lambda^2} + \frac{1}{2^2} \frac{4\pi^2 n^2}{F^2 \lambda^2} - \frac{1}{2^3} \frac{4\pi^2 n^2}{F^2 \lambda^2} \dots \right) \right] \quad [2]$$

where u^2 is the intensity of turbulence of the stream,
 λ is Taylor's λ_1 (14), a measure of size of eddy of the stream,
 n is the frequency
 and F is equal to $18\mu / (d_p^2 \rho_p)$; based on stream viscosity, particle diameter, and particle density respectively.

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The determination of the distribution function is deemed necessary toward further understanding of the statistics of momentum transfer and our effort toward determining other transport characteristics. This lead to the conclusion of relative Reynolds number of particles:

$$\bar{Re}_r = \frac{d_p \sqrt{(\Delta u)^2} \rho}{\mu} = \frac{\sqrt{\pi}}{18\sqrt{2}} \bar{Re}^2 \left(\frac{d_p}{l_1} \right) \left(\frac{\rho}{\rho_p} \right) \quad [3]$$

where $\frac{(\Delta u)^2}{u^2} = \frac{u^2 - u_p^2}{u^2}$ is the relative intensity between the particle (intensity $\sqrt{u_p^2}$) and the stream (intensity $\sqrt{u^2}$),

\bar{Re} is the Root-mean-squared Reynolds number, $\frac{d_p \sqrt{u^2} \rho}{\mu}$,

and l_1 is the Lagrangian scale of turbulence of the stream.

Ref. (8) presents this relation as

$$\bar{Re}_r = \frac{2\sqrt{2}}{8\pi^2} [2 (\rho_p/\rho) + 1] \bar{Re}_\lambda^2 \left(\frac{d_p}{\lambda} \right)^3 \left(\frac{\lambda}{\lambda_3} \right) \quad [4]$$

where $\bar{Re}_\lambda = \frac{\sqrt{u^2} d_p \rho}{\mu}$

and $\lambda_3 = \sqrt{u^2} \tau_L$; τ_L being the Lagrangian microscale for time.

Eq. [3] and [4] are identical for small particles ($\lambda_3 \sim \lambda$); the correction for the apparent mass (4) is a direct one, applicable to the case where ρ_p and ρ are close to each other.

Further sharpening of the results from Eq. [2] calls for a more accurate determination of the distribution function from statistical mechanics of this type of system. This is part of our current effort.

Removal of the restrictions of small particles and moderate turbulence lead to experimental determination of stream and particle motion (11, 12) in our present phase. Some of the results will be discussed in the next part.

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In this study, we are also concerned with the interaction between the particles which is significant in the case where solid to fluid weight ratio is high (13). To understand the phenomena associated with the wall effect, interaction of particle motion with the wall and non-isotropic turbulence has been formulated and analyzed through extending the concept of local isotropy (15).

Discussion

Experimental work to date has yielded data on the turbulence characteristics of both the stream and the particles in the middle third of a 3" x 3" duct. Within this range, the stream is nearly isotropic. For the range of weight ratio of particles (spherical glass beads) to fluid (air), no significant interaction between the solid particles and stream has been observed. This assumption was made in our analytical work on the particle interaction and wall effect.

The stream measurements so far made with helium tracer diffusion technique compare favorably with results obtained by other methods (Table 1) (16). The tracer diffusion technique enables us to determine intensity, diffusivity and scale of turbulence [Row (1) to (8) of Table 2]. The basic technique is presented in Ref. 11 and 12.

The particle motion evaluated from photographic record obtained by high frequency (6000 to 8000 cycles) successive exposure gives directly the mean intensity of the particles and the particle diffusivity. Some of the results so far obtained are presented in Row (9) to (16) of Table 2.

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It is interesting to note that for particles giving \bar{Re} much greater than 1, the particle diffusivity (17) is less than stream diffusivity as contrary to the analytical result. This may be attributed to significant deviation from Stokes Law in the cases experimented. Further, the intensity of particles as measured in some cases of low duct Reynolds number, is greater than that of the stream. This is attributed to increased significance of wall interaction at low stream velocities. In the case of low mean velocity of the stream, contribution of exchange of particles between the middle third and the turbulent field (greater intensity than in the middle) near the wall is more significant than in the case of high stream velocity (Row 14, Table 2). The gravity effect for low mean stream velocity case is also expected to be more significant (Row 15).

The method suggested by Ref. (8) for calculating particle motion was found to be rather difficult and expensive to carry out. For the case of particles under isotropic turbulence, with or without the effect of particle interaction due to Bernoulli force (18), we are working toward improving the distribution function as approximated by Eq. [2] by solving the Boltzman equation to obtain its higher order perturbations (19).

The wall effect on single particle was formulated by considering the drag force, fluid resistance due to relative particle acceleration, the fluid inertia, force due to wall turbulence and the buoyancy force. Effort is made toward solving this integral-differential equation.

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Table I

Intensity of Turbulence

Reynolds number of duct	Intensity/mean velocity			Source
12000	.031	.034	.040	Ref. 16
38000	.028	.030	.035	Ref. 16
38000	.0275			Ref. 12
83500	.0224			Ref. 12
129000	.0196			Ref. 12

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Table 2

Statistical properties of particle and stream motion

Item Case	1	2	3	4
1 Mean velocity of air, U, fps	25	25	25	25
2 Reynolds no. of duct flow	37940	37940	37940	37940
3 Particle flow rate, lb./min.	0	.403	.270	.394
4 Particle size, micron		250	250	110
5 Stream intensity, $\sqrt{u^2}$, fps.	.690	.692	.549	.690
6 $\sqrt{u^2}/U$.0276	.0277	.0220	.0276
7 Scale of turbulence of stream, l_1 , ft.	.0562	.0299	.0423	.0435
8 Eddy diffusivity, E , ft ² /sec.	.0399	.0207	.0232	.0300
9 Particle intensity $\sqrt{u_p^2}$	2.45	1.84	3.06	
10 Particle diffusivity, E_p , ft ² /sec.	1.53	1.53	1.22	
11 Scale of turbulence of particles, ft.	.003/.0017*	.0028/.0017	.0011/.0007	
12 Reynolds number of particles	.002	.0016	.0007	
13 K (Ref. 10)	3.58	2.75	.53	
14 $(\overline{u^2} - \overline{u_p^2})/\overline{u^2}$	321	101	5.65	
15 g/F, fps (ref. 10)	-3.9	-6.76	-2.1	
16 E_p/E	161	161	40.5	
	.1	.1	.026	

* at two stations 2.076 in./1.038 in.

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Table 2

Statistical properties of particle and stream motion

Item Case	5	6	7	8	9
1 Mean velocity of air, U, fps	55	55	55	85	85
2 Reynolds no. of duct flow	83480	83480	83480	129000	129000
3 Particle flow rate, lb./min.	0	.393	.406	0	.395
4 Particle size, micron		250	110		110
5 Stream intensity, $\sqrt{u^2}$, fps.	1.14	1.18	1.27	1.68	1.58
6 $\sqrt{u^2}/U$.0207	.0215	.0231	.0198	.0186
7 Scale of turbulence of stream, l_1 , ft.	.0412	.0503	.0469	.0291	.0337
8 Eddy diffusivity, E , ft ² /sec.	.0470	.0593	.0568	.0489	.0533
9 Particle intensity		2.14	1.84		3.06
10 Particle diffusivity, E_p , ft ² /sec.		1.22	.98		.86
11 Scale of turbulence of particles, ft.					.0014/.0007
12 Reynolds number of particles					.0016
13 K (Ref. 10)		4.95	2.81		3.50
14 $(\overline{u^2} - \overline{u_p^2})/\overline{u^2}$		330	16.42		49.2
15 g/F, fps (ref. 10)		-0.662	.404		.702
16 E_p/E		161	40.5		40.5

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STUDIES OF HEAT TRANSFER TO GASES
AND
THE MECHANISM OF TWO PHASE FLOW

Purdue University - Phase 11

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Introduction

The research reported herein is concerned with the following two problems.

Problem 11 R1 A Study of the Heat Transfer to and from Gases with
Large Temperature Differences Between the Gas and
the Wall.

Problem 11 R3 The Investigation of Two-Phase Annular Gas-Liquid
Flow in a Vertical Tube.

The progress made with respect to each problem is reported under separate
sub-headings.

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Discussion

Problem 11 E1 A Study of the Heat Transfer to and from Gases with Large Temperature Differences Between the Gas and the Wall. The research program discussed herein is concerned with the investigation of the heat transfer phenomena occurring between a gas in turbulent diabatic flow and the wall of a smooth round duct.

During the subject report period the research effort has been concerned with the following items:

- (A) Completion of the analysis of the data for cooling the gas with the wall temperature of the duct (a) constant and (b) variable with axial distance.
- (B) Adaptation of the theory developed by Rubesin for flat plates, to the prediction of the influence of the wall temperature gradient upon the heat transfer to or from a gas in turbulent diabatic flow in a circular tube.
- (C) Completion of the theoretical analysis of heat transfer in the entrance regions of smooth round ducts.
- (D) Revision of the existing apparatus for conducting heat transfer experiments with hydrogen.

The afore-mentioned items are discussed in detail in the following paragraphs.

- (A) Cooling Experiments. For these experiments, the local and the average values of the heat transfer coefficient, Nusselt number, and Reynolds number

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were computed. The experiments were conducted with air and with carbon dioxide in a test section having $L/D = 60$ (see Reference 1).

Figure 1 presents the thermal entrance lengths L_{hl}^* (for air and carbon dioxide) as functions of the bulk Reynolds number for conditions where the wall temperature was invariant with axial distance. Included in the figure are the values of thermal entrance length (L_G) predicted by the theory described in (C). Figure 1 shows that the predicted values of thermal entrance length are conservative. Table I summarizes the range of values obtained for L_{hl} for the stated ranges of bulk Reynolds number \bar{N}_{Re} .

TABLE I
Range of Experimental Values for the Thermal Entrance Length
(Cooling Experiments)

Gas	L_{h5}	L_{hl}	\bar{N}_{Re}
Air, cooling CWT**	7-12	16-25	25,000 to 152,000
Air, cooling VWT	8-43***	16-48***	20,000 to 94,000
CO ₂ , cooling CWT	5-14	12-26	23,000 to 218,000
CO ₂ , cooling VWT	12-28	20-38***	24,000 to 127,000

- * The thermal entrance lengths L_{hl} and L_{h5} are defined as the distance from the entrance to the cross section where the local heat transfer coefficient is equal to 1.01 or 1.05 times the asymptotic value of the heat transfer coefficient.
- ** CWT denotes wall temperature constant with axial distance.
- *** VWT denotes variable wall temperature with axial distance.
- *** Estimated values.

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The increase in the local Nusselt numbers Nu_b downstream from the entrance region is attributed to the decrease in the thermal conductivity of the flowing gas with decrease in the local bulk temperature.

The local heat transfer coefficient decreased rapidly just beyond the entrance section and then decreased to a substantially constant value for x/D values ranging from 12 to 26 diameters depending upon the Reynolds number.

The average heat transfer results for the cooling experiments conducted with air and carbon dioxide, for a constant wall temperature, were best correlated by evaluating the physical properties of the gases at the average bulk temperature. Figure 2 presents the bulk Nusselt number \bar{Nu}_b as a function of the bulk Reynolds number \bar{N}_{Reb} for the cooling experiments. The aforementioned results are correlated with a maximum deviation of ± 6 per cent by the following equation.

$$\bar{Nu}_b = 0.0181 \bar{N}_{Reb}^{0.8} \quad (1)$$

The subscript b denotes that the physical properties were evaluated at the average bulk temperature. Including the Prandtl number to the 1/3 power in equation 1 increased the maximum deviation of the results from the correlating line to ± 7 per cent. Correlation of the results presented in Fig. 2 by the Colburn modulus as a function of the Reynolds number yielded a maximum deviation of ± 7 per cent when the properties were evaluated at the bulk temperature and ± 10 per cent when the properties were evaluated at the average film temperature $\bar{T}_f = (\bar{T}_b + \bar{T}_w)/2$, where \bar{T}_w is the average wall temperature.

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The results briefly described above are discussed in detail in Reference (2).

(B) Prediction of Influence of Wall Temperature Gradient. Analytical studies of heat transfer from non-isothermal surfaces (3) (4) demonstrated that the variation of the surface temperature with distance has a significant effect upon the heat transfer to or from the surface. A calculation of the total amount of heat per unit width $Q(W)$ transferred from a flat plate of length W with an unheated starting length L to a gas flowing turbulently over the surface is presented in Reference (2). The results of the afore-mentioned calculation are given by the following equation.

$$Q(W) = \frac{h(W,0)}{W} \left[\frac{1}{5} - \frac{L}{5} \right] \left[(T_{w2} - T_{w1}) I_1 + 1.25 L \left(\frac{\partial T_w}{\partial x} \right) I_2 \right] \quad (2)$$

where

- $Q(W)$ = the total amount of heat transferred per unit width and time from the heated portion of the plate.
- $h(W,0)$ = the local heat transfer coefficient at the end of the plate, $x = W$.
- W = the distance from the leading edge to the end of the heated section.
- L = the distance from the leading edge to the point of discontinuity in the surface temperature.
- T_{w2} = the surface temperature at $x = L^+$.

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- T_{w1} = the surface temperature at $x = L^-$.
 T_w = the surface temperature at location x .
 x = the distance along the plate, the leading edge being the point $x = 0$.

$$I_1 = \int_{(L/W)^r}^1 (1-\eta)^s \eta^{-(4+5r)/5r} d\eta$$

$$I_2 = \int_{(L/W)^r}^1 (1-\eta)^{(s+1)} \eta^{-(9+5r)/5r} d\eta$$

$$\eta = (L/x)^r$$

$$r = (28m + 39)/40$$

$$s = (7 + 28m)/(28m + 39)$$

$$m = \text{a constant, the value of which is restricted to the interval } -1/4 \leq m \leq 9/28. (3)$$

For given values of L , W , and Reynolds number the integrals I_1 , I_2 , and the term $h(W,0)$ are constants. The term $1.25 L (\partial T_w / \partial x) I_2$ then represents the contribution to the total quantity of heat transferred because of the surface temperature gradient; the latter was assumed to have a constant value in the derivation. If it is assumed that the heat transferred from a gas to a tube of length W with an uncooled length L is similar to $Q(W)$ for a flat plate, then equation 2 may be employed for predicting the influence of $\partial T_w / \partial x$. Equation 2 demonstrates that for the case of cooling ($T_{w2} < T_{w1}$) the total amount of heat transferred from a gas to the tube wall should be

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larger when the surface temperature decreases with distance than if the surface temperature were constant with distance; conversely for a positive surface temperature gradient the heat transferred would be less than that for zero gradient. Figure 3 presents the results of cooling experiments conducted with air in a tube having positive and negative values of $\partial T_w / \partial x$; it is seen from the figure that the experimental results are in qualitative agreement with the trend predicted by equation 2. A choice of the constant $m = 1/7$ results in better quantitative agreement between the predictions of equation 2 and the experiments conducted with the wall temperature invariant with distance. Figure 4 presents the experimental results (see Fig. 3) adjusted to conditions of constant wall temperature by assuming the heat transferred in the tube to be proportional to the quantity enclosed by the brackets on the right-hand side of equation 2, and that $28m = 4$. Included in Fig. 4 are the adjusted results of heating experiments with Reynolds number less than 100,000. It is seen from Fig. 4 that the theory adequately predicts the influence of $\partial T_w / \partial x$ for values of \bar{T}_w / \bar{T}_b less than approximately 1.6. It should be pointed out that in applying the modified theory of Rubesin to the heating experiments it was assumed that $\partial T_w / \partial x$ was constant along the tube which is not the case. The assumption that $\partial T_w / \partial x$ is constant appears to be satisfactory for those experiments where $\bar{T}_w / \bar{T}_b < 1.6$. The experimental results obtained with carbon dioxide under the above-mentioned conditions and the predicted influence of the surface temperature gradient directly parallels that illustrated for air.

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(C) Theoretical Analysis of the Heat Transfer in the Entrance Region. Calculations were made of the heat transfer characteristics for air and carbon dioxide in turbulent diabatic flow in the thermal entrance region of a smooth round tube. It was assumed that the flowing fluid had a fully developed velocity profile and a uniform temperature profile at the cross section where energy exchange was initiated. The thermal boundary layer thickness was computed according to the method of Deissler (5) for both the constant heat flux, and the constant wall temperature boundary conditions. The variations of the physical properties of the fluid with temperature were assumed to approximate those for air and for carbon dioxide. The velocity and temperature profiles employed in the region between the wall and the edge of thermal boundary layer were those calculated by Botje (6) for fully developed flow. In the region outside the thermal boundary layer the temperature of the fluid was assumed constant with distance from the wall and the velocity profile was assumed to be that for adiabatic flow. The derivation of the relationship for the thermal boundary layer thickness with axial distance, and the method of calculating heat transfer and flow parameters in the entrance region are presented in complete detail in References (2) and (7).

Figure 5 compares the results of the afore-mentioned analysis with the experimental results, described under (A) above, for cooling carbon dioxide in a test section having $L/D = 60$. Figure 6 compares the predicted and experimental results for heating air. It is seen from Figs. 5 and 6 that the agreement between theory and experiment is satisfactory for practical purposes.

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(D) Revisions to Apparatus. The apparatus for conducting heating experiments is being revised so that hydrogen gas can be used as the flowing medium and average wall temperatures exceeding 2000 R can be obtained. A new test section has been fabricated of Haynes Alloy 25 tubing 0.306 inches ID and 40 diameters long. An isothermal starting length 46 diameters long is provided upstream to the test section. It is estimated that Reynolds numbers up to 50,000 can be achieved with hydrogen gas as the heat transfer fluid. The revision is approximately 75 per cent complete and it is anticipated that exploratory experiments will be in progress by May 1958.

Problem 11 E3 The Investigation of Two-Phase Annular Liquid Flow in a Vertical Tube. This investigation is concerned with the analytical and experimental study of the mechanism of the downward or "gravity" flow of a liquid film on the inside wall of a vertical circular tube with co-current gas flow in the core of the tube.

A report analyzing the status of knowledge on the subject is in preparation and should be ready for distribution by June 1958. The most pertinent findings obtained from the literature review (8) are summarized below.

1. The theory proposed by Nusselt (1916) for describing the mechanics of liquid film flow and the transfer of heat through liquid films is inadequate for predicting the rates of heat, mass, or momentum transfer in annular two-phase flow after surface disturbances have appeared upon the interface separating the liquid phase from the gaseous phase.

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2. The increase in the surface area, due to the surface disturbances, is insufficient for accounting for the increases in the transfer rates after those disturbances occur.

3. Initial theoretical approaches to a solution of the problem of two-phase flow were semi-empirical in nature and attempted to solve the problem by neglecting the specific flow pattern.* Experimental evidence indicates that the flow pattern must be considered in any complete solution of the problem.

4. More recent theoretical solutions appear to yield good results for some flow conditions but are inadequate for other. Insufficient experimental data are available for determining conclusively the applicability of any of the theoretical solutions.

5. From two-phase annular flow experiments there is evidence that the pressure drop may be correlated in a fashion analogous to that employed by Moody for single-phase flow in rough pipes. That method has not been generalized, however, because the exact effect of the liquid flow rate is not known.

6. Since the surface disturbances are random in nature, a statistical approach to solving the problem would appear to be most promising. The results of such a study for the single-phase flow of a liquid film was reported recently by von Brauer (9).

* Flow pattern - slug, bubble, mist, annular, etc.

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7. Most of the investigators realize that there is a need for a more detailed description and a more thorough understanding of the surface disturbance phenomena.

8. It is apparent that currently there is no general solution, either theoretical or experimental, for two-phase annular flow.

The construction of the experimental apparatus has been completed. Currently the instrumentation is being calibrated, and some exploratory experiments are being conducted for the purpose of obtaining experience with the new apparatus.

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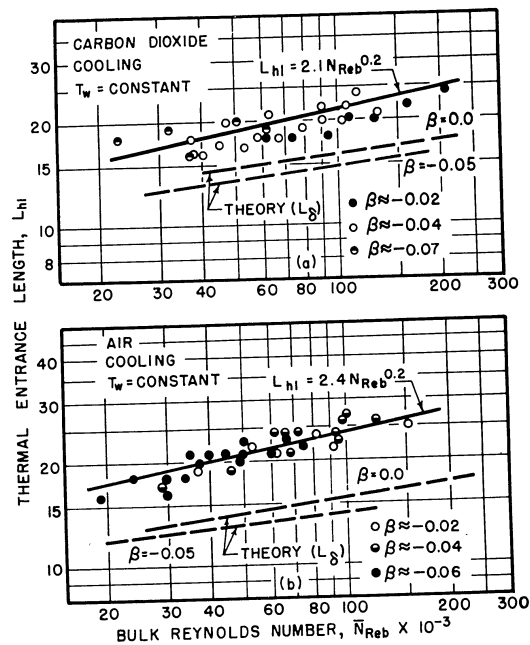


Fig. 1 Variation of Thermal Entrance Length with Bulk Reynolds Number and β for Air and Carbon Dioxide; Cooling, Constant Wall Temperature.

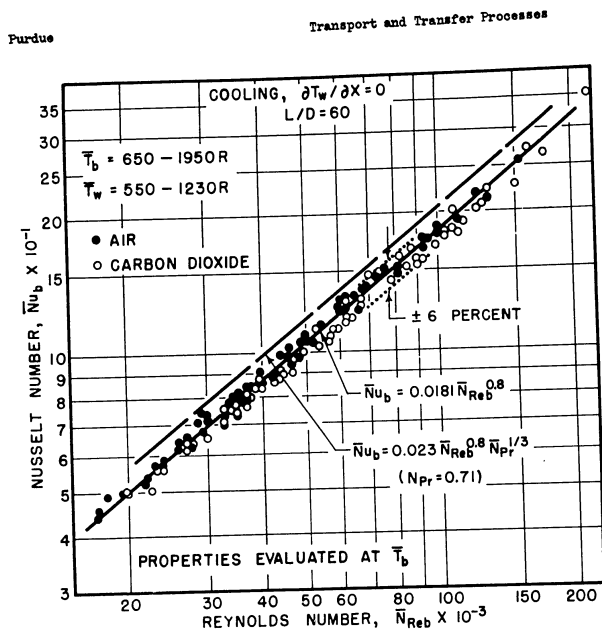


Fig. 2 Correlation of Bulk Nusselt Number With Bulk Reynolds Number for Air and Carbon Dioxide; Cooling, Constant Wall Temperature.

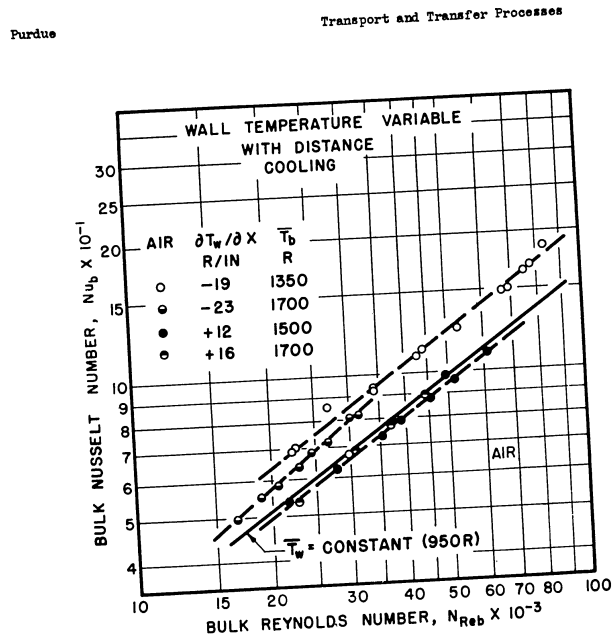


Fig. 3 The Influence of Variable Wall Temperature Upon the Nusselt Number for Air; Cooling.

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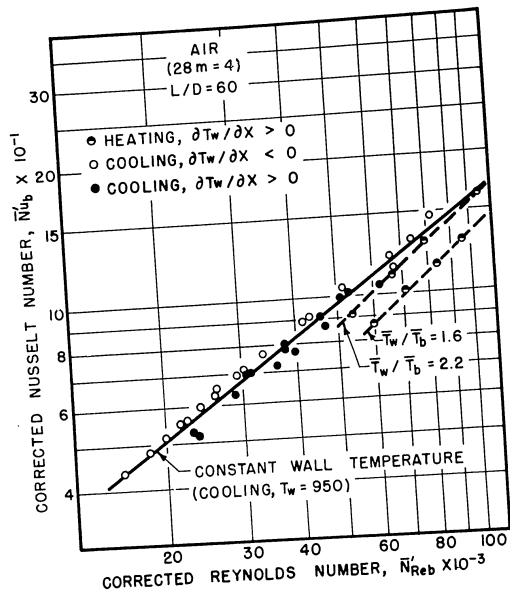


Fig. 4 Variable Wall Temperature Results for Air Corrected to Conditions of Constant Wall Temperature; Heating and Cooling, Properties Evaluated at the Bulk Temperature.

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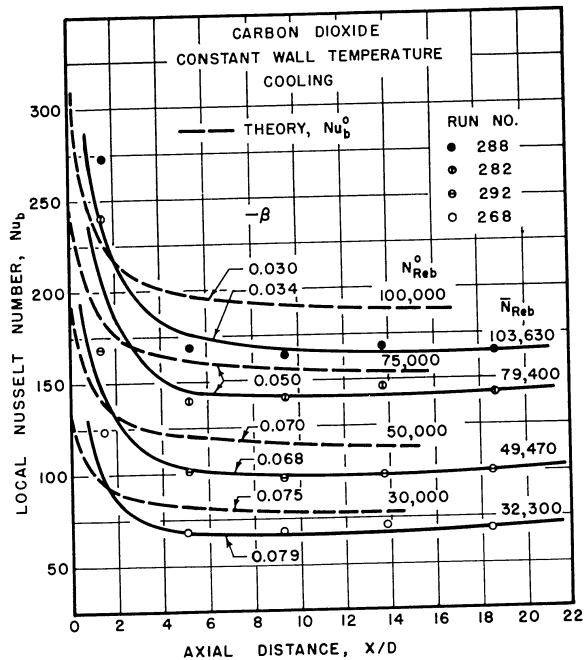


Fig. 5 Comparison of Experimental and Predicted Values of Local Bulk Nusselt Number for Carbon Dioxide; Cooling, Constant Wall Temperature.

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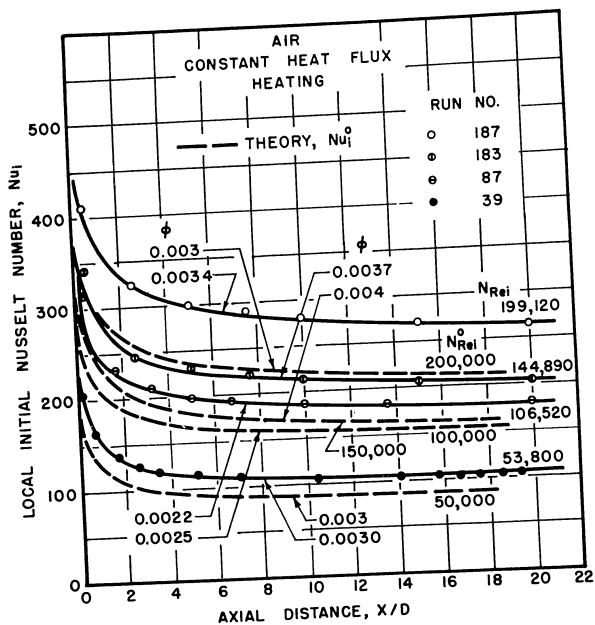


Fig. 6 Comparison of Experimental and Predicted Values of Local Initial Nusselt Number for Air; Heating, Constant Heat Flux.

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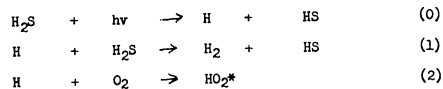
REACTIONS OF HYDROGEN ATOMS

Contractor: The Catholic University of America
Contract No. N60ri-105, Task 3

Personnel: B. de B. Darwent, Phase Leader
V. J. Krasnansky, Investigator
L. J. Stief, Investigator

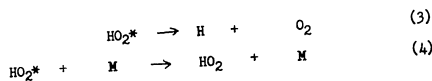
Introduction

In the last Semi-Annual Progress Report (April 1957), results were presented showing that the H atom produced in the photolysis of HI was "hot" and, therefore, that the results obtained by Bates, et.al. on the reaction of H with O₂ should not be accepted without reserve. The results included in the present report were obtained by photolyzing H₂S in the presence of O₂. There is good experimental evidence that the H atoms produced in the photolysis of H₂S have thermal velocities. The following simple mechanism:



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assumed for the process, and leads to the identity:

$$\gamma = (q/1-q) = (k_1/k_2r) \left\{ 1 + \frac{k_3/k_4m}{1} \right\} \quad (A)$$

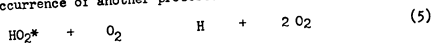
where q is the quantum yield of H_2 , r is P_1/P_2 , P_1 being the concentration of H_2S and P_2 of O_2 , and m is the concentration of all species. If HO_2^* is long lived (i.e., $k_3 = 0$), we get

$$1/q = 1 + k_2/(k_1r) \quad (B)$$

Results

A plot of $1/q$ against $1/r$ showed a considerable deviation from linearity, indicating that equation (B) did not account adequately for the results. However plots of γ vs $1/m$ did provide straight lines with small but definite intercepts, in conformity with equation (A). This suggests strongly that the simple mechanism is essentially correct and that k_3 is not negligible.

Linearity of γ vs $1/m$ is obtained, at constant temperature and r , whether the variation in m was accomplished by varying P_1 and P_2 , but keeping the ratio constant, or by maintaining P_1 and P_2 constant and adding varying amounts of CO_2 to alter the total pressure. However, the intercepts in the former case were considerably larger than in the latter. This suggests the occurrence of another process:-



the inclusion of which alters the kinetics slightly to give:

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$$\gamma = (k_1/k_2r) \left\{ 1 + \frac{k_3P_2}{k_4m} + \frac{k_3}{k_4m} \right\}$$

The ratios k_1/k_2 and k_3/k_4 were measured at 50° , 93° and 150° C. giving the differences in activation energies, and k_5/k_4 at 50° C. The following data were obtained for the ratio of rate constants:-

T, °C.	50	93	150
k_1/k_2	0.060	0.137	0.171
$(k_1k_3/k_2k_4) \times 10^3 (\text{mm}^{-1})$	0.395	0.765	1.45
$(k_3/k_4) \times 10^3 (\text{mm}^{-1})$	6.58	5.58	8.48
k_5/k_4	33.		

It seems likely that the ratio k_3/k_4 is independent of temperature, so that $E_3 - E_4 = 0$. The Arrhenius plot of k_1/k_2 and k_1k_3/k_2k_4 both give activation energies of 2.8 kcal. mole⁻¹. There is some uncertainty in the magnitude of E_1 which may be 4.88 or 7.5 kcal. mole⁻¹. Hence E_2 will be 2.05 or 4.7 kcal. mole⁻¹. From the magnitude of k_3/k_4 we find that, if reaction 4 occurs on every collision, k_3 will be 1.9×10^{10} sec.⁻¹ or 3×10^{11} sec.⁻¹, the minimum average life of HO_2^* , will be about 5×10^{-11} sec.

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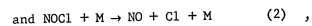
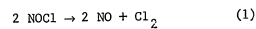
HIGH TEMPERATURE REACTIONS

The Pennsylvania State University, Phase I

Dr. Howard B. Palmer, Phase Leader
Mr. Bernhard Deklau
Mr. Bruce Knox

Introduction

The objective of our work on high temperature reactions is to add to the basic understanding of reaction rates at high temperatures. The general procedure in this effort is to observe a gas as it undergoes very rapid heating in a shock wave and to attempt to follow the rates of reactions of pertinence, as they set in behind the shock front. We have begun measurements of the high temperature dissociation rate of gaseous NOCl. This molecule is of interest first because it probably can decompose by two mechanisms,



the second process presumably proceeding via the Lindemann mechanism. It

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is well known that process (1) occurs at low temperatures, and there are indications in the literature that process (2) is already making a significant contribution at temperatures as low as 400°K. Literature data on the decomposition rate extend up to 573°K, with one rough value available at 1020°K. The second reason for interest in NOCl is that it is triatomic. If appreciable contribution to the dissociation rate is made by transfer of energy from rotational and vibrational energy modes to the O-Cl bond, the contribution might be expected to be quite large and should show up at relatively low temperatures. The literature data allow an estimate to be made of the rate constant of reaction (2), assuming second order behavior (i.e., "low pressure" behavior, in the Lindemann scheme). The estimate is

$$k \approx 10^{15} \exp(-30\text{kcal/RT}) \text{ cc/mole sec.}$$

This conforms to expectations in having a large pre-exponential factor, indicative of extensive energy coupling, and an empirical activation energy below the O-Cl bond energy, 38 kcal. It seems that detailed study of the rate at high temperatures should be interesting and worthwhile.

Discussion

Our shock tube is operating satisfactorily now, and a number of preliminary runs have been made with commercial NOCl. This is not of adequate purity to give usable rate data, so will be further purified by

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distillation. Calculations of shock conditions corresponding to various measured velocities in pure NOCl and in NOCl diluted with argon are being completed. Calculations of shock conditions expected from initial pressure ratios across the diaphragm (He driver) have also been made for guidance in making experimental runs.

From one of the preliminary runs we have made a rough estimate of the dissociation rate and computed a rate constant (at ca. 800°K) that appears to conform reasonably well to the above estimated rate constant of reaction (2). It appears from this that a study of NOCl decomposition may be particularly worthwhile by the shock wave technique because the rate should be fast enough at low enough temperatures for careful examination of agreement between kinetic data from shock wave experiments and those obtained by more conventional methods.

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SURFACE-CATALYZED ATOM AND FREE-RADICAL REACTIONS

Stanford Research Institute - Phase II

Henry Wise - Phase Leader
Clarence M. Ablow
Bernard J. Wood

Introduction

The heterogeneous interaction of labile species such as atoms and free radicals is associated with various aspects of combustion and propulsion. In this investigation, the surface activity of various solid surfaces for the recombination of atoms is quantitatively examined.

Discussion

The experimental procedure employed in the measurements of the activity of metallic and nonmetallic surfaces for the recombination of atoms has been described in the previous semi-annual progress report (dated October 1, 1957).

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The dynamics of heterogeneous radical reactions in a system such as employed in our measurements have been examined from a theoretical viewpoint. This theoretical analysis includes the effects of radial and longitudinal diffusion in a cylinder of finite length containing "atom sinks" of different relative magnitude. The mathematical treatment is contained in a forthcoming Squid report.¹

The measurements of surface activity have included the interaction of hydrogen atoms with transition metals. In particular, the recombination coefficients γ of the first series of transition metals have been studied.² The results of our determinations are summarized in Table I, which includes also several other surfaces of interest. It is to be noted that in the case of a very active surface such as platinum, one in every four collision leads to recombination and the formation of a hydrogen molecule. For a less active transition metal such as titanium, the recombination coefficient is reduced by a factor of about 2.5. Pyrex glass exhibits a relatively low value of γ . The experimental measurements are being extended to other metallic and non-metallic surfaces including semiconductors.

Notes and References

1. Henry Wise and C. M. Ablow, "Diffusion and Heterogeneous Reaction I. The Dynamics of Radical Reactions." (Squid Report, March 1958)
2. The recombination coefficient γ is defined as the ratio of the number of atoms striking the surface and reacting to the total number of atoms hitting the surface.

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Table I

RECOMBINATION EFFICIENCY OF VARIOUS SURFACES FOR HYDROGEN ATOMS

Surface	Ti	V	Cr	Mn	Fe	Co	Ni	Pt	Cu	Pyrex
Recombination Coefficient	0.10	0.15	0.16	0.22	0.17	0.18	0.18	0.24	0.19	7.5×10^{-4}
Percent "d" character*	27	35	39	40.1	39.7	39.5	40	44	-	-

*L. Pauling, Proc. Roy. Soc. A196, 343 (1949)

Atlantic Research

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STRUCTURE AND BURNING MECHANISM OF LAMINAR FLAT FLAMES

Atlantic Research Corporation - Phase 3

R. Friedman, Phase Leader
R. G. Nugent

Introduction

The program to date has been centered on the problem of measuring temperature and composition gradients in low-pressure premixed carbon monoxide flames with small known amounts of either hydrogen or water vapor present. The ultimate objects are to gain understanding of the rate-controlling process in the oxidation of carbon monoxide under flame conditions, and to develop generally applicable techniques for measuring flame reaction rates.

The work naturally divides itself into three sections, the obtaining of traverse data, the primary analysis of these data to yield heat-release and reaction rates, and the final analysis of these rates to define the underlying mechanism. Progress in each of these sections will be briefly described.

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Experimental

Flat flames are stabilized on a burner of 25-cm diameter, at pressures of the order of 20-50 mm Hg abs. Suitable flow-metering, ignition, and vacuum-pumping equipment is utilized. Flame and probe positions are measured through a window with a traveling telescope. The probe may be moved with 6 cm of travel along the burner center-line, by means of a traverse mechanism. Two types of probes are used, a thermocouple probe made of 13-micron wire and a sampling probe consisting of a quartz tube with capillary tip. Other instrumentation includes a precision potentiometer for the thermocouple and a gas-handling system and mass spectrometer (Consolidated Electrodynamics Corporation, Model 21-620) in conjunction with the sampling probe.

To date, traverses of both temperature and composition have been made in two lean $\text{CO-O}_2\text{-H}_2$ mixtures, one of which was adjusted to be 142°C hotter than the other, and two lean $\text{CO-O}_2\text{-H}_2\text{O}$ mixtures, each at the same temperature but with differing H_2O contents. In all cases, the pressure was 30 mm Hg. Some exploratory tests have been made with rich mixtures and at other pressures, but no data have been obtained.

Discussion

From composition-traverse data, the rate of disappearance of carbon monoxide is obtained by suitable mathematical procedures which take into account the diffusion flow. The results may most conveniently be expressed in terms of a first-order decay constant k for the rate of disappearance of carbon monoxide in the "tail" of the flame; k comes out to be of the magnitude 200-300 reciprocal seconds for flame temperatures of the order of 1800°K.

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An independent way of obtaining values for k is by analysis of the temperature distribution to obtain a heat-release rate, and then to convert this to a reaction rate by means of the known heat of reaction. Agreement better than a factor of two has been obtained between the two methods for several mixtures.

Certain trends of interest may be discerned from the results. The most striking is the comparison of reactivity as determined above in a carbon monoxide flame with the reactivity as deduced from the magnitude of the burning velocity of that same flame. The reaction in the "tail" of the flame seems to be an order of magnitude slower than the reaction governing the burning velocity, even after allowance is made for the concentration level of carbon monoxide on the basis of a reaction first-order with respect to carbon monoxide.

A second interesting finding has to do with a comparison of two lean mixtures of the same flame temperature, one containing three per cent hydrogen and the other, three per cent water vapor. In the former, sampling shows that the hydrogen is converted to water early in the flame, as one would expect, but the rate of carbon monoxide "clean-up" in the "tail" of the flame is much faster in the hydrogen flame than in the water-vapor flame, which is unexpected.

A detailed discussion of these findings is presently being prepared as a Technical Report. Future plans call for study of rich mixtures, to find out whether the reaction is really first-order with respect to carbon monoxide, and study of the relative intensity of light emission from the initial highly luminous part of the flame (which presumably controls the flame speed) and the much less luminous "tail" of the flame in which the last of the reaction occurs.

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RESEARCH ON HIGH PRESSURE COMBUSTION

United States Department of the Interior
Bureau of Mines, Region V
Division of Explosives Technology
Pittsburgh, Pennsylvania

Phase 1

Phase Leaders: J. Grumer (1R1), H. G. Wolfhard (1R2)
Investigators: E. B. Cook, T. A. Kubala, M. Vanpee

Introduction

This program seeks to advance the understanding of combustion of explosive gas mixtures. (1) In continuation of established work, burning velocities, peak pressures, end pressures, chemical composition of the burned gas, and expansion ratios are being measured at elevated pressures and temperatures by means of a spherical vessel method. (2) Ignition phenomena are studied which are relevant to the flame-holding of ramjet burners, where fresh cold fuel-air mixture is continuously reignited behind the baffle in contact with hot burned gases.

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DiscussionProblem 1R1 - Determination of Standard Burning Velocities and ExpansionRatios

(1) Burning velocities and their pressure dependence - The immediate interest is in the influence of elevated initial pressure and later of initial temperature on the propagation of spherical laminar flames in a closed vessel. To facilitate this study, a new 8-inch I.D. stainless steel spherical vessel is being constructed to replace the present 12-inch I.D. iron vessel which can be operated only up to about 470 p.s.i. peak pressure. The main sections of the new equipment have been cut. The pressure rise history during combustion will be measured in the new vessel by means of a transducer. Recent experiments with methane-air mixtures in the 12-inch I.D. vessel have shown good agreement between pressure rise data taken by means of the transducer and the heretofore employed mechanical-optical system based on the deflection of a wide diameter diaphragm. New data taken with 10.5 percent methane-air mixtures in the range of 1-4 atm, initial pressure have yielded burning velocity values in good agreement with published values for stoichiometric methane-air mixtures (1). The pressure dependence of the burning velocity of the 10.5 percent methane-air mixtures corresponds to a pressure exponent of minus 0.36 and closely parallels the reported pressure dependence for stoichiometric mixtures at these elevated initial pressures. The data in reference 1 were obtained with a 10-inch spherical vessel. The close agreement between the data from the 10-inch and the 12-inch vessel indicates that a vessel diameter

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effect is not likely to complicate future work with the 8-inch I.D. new vessel under construction.

Other measurements were made with this slightly rich methane-air mixture at initial pressures in the range of 1-4 atmospheres. These were peak pressures, end pressures after cooling of the burned gases to initial temperature, and analysis of the composition of the burned gas. The end pressures and chemical composition of the burned gas indicated that the water-gas shift was being followed as the burned gases cooled to room temperature. The computed equilibrium temperature for the water-gas shift was in the neighborhood of 1200-1500° K. in runs where the theoretical flame temperature averaged about 2200° K.

(2) Expansion ratios - This laboratory has for some time been concerned with the accuracy of the thermodynamic assumptions involved in converting pressure rise and flame growth data to burning velocities. The problem has been approached through examination of existing theory and experimental measurements of expansion ratios. Particular attention was given to the relation between the pressure rise and the fraction of charge burned as the combustion wave traverses the vessel contents. It is now clear that the heretofore employed expression relating these two is inexact. In 1917, Flamm and Mache (2) derived the relation between the pressure rise and the fraction of charge burned as being

$$1 - n = \frac{RT_1(P_e - P)}{P_1 \left[RT_{1u} \frac{\gamma_b - \gamma_u}{\gamma_u - 1} + K(\gamma_b - 1) \right]} \quad (1)$$

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In equation 1, n is the fraction burned, R is the gas constant, K is a constant, γ is the specific heat ratio, T is the temperature, P is pressure, and the subscripts i , u , b and e indicate the initial, ambient, burned and end states of the combustion process. Later, the assumption was made that T_i may be substituted for T_u , changing equation 1 to equation 2 (3, 4).

$$n = \frac{P - P_i}{P_e - P_i} \quad (2)$$

The substitution was justified by noting that it changed the value of $1 - n$ very little. However, for an error of y in $1 - n$, the error in n is $(y/n)(1 - n)$. When measuring burning velocities, small values of n are employed and errors in n result in about equal errors in the burning velocity. In this way, when $n \sim 0.03$, a change in $1 - n$ of 0.3 percent will change n and the burning velocity by about 10 percent.

Instead of the above substitution, T_u has been evaluated when $P/P_i \leq 1.1$, using the information that the rise in pressure in the unburned gas is due to the adiabatic compression of the unburned gas by the expansion of the burned gas formed. In this way, equation 1 has been transformed into equation 3, with an estimated error in n of less than one percent.

$$n = \frac{P - P_i}{P_i \gamma_u (\gamma - 1)} \quad (3)$$

Here, $E = (m_b T_b) / (m_i T_i)$ is the expansion ratio for constant pressure burning at $P_i T_i$; m is mole.

Equations 2 and 3 for the fraction burned are in the ratio to each other of about the ratio of the specific heat ratios of the unburned and burned

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gases--a factor of about 1.1. This 10-percent difference is about the difference in the burning velocity that one gets from these two expressions. The substitution of equation 3 for equation 2 has now been justified both by analytical mathematics and experimentation. The details of these efforts have been included in a new publication from this laboratory on spherical vessel combustion (5).

Problem 1R2 - Study of High Pressure Combustion - The work on high pressure flames was discontinued mainly because A. Strasser, who conducted the experiments of this phase of the program, was no longer available and partly because the ignition work (see below) proceeded more satisfactorily. Dr. M. Vanpee has joined the program.

The ignition of methane-nitric oxide mixtures by pilot flames was first investigated. The results will not be discussed here as they are now available on microcards (6). Supplementary measurements concerning "spontaneous ignition temperatures" of nitric oxide-fuel mixtures are also available on microcards and have been published (7).

As a next step, hydrocarbon-air mixtures were ignited by jets of hot gases which were heated in ceramic furnaces. It was found that the "hot-gas ignition temperature" is a well-defined value which depends on mixture strength and jet diameter, but only little on jet velocity as long as the flow is laminar. No correlation seems to exist between spontaneous ignition

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temperature and "hot-gas ignition temperature." A paper has been written on this subject which is available on microcards (8).

The research now in progress is aimed at a closer understanding of the hot-gas ignition process and its correlation with the problem of flame-holding in ramjet burners. The influence of inhibitors on hot-gas ignition has been investigated. It was found that iron carbonyl and tetraethyl lead have no influence on hot-gas ignition, although they influence spontaneous ignition greatly. Methyl bromide, which influences flame propagation, also increases the temperature of the hot jet necessary for ignition. The close parallel between hot-gas ignition and limit flame temperatures is now further investigated and limit flame temperatures are measured with a spherical diffusion flame arrangement. It is planned to measure hot-gas ignition temperatures also at reduced pressures and to study the kinetic processes in detail.

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4. B. Lewis and G. von Elbe, J. Chem. Phys., 2, 667 (1934).
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INVESTIGATION OF FLAME PROPAGATION AND STABILITY
WITH PARTICULAR REFERENCE TO THE INTERACTION BETWEEN FLAME AND FLOW

Cornell Aeronautical Laboratory, Inc. - Phase 2

G.H. Markstein, Phase Leader
L.M.Somers, H.M.Preston

Introduction

This investigation is primarily concerned with mutual interactions between flow disturbances and flames. Flame structure is studied in the presence of artificial or spontaneous flow disturbances, comprising fluctuations of a more or less random nature as well as pipe resonance oscillations and pressure waves. The experimental methods include still, motion picture, and streak camera photography of flame structure, sampling of burned gases for chemical analysis, oscillographic recording of pressure and radiation transients, use of ionization probes for timing of flame propagation, and smoke or particle tracer techniques of flow visualization. Concurrently, the interaction of flow disturbances with flames is being investigated by methods of perturbation analysis.

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Discussion

Work on preferential diffusion effects and other transport effects across flow lines in curved laminar flame fronts has been started. Steady, two-dimensional cellular flames are being used thus far as a convenient system for this study. A slot burner previously developed for obtaining these flames^{1,2} was slightly modified in order to facilitate introduction of a sampling probe into the flame from the burned-gas side. One modification consisted of reducing the height of a flame enclosure, used for preventing entrainment of air into the burned gas, to 3/4 in. The other one consisted of introducing two steel wires of 1/16 in. diameter into the flame near the flame base, for the purpose of preventing the tendency of the flame cells for irregular lateral motion. These wires were mounted on supports that could be moved along the slot and clamped in any position. By placing one of these wires on either side of the sampling probe, the cells near the probe could be completely immobilized.

Two types of probes were tried for sampling of the flame gases. Quartz capillaries similar to those used by others^{3,4,5} were first employed. While otherwise satisfactory, they tended to close off gradually when exposed to the hot flame gases. Recently an uncooled stainless steel capillary pinched off at the end into a narrow slit has been tried. This probe appears to remain open indefinitely as long as it is not exposed to partially burned oxidizing gases. At present both probe types are being used and their relative merits are being evaluated. The probes are mounted on a slide compound,

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so that traverses along the wavy flame front in the burned gas as well as through the flame front in a normal direction could be carried out.

The analysis of the gas samples is carried out by gas chromatography. Molecular sieve 5A is used as column material for the separation of H₂, N₂, O₂ + A, CO and CH₄. C₂ to C₄ hydrocarbons and CO₂ are analyzed with a silica gel column. The analysis of water is carried out with a partition column of 2-aminobiphenyl on firebrick. Except for the analysis of water concentration, the gas samples withdrawn by the probe are dried and pumped into glass sample flasks at a pressure of 200 mm Hg, and are then pressurized with mercury for introduction into the chromatograph at atmospheric pressure.

A special technique was developed for analysis of water, in order to overcome absorption and adsorption difficulties. For this purpose the gas sample is pumped continuously from the probe through the sample valve of the chromatograph at a pressure of 200 mm Hg. The connecting hoses and the sample valve itself are heated electrically to about 120° C for preventing condensation and adsorption. The temperature of the sample volume on the sample valve is measured with a thermocouple.

As a consequence of a highly nonlinear partition isotherm, water in small concentrations moves much slower through the chromatograph column than at higher concentrations. As a consequence, the chromatogram peaks exhibit a steep rise and very gradual drop, and moreover, consecutive peaks corresponding to samples of the same water concentration taken at constant time

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intervals tend to increase in height and area and approach constant values only asymptotically. Therefore, several samples (usually at least five) are taken at eight-minute intervals until the peaks become reasonably constant.

Calibration of the chromatographs is carried out by means of prepared gas mixtures. The mole fractions of the components of the calibrating mixtures were chosen close to those to be encountered in the flame gas samples. The calibration procedures are in every respect identical with those for analysis of the unknown gas samples. In particular, calibration for water vapor is carried out under conditions of steady flow through the sample valve at 200 mm Hg pressure and about 120° C.

Thus far, measurements of gas composition were carried out on propane and n-butane flames. The equivalence ratio was about 1.50 in both cases. The results obtained by sampling along the flame front about 1.2 mm downstream of the luminous region showed definite shifts of composition between the ridge and the valley of the flame structure. As expected on the basis of the preferential diffusion hypothesis⁶, the carbon-oxygen ratio was somewhat higher at the ridge, and somewhat lower at the valley, than that of the unburned gas. This shift of composition was, however, rather small; the total change between ridge and valley was about five per cent. The oxygen-nitrogen ratio remained entirely unchanged, within the limits of accuracy of measurement. Carbon-hydrogen ratios tended to be too large, both at the ridge and at the valley, compared to those of the fuels, an effect which is as yet unexplained and is being further investigated.

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The most pronounced effect, however, was an apparent shift of the water-gas equilibrium, $\text{CO}_2 + \text{H}_2 \rightleftharpoons \text{CO} + \text{H}_2\text{O}$, between the ridge and the valley, corresponding to a temperature change from about 1800° K at the valley to about 2000° K at the ridge in the case of the butane flame. A similar observation had been made previously by Jost⁵ on polyhedral benzene flames. It is planned to measure the temperature distribution in the burned gas by means of fine-wire thermocouples, in order to determine whether the observed effect is due to real temperature changes or to nonequilibrium conditions.

Preliminary results of traverses normal to the flame front at a ridge and at a valley showed the usual presence of pyrolysis products of the hydrocarbon fuel in the expected sequence. The differences between the compositions at the ridge and at the valley were not very pronounced, the most notable one being a higher maximum of acetylene mole fraction at the ridge than at the valley.

Work on pressure wave - flame front interactions has been continued. Previous studies⁷ dealt with the effect of shock waves on laminar flames of roughly hemispherical shape, so that the characteristic dimension of their structure was the width of the combustion chamber. A two-dimensional periodic structure of smaller scale was impressed on the flames in recent work, by passing them through a grid of parallel wires. The response of this structure to shock wave interaction agreed qualitatively with that predicted by the analysis of modified Taylor instability⁸. Moreover, the disturbance velocity amplitude predicted by the analysis from the known ratio

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of initial distortion amplitude to wavelength, the flow velocity behind the incident shock wave, and the density ratio across the flame front, agreed within 20 per cent with the velocity amplitude deduced from the observed rate of change of flame front deformation.

The results of this work showed further that while an initial period of about 0.3 milliseconds after passage of the shock wave was dominated by the small-scale features of the flame structure, the large-scale flow disturbances that correspond to the overall hemispherical shape of the flame came increasingly into play later on. A rough dimensional analysis was carried out for correlating this result and previous results obtained in the absence of small-scale structure. For this purpose, a dimensionless parameter $\delta U/L$ was computed, where δ is a characteristic response time, U the flow velocity behind the incident shock wave and L a characteristic length. In the earlier work, the radiation emitted by the flame had been recorded, and the time δ was taken as the interval between the beginning of the interaction and the instant of maximum radiation.

The width of the combustion chamber was regarded as characteristic length. The parameter $\delta U/L$ was found to vary by about ± 20 per cent over a range of incident-shock pressure ratios between 1.16 and 1.61. For the work with small-scale disturbances, the interval δ could only be estimated from spark photographs; here, the wavelength of the initial flame distortions was regarded as characteristic length. For this case, the parameter $\delta U/L$ was about half that for the large-scale disturbances.

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The correlation is thus not very good, but may provide a means for estimating the response time of flames of given structure during shock wave interaction. The present correlation was obtained with the same combustible mixture and under similar experimental conditions. It is planned to study the dependence of the dimensionless parameter on density ratio across the flame front and on other variables.

Work on another case of flame front-shock wave interaction has been started in which vortex formation is the most prominent feature. In this case the gas mixture was ignited in the center of the combustion chamber so that the flame front initially was approximately spherical. Interaction of the shock wave with this flame transformed it into a relatively smooth vortex ring and a very fine grained turbulent burning zone in the axial region. As in the case of interaction of shock waves with helium jets or spheres⁹, the displacement of the vortex ring by the shock wave exceeded that derived from one-dimensional theory, but was smaller than that computed on the basis of the full buoyancy effect for the density ratio across the flame front.

A brief account of the recent work on shock wave-flame front interaction has been included in comments to be presented at the Third AGARD Combustion and Propulsion Colloquium.

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INVESTIGATION OF THE BASIC PROBLEMS
ASSOCIATED WITH GASEOUS COMBUSTION

University of Delaware - Phase 2

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Introduction

The objective of this study is to obtain information on the processes occurring in laminar and turbulent gaseous flames. The work has been divided into three main problems: Problem 2R1: An investigation of premixed turbulent flames burning above tubes. The approach is to determine local turbulent burning velocities and rates of burning by chemical analysis and measurement of pitot pressure, and to observe flame structure and behavior in more detail by taking time-photographs of flames at various wave lengths, instantaneous photographs and high speed motion pictures. Problem 2R2: An investigation of premixed turbulent flames burning in ducts. Purpose and approach are similar to those of problem 2R1. Problem 2R3: An

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investigation of the structure and kinetics of laminar flames at various pressures by taking spectrophotometric traverses through flat flame fronts at wave lengths ranging from the near infrared (5.7μ) to the ultraviolet (0.3μ).

Discussion

Problem 2R1 - A Study of Turbulent Flames Burning Above Tubes. The optical study of the open turbulent flame has been continued. The flame was a stoichiometric butane-air flame burning from a 1-inch tube at an average cold stream velocity of 60 ft./sec. and was stabilized by a ring-shaped pilot flame at the tube rim. In (1) it had been reported that the turbulence of the approach stream had a strong effect on the separation of the maxima of the CC- and CH-radiation, indicating that at high degrees of turbulence, especially in the upper sections of the flame, the wrinkled laminar front was not the appropriate model of a turbulent flame. Similar observations have now been made with the CO_2^* (or continuous background) radiation. The maximum of the latter appeared, at higher degrees of turbulence, prior to the maxima of CC- and CH-radiation, which is neither the case with laminar flames nor with enclosed turbulent ones (though in some of these flames the

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points of incipient radiation are in this order (see below)).

The intensity at the maxima of CC-, CH- and CO_2^* -radiation decreased with increasing flame height corresponding to a widening of the flame zone with height. At low turbulence (wrinkled flame front) the decrease was linear and was the same for all three types of radiation. At higher turbulence the behavior was less uniform. Measurements at these conditions were extended beyond the points at which the various radiation maxima occurred in the axis. At these points a sharp drop of the individual radical radiation set in as may be expected.

The radiative flux emerging from the total flame was measured with a Photronic Cell at wave-lengths characteristic of the three radicals mentioned and of the infrared water vapor radiation. All of these types of radiation decreased by roughly 27% on passing from low turbulence via medium to high turbulence. It is intended to check by chemical analysis whether this is due to flame quenching by entrained air or to an influence of turbulence on the chemical mechanism of combustion (2).

Experiments are under way with two-dimensional open turbulent flames burning above rectangular burners between two quartz plates. One of these flames forms an upright wedge which is held at two sides of the burner rim, the other one forms an inverted wedge which is held on a slit pilot flame

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across the opening of the duct. The former flame type will serve to check the effect of burner dimensions on the flame for the case that the scale of turbulence is kept constant by the use of grids.

Problem 2R2 - A Study of Turbulent Flames Burning in Ducts.

The flame studied is a propane-air flame burning in a 2 inches x 1.5 inches rectangular duct of 10 inches length from a flame holder placed between the center lines of the 2-inch walls which consist of quartz. The velocity was 60 ft./sec.; the composition was varied from a fuel equivalence ratio of 0.87 to 1.21; the turbulence of the approach stream was either about 0.5% or about 9%. In (1) the points of incipience of the CH-, CC- and H₂O-radiation, and the points of maximum slope of the H₂O-radiation and of maximum CH- and CC-radiation in the cross-sections of the duct, had been reported. It was concluded from the large distances between these points that these flames burned by way of distributed reaction zones, and it was concluded from the difference between the order of these points and those in the laminar flame that the kinetic mechanism of turbulent burning differs in some respects from that of laminar burning.

The observations of the CO₂*-radiation fit well into this general scheme: In laminar flames the order of incipient radiation is always CO₂*, CC, CH, in turbulent flames CH, CO₂*

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CC except for rich turbulent flame at large distances from the flame holder where the points of incipience of CC and CO₂* coincide. The order of the maxima of radical radiation in laminar flames shifts from CC, CH, CO₂* for lean mixtures gradually to CO₂*, CC, CH for very rich mixtures. In turbulent flames the order is as follows:

	lean	stoichiom. and rich
low turbulence	CH, CO ₂ *, CC	CH, CC, CO ₂ *
high turbulence	CO ₂ *, CH, CC	on the average CH CO ₂ *

It can be seen that the transition from lean to rich mixtures shifts the CO₂*-maximum in laminar and in turbulent flames in an opposite direction, and that an increase of turbulence shifts the CO₂*-maximum in an upstream direction.

Preparations for investigating turbulent flames in a 20-inch duct (as compared with the 10-inch duct presently used) are completed. The Perkin-Elmer Vapor Fractometer needed a number of further improvements of which a built-in thermostat is outstanding. Sensitivity and reproducibility are satisfactory now. The flame in this burner will be studied with all the tools developed (chemical analysis, pitot and static pressure measurement, filter photography and direct and schlieren high-speed motion photography.)

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Problem 2R3 - Spectrophotometric Traverses Through Flame

Fronts. The aim of this project is to follow the radiation intensity due to various emitters while the stream of a combustible gas mixture passes through a steady flame zone. The arrangement used for this purpose is a horizontal flat flame front burning above a cooled porous metal plate at various pressures. It is viewed edgewise by the spectrophotometer and can be shifted normal to the optical axis. The average thickness of the flame zone seen by the instrument has been made for some purposes as small as 0.09 mm.

Measurement of radical radiation which so far had been carried out at 1 and 1/3 atm. has been extended to 1/6 atm. If the pressure dependence of the maximum radiation intensity of the chosen band peaks (which is found at some point in the reaction zone) is expressed by the equation $I = k p^n$ it may be stated that between 1 and 1/6 atm. the exponent n for CH, CO and OH has a value below 1 while for CO_2^* n is found to be 1.3. The higher value of the latter exponent is to be expected since the continuous CO_2^* -radiation is proportional to a collision number while the banded radical radiation is proportional to a concentration. Also the mean width of the zones of radical radiation has been measured. The pressure exponents for the width lie between 0.8 and 1.1. The experiments are being continued, e.g. with the purpose of obtaining decay-curves

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of radical radiation at 1/6 atm.

Measurement of the infrared CO_2 -radiation with the help of a lead telluride cell has started. Quantitative evaluation of the data requires a standardized tungsten ribbon lamp with a sapphire window. Delivery of this lamp was delayed far beyond expectation but is expected very soon.

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BURNING VELOCITY, FLAMMABILITY LIMITS, AND
IONIZATION IN FLAMES

Experiment Incorporated - Phase I

I. R. King and W. E. Meador, Jr., Phase Leaders

Introduction

This investigation is concerned with (a) obtaining accurate determinations of the lean flammability limit and burning velocities near this limit, (b) learning more about the anomalous behavior of carbon disulfide-air flames, and (c) calculating the theoretical reasonableness of certain elementary ion-producing reactions.

Discussion

Problem 1R1 - Burning Velocities and Flammability Limits. This phase of our program was initiated on October 1, 1957, and is concerned with obtaining

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accurate determinations of lean flammability limits and burning velocities near these limits. Justification for such an investigation lies in the wide discrepancy found in existing limit data and in the almost complete lack of burning-velocity data at and near the lean limit. The method of investigation utilizes the flat-flame burner technique previously used in our ionization work. Since this type of burner produces a plane, flat, stationary flame, floating in space, out of contact with any surfaces, it is ideal for investigating limits and burning velocities near these limits. The burning velocity is determined by simply measuring the diameter of the flame (usually from several different points), using a cathetometer or traveling telescope, and the total flow of gases to the burner. The limit of flammability is obtained from a plot of burning velocity versus composition and is taken as the last point (on the lean side) at which it was possible to stabilize a flame. With most of the fuels tested to date, this occurs at a burning velocity of about 4 cm/sec. Whether or not this is the true limit, or simply an apparent limit due to our inability to stabilize flames at velocities much lower than this, is still a point of debate. However, some flames (CO-air for example) have been stabilized at velocities as low as 3 cm/sec.

In determining the limiting fuel-air composition, it is necessary to correct the measured values for the preheating effect. As the gas-air mixture passes through the burner tube, it is heated to some extent by the screens and walls of the burner so that the limit measured is for an elevated temperature. In order to compare these limits with those in the literature (normally given at room temperature) it is necessary to correct the measured values for this preheating effect. White (1) has shown that when a

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gas is preheated, the limit is lowered by an amount equal to the amount of additional fuel that would be required to raise the temperature of the gas-air mixture from ambient to the preheat temperature. Similar observations have been made by Egerton and Thabet (2). Since previous flat-flame burners used a corrugated matrix rather than screens to produce laminar flow, the gas was preheated to a greater degree than in the present investigation, thus necessitating the use of a larger preheat correction. In this investigation it has been found that for all fuels used to date, the preheating effect amounts to only about 50°C.

A comparison of lean limits obtained to date in this laboratory and elsewhere are shown in the following table. All values have been corrected for preheat.

Method	Lean Limit, volume percent	
	Propane	Methane
Tube (3)	2.37	5.26
Flat Flame		
Egerton and Thabet (2)	2.01	5.1
Badami and Egerton (4)	1.89	5.31
Experiment Incorporated	1.91	5.15

In most cases, values obtained using the flat-flame burner technique are considerably lower than those using the conventional tube method.

Burning-velocity curves in the range of 4 to 10 cm/sec have also been obtained for these fuels and compared with corresponding values extrapolated from existing burning-velocity data obtained using other methods. Since the lowest burning velocities obtainable using other methods is only about 20 to 25 cm/sec, the necessary extrapolation covers a fairly wide range and so is

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not very definite. However, the agreement is quite good, and the present points do help to define the complete burning-velocity curve.

The effect of moisture on the lean flammability limit and burning velocity of CO-air flames has also been investigated. For very dry mixtures (Matheson premixed air) a lean limit value of 17.3% CO in total mixture at a burning velocity of 3.15 cm/sec was obtained. With 0.18% H₂O, the lean limit dropped to 15.3% CO at a burning velocity of 3.66 cm/sec, indicating that for this fuel the lean limit is very sensitive to minute traces of water vapor. Burning velocities show a similar effect, that is, an increase with increasing moisture content.

In some of our previous work it was observed that carbon disulfide flames are also quite sensitive to minute traces of water vapor, although in this case water acts as an inhibitor rather than as an additive. Additional tests have shown that these flames are quite sensitive not only to water vapor but to many other hydrogen-containing compounds as well. Some preliminary results, obtained for upward propagation in a 5-cm-diameter tube, are shown below:

Additive	% CS ₂ Necessary for Propagation
0.0%	1.30
0.13% H ₂	1.52
0.50% H ₂ O	1.75
0.13% C ₂ H ₄	3.60
0.34% C ₂ H ₄	3.58
0.13% C ₂ H ₆	3.34

Part of our program is concerned with making accurate determinations of the effect of water vapor on the burning velocity and flammability limits

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of the CS₂-air flame. Because this flame is one of the most difficult of all flames to work with because of its great sensitivity to wall or surface effects, the flat-flame burner offers an ideal method of study since the flame floats in air out of contact with any surfaces. These studies are now underway.

Problem 1R2 - The Source of Ionization in Flames. The purpose of the present research is to investigate the theoretical reasonableness of certain ionized-product reactions taking place under flame conditions, and then perhaps to account for part of the abnormal ionization observed in reaction zones. A typical such reaction would be $\text{CO}^*(A^1 \Pi) + \text{O} \rightarrow \text{CO}_2^+ + e^-$ (where * denotes an excited state), where $\text{CO}^*(A^1 \Pi) + \text{O} \rightarrow \text{CO}_2 + 313 \text{ kcal/mole}$ and the ionization potential of CO₂ is 318 kcal/mole.

The first step in a problem of this sort is to calculate the pertinent potential-energy surfaces for a given reaction. A mass point sliding about on this surface can then be made to represent the analogous motion of the reacting system as a function of the nuclear coordinates. Finally, if the energy surface of the ionized product (say CO₂⁺) crosses or approaches that of the activated complex, the probability of a transition to the ionized state may be calculated quantum mechanically and the result used in a theory of reaction rates.

During the present report period, work has continued on the above reaction with emphasis on the linear symmetrical configurations of CO₂ and CO₂⁺, the outer regions of the surfaces having been completed. Many of the

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difficult three-center integrals for the inner regions have already been computed. A modified Roothaan (5) self-consistent field procedure (molecular orbital theory) is being employed and the complex iterations being performed on the NORC calculator at Dahlgren, Virginia.

In contrast to the work of Mulligan (6) at Catholic University on the ground state of CO_2 at its equilibrium configuration, localized molecular orbitals are being used to describe certain of the electrons. Although Mulligan's method is more general in form than the present one and does not predict localization, reasons for this have been discovered and corrections made. The result is a reduction in the number of variational parameters from fourteen to two (not counting screening constants), an enormous mathematical simplification in view of the exceedingly complicated iterative procedures involved. Recent rough calculations have resulted in orbital ionization potentials that are not far different from those of Mulligan, whenever comparisons can be made.

Furthermore, there are certain preliminary restrictions on several of the screening parameters which are inherent in the present setup and not in the nonlocalized one. This further simplifies the procedure. It is the opinion of this author (W. E. M.) that the net result will be a considerable improvement over all previous work on this molecule. It might be mentioned here that the ideas involved are not restricted to CO_2 , and if the method works, general molecular orbital theory will be considerably simplified mathematically for complex molecules.

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During the remainder of this contract period, it is hoped that the investigation of the $\text{CO}^* + \text{O}$ reaction will be completed, with a publication in the near future on the ground-state energy of CO_2 using the aforementioned modifications.

Preliminary work has also begun on several of the other more promising reactions.

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HIGH OUTPUT COMBUSTION

Massachusetts Institute of Technology - Phase 1

Hoyt C. Hottel and Glenn C. Williams, Phase Leaders
Olav E. Blichner, Noble M. Nerheim, and W. Paul Jensen

Introduction

The studies made under this program pertain to burning rates and mechanisms in well-stirred reactors. In the most recent experimental work the influence of flow characteristics and mixing on overall reactor performance was systematically studied. The object of the present phase of the work is to determine chemical kinetic parameters for several fuels, from measurements of temperature and composition in a new small model of the stirred reactor.

Discussion

Problem 1R1 - Burning Rates in Well-Mixed Reactors. During nine months as a Visiting Fellow at MIT, Mr. Olav Blichner conducted an experimental investi-

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gation of the fluid dynamic features of stirred-reactor performance. His reduction of the data was unavoidably deferred, so that the results of the work have only recently become available here and only in graphical and tabular form. In the absence of a written appraisal of the results by Blichner, it seems advisable in this report simply to indicate obvious features of the results, with the expectation that a SQUID technical report on the subject can be written fairly soon.

In Blichner's work there were three primary objectives: (a) to determine by tests with a readily-controlled feed mixture the effect on blowout flow rates of the size of feed holes in the reactant-feed sphere; (b) to assess the influence on mixing conditions (and thus on blowout) which might result from variations in pressure drop, as required to maintain flow rates; and (c) to determine as clearly as possible the value of "n", the pressure exponent in the loading parameter N_A/\sqrt{P}^n (where N_A indicates moles of air per second, V the reactor volume in liters and P the pressure in atmospheres.) An additional objective, that of visual study of flow patterns in a stirred reactor, was added late in the program and partially realized by brief tests with a vycor-walled cylindrical reactor.

In the main experimental work, a spherical reactor of 4-inch i.d., 7 1/2-inch o.d., and having 80 exhaust holes was made. The reactor was fed by either of two 3/4-inch o.d. inner spheres, one with 24 holes each 0.055 inches in diameter, the other with 80 holes each 0.030 inches in diameter. Earlier work (1) had indicated that, at lean blowout, higher loading was pos-

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sible in the 80-hole feed source when the holes were 0.030" diameter than when they were 0.055. This was presumably because of the faster mixing made possible thereby, - a conclusion at variance with earlier literature (2) claiming that the stirred reactor operates under conditions in which mixing has been eliminated as a factor. In the present work (and not in the earlier work) the total feed hole area was kept constant so that the pressure drop required for a given mass flow rate was the same through either 80 holes or 24. The fuel used was commercial propane, approximately 96% pure.

The present results have been plotted as $N_A/\sqrt{P}^{1.8}$ vs. generalized fuel fraction, F, and equivalence ratio, ϕ , for convenience in comparing with the results of Longwell and Weiss (2) and the MIT work (1). If half a dozen wild points (out of nearly 200) can be ignored, it appears that (a) from a lean ϕ of 0.4 to the stoichiometric value the band covered by Blichner's data for a four-fold range of mass flow rates and for both feed spheres nicely spans the Longwell and Weiss data obtained with isooctane, and lies below Bakcr's data at ϕ 0.65 but decidedly above these at stoichiometric. On the rich side Blichner's blowout points are richer than those of both previous investigations. Blichner's lean (but not his rich) data cover as wide a range on the loading parameter scale as do those of Longwell and Weiss.

Considering the effect of feed hole size on allowable loading the following results are clear: (a) At $N_A/\sqrt{P}^{1.8}$ values between about 1.0 and 3.0, there is no distinction in blowout points due to differences in feed spheres, (b) At higher loading rates and ϕ 's up to about 0.7, the blowout points are

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leaner for the 80-hole feed sphere. These results are most clearly evident in a series of plots showing results with nearly constant mass flow rates, and the maximum difference is somewhat less than 0.1 unit on the ϕ scale.

(c) A transition occurs at $0.7 < \phi < 0.8$ for all mass flow rates, with the performance of the reactor with a 24-hole feed source being consistently superior for the richer mixtures. Near the peak of the curve, data points for the 24-hole source are as much as 20% above those for the 80-hole source and above the Longwell and Weiss curve. (d) Although data on fuel-rich operation are sparse, those available consistently show blowout at richer fuel/air ratios with the 24-hole than with the 80-hole feed.

The data for both feed sources have also been plotted separately to show any influence of mass flow rate on blowout, but it is not possible to discern a consistent trend in this respect, at least none that can clearly show through the scatter of the data.

Blichner has plotted N_A/V , flow rate per unit volume, against the pressure at various values of F for lean blowouts, to determine the best value of the pressure exponent, n . (F is the ratio of fuel actually fed to the sum of fuel fed and the fuel-equivalent of the air). The mean values of n vary from about 1.4 at $F = 0.34$ for both feed sources to about 2.1 at $F = 0.43$ for the 24-hole source and to about 1.9 at $F = 0.43$ for the 80-hole source. These results can be submitted only with reservations. The variation of n with F is quite clearly discernible but any variation from one feed sphere to another is almost completely masked by scatter of the data.

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Problem 1R2 - Study of Global Combustion Kinetics. Studies of burning rates and combustion kinetics in the spherical reactor as developed by Longwell and Weiss are limited to relatively inexpensive fuels because of the large flow rates required. Since significantly smaller models are difficult to fabricate, a modification of the well-stirred reactor has been designed which consists of a 1-inch spherical combustion zone surrounded by a 3/4-inch thick spherical shell of kaolin insulating brick. Two fuel sources of 0.020-inch diameter located on the perimeter of the combustion zone will feed the reactor. The feed sources will be on opposite sides of the sphere, but the flow will be directed away from the center at an angle of about 10° so that the two jets will not impinge at the center. The burned gases will exhaust through numerous small holes in the combustion chamber wall. In order to minimize the heat losses from the combustion zone the reactor will be surrounded by another spherical shell of insulating fire brick, spaced 3/4-inch from the outer wall of the chamber and providing a hot-gas guard zone to keep the outside wall of the reactor hotter than would otherwise be possible. This shell will be about 2" thick and will be pierced with exhaust ports.

Provisions have been made to measure the reactor temperature with a specially modified optical pyrometer. A tube tapered down to an inside diameter of .020-inch at one end will extend from the inside surface of the combustion chamber to the wall of the altitude chamber in which it is housed, a distance of about 14 inches; there it will be sealed to prevent air leaks. The modified pyrometer will then be inserted into the tube from outside the chamber.

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In order that this tube may also serve as one of the feed sources, a seal consisting of an optically flat glass window will be placed between the pyrometer and the feed line leading to the tube. If the temperature of the inside wall of the reactor is uniform, this configuration will represent a black body furnace and, with the pyrometer sighted on the small feed port, the temperature read will be independent of the emissivity of the combustion chamber wall. If there were no heat transfer to or from the combustion zone, this temperature would also be that of the reacting gas.

The main aim in this work will be to make independent determinations of the activation energy, not limited to blowoff conditions but made from temperature measurements and sampling data. Since the temperature and composition are related by the energy balance, only one must be measured if the loss term in the energy balance is calculable. A measurement of both, however, will eliminate the need for reliance on a questionable energy balance.

The relation of the loading factor at blow-off, $(N_a/\sqrt{P})_{B.O.}$, to equivalence ratio ϕ will also be established. This relationship plus sampling data will provide a means of comparing the performance of the two-jet reactor with that of the larger well-stirred reactors. A further comparison will be made by determining n by varying P at fixed ϕ . The "overall" activation energy obtained by fitting the previously proposed reaction schemes to the blow-out curve will be compared with the value of E obtained from the pre-blowout experiments described above. In this correlation, the activation energy should be that value of E which best predicts the blowoff curve according to the

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assumed reaction scheme.

In order to make a comparison between this reactor and earlier versions of the well-stirred reactor, propane has been selected as the first fuel to be investigated. Since the possibility of postulating an actual mechanism should improve if the number of possible species present is decreased, H_2 and CO have also been selected. The mechanisms involved in the H_2 explosion limits have been fairly well established, and while these same mechanisms are not necessarily important for high temperature homogeneous combustion, they should be helpful in selecting a controlling mechanism.

The combustion of CO is not nearly as well understood as that of H_2 , but it has the advantage of reacting much more slowly than hydrogen or hydrocarbons when it is pure. Since the residence time of the gases in the reactor increases as the reaction rate decreases, it appears probable that the effect of "unmixedness" on the pressure exponent, n , would diminish as the reaction velocity decreases. The presence of minute quantities of H_2O or H_2 , however, affects the burning velocity of CO greatly, and the problem of obtaining sufficiently pure CO has not yet been solved.

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IONIZATION IN DETONATION WAVES

Massachusetts Institute of Technology - Phase 3

James A. Fay, Phase Leader
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Introduction

The purpose of this study is to measure experimentally the degree of ionization in detonation waves and to determine whether or not thermodynamic equilibrium is achieved with respect to ion formation. In addition, aerodynamic measurements of the flow in detonation waves are being made to permit a better understanding of some high temperature gas dynamic phenomena.

Discussion

Measurements have been made of the electrical conductance of oxy-acetylene detonation waves at one atmosphere initial pressure with the concentration of acetylene in the initial mixture varying from 30% to 80%. The method of measurement used was described in the Squid Semi-Annual Report dated April 1, 1957. Hot-wire initiation was used for all mixtures except for those with more than 65% acetylene; detonations were initiated in these by detonating an equi-molar oxy-acetylene mixture . . .

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separated from the test mixture by a cellophane diaphragm.

The theoretical gas conductance was calculated using the procedure outlined in the preceding Squid Semi-Annual Report, and includes the following effects:

(a) At 30% and 40% acetylene in the initial mixture the principal species contributing to ionization were H_2O^+ (12.6 ev) and O_2^+ (12.2 ev). At 53% and more acetylene in the initial mixture the important species were $C_2H_2^+$ (11.6 ev) and C^+ (11.265 ev).

(b) The gas behind the detonation wave consisted mainly of H_2 and CO in the mixture range studied. Both of these species have electron collision cross-sections of 10^{-15} cm^2 at temperatures under question, i.e., 3500°K to 4200°K (1), and this value was used in the computation of the electrical conductivity.

Kistiakowsky and Zinman (2) have measured the velocities of the oxy-acetylene detonation waves in the composition range we have used. They found that in the range 60% to 70% acetylene in the initial mixture the measured velocities corresponded to homogeneous rather than total equilibrium behind the detonation wave, i.e., solid carbon was not precipitated behind the wave. Two values of the gas conductance were therefore calculated, one assuming homogeneous equilibrium and the other assuming total equilibrium.

The adjoining graph shows a semi-log plot of the electrical conductance (Σ mhos) against the concentration of acetylene in the initial mixture. At 30%, 40%, and 53% acetylene the experimental values are about a factor of two higher than the theoretical. This could be due to an uncertainty in the electron-molecule collision cross-sections which are not known very accurately. If we assume this discrepancy to be due to the cross-section, then the conductance at 66% acetylene is found to correspond to homogeneous equilibrium which is in agreement with the conclusions of Kistiakowsky and Zinman (2). At richer mixtures the conductance is higher than the theoretical by as much as a factor of

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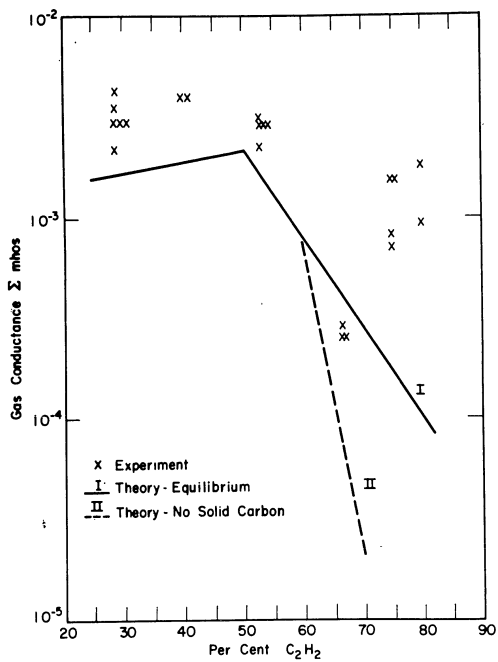
ten. This abnormally high ionization may be due either to the ionization of solid carbon or the formation and ionization of other hydrocarbons with lower ionization potentials than C_2H_2 , such as Benzene (9.3 ev).

The problem of high ionization in rich oxy-acetylene flames has been encountered by Shuler and Weber (3). They attribute it to the formation of small carbon aggregates and polymers in the flame and their subsequent ionization at an ionization potential intermediate between that of graphite (4.35 ev) and atomic carbon (11.265 ev). Some low pressure experiments are now being performed in our laboratory and these may shed some light on the source of the high ionization.

Schlieren photographs of detonation waves in a stoichiometric oxy-hydrogen mixture have been made using a two inch square detonation tube. The photographs show a weak oblique wave, apparently originating from the point of intersection of the wave front with the tube wall, which is stationary with respect to the moving detonation front. The wave clearly shows that the product gas flow is supersonic with respect to the detonation front, having a Mach number of about 1.15, in contrast with the one-dimensional theory which predicts sonic flow. This effect is being studied further.

References

1. Massey, H. S. W., and Burhop, E. H. S., Electronic and Ionic Impact Phenomena, Oxford, 1952, p. 206.
2. Kistiakowsky, G. B., and Zinman, W. G., *J. Chem. Phys.*, **23**, 1889, (1955)
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Electrical Conductance of Oxy-Acetylene Detonation Waves at one Atmosphere Initial Pressure

PHYSICAL PROPERTIES OF VARIOUS TYPES OF FLAMES

Princeton University - Phase 10

Martin Summerfield, Phase Leader
K. P. Hall, E. K. Bastress,
D. Blair, H. J. Taback

Introduction

This research phase is concerned with the physical and chemical properties of flames and the relation between such flame structure and the mechanism of propagation. From a fundamental standpoint, the burning velocity of a flame is determined by the internal processes in the reaction wave. Detailed experimental studies have been proceeding during the past period on two flame types: (1) One-dimensional (flat) laminar flames in premixed gases; (2) Solid propellant flames (with special emphasis on composite type propellants).

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Discussion

Problem 1OR1 - Laminar Flame Speeds in Pre-Mixed Gases. The purpose of this research is to obtain accurate measurements on laminar flame speeds under various conditions and with various combustible media with the object of making systematic comparisons with fundamental flame theory. The experimental apparatus that has been chosen is the Botha-Spalding flat flame porous burner. The main parameters to be varied in the flame speed determinations are: fuel type with air and with oxygen; mixture ratio; combustion pressure; percentage heat removal through the porous disk; chemical treatment of the porous disk surface.

Since the design of the apparatus was guided by a previous detailed analysis of all possible sources of error, we believe that flame speed data having a high order of precision will be obtained. Special design features were discussed in the report of April 1, 1957; and the value of the method (with its heat removal feature) for the investigation of kinetic factors in flame theory was expounded in the report of October 1, 1957.

The status of the project at the present time is as follows: The burner and associated instrumentation have been installed, and the burner has been operated with propane-air flames. Attention during the present period has been directed primarily to refinement of the operating procedure. A major factor requiring detailed attention has been the uniformity

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of the porous plugs through which the premixed gas flows prior to combustion. Porous plugs obtained from commercial sources have shown serious nonuniformities in porosity as measured by pressure traverses made with a pitot tube across the face of the plug. (For the purpose of such traverse surveys, air pressure approximately 10 times as great as the anticipated operating pressure is applied upstream of the plug.) Facilities for fabrication of our own porous plugs under carefully controlled conditions have been installed and the technique of plug manufacture is being evolved. Of the several plugs fabricated to date in this equipment the best show marked improvement in uniformity over the plugs obtained from commercial sources.

This project is being carried out by Mr. David Blair and Mr. E. Karl Bastress, as a joint Ph.D. thesis. Mr. Blair is an instructor and graduate student at Columbia and ultimately will present his thesis to Columbia; Mr. Bastress is a Princeton student. Part of the cost of the project is being borne by a research grant of the Air Reduction Company. Mr. Bastress holds an Air Reduction Fellowship in Aerochemistry.

Problem 1OR2 - The Mechanism of Burning of Composite Solid Propellants.

The purpose of this research is to determine the basic factors that control the burning rates of composite propellants. We have started our research with ammonium perchlorate type propellants. Up to the present time, no theory has appeared that even approximately explains the effect of such parameters as chamber pressure and particle size upon the rate of burning of ammonium perchlorate solid propellants. At the outset,

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It is to be noted that there are important differences in the physical chemical behavior of the various oxidizing salts that have been used in solid propellants, and that different theoretical approaches may be required. For example, ammonium perchlorate differs from the case of ammonium nitrate in that the ammonium nitrate melts prior to its breakdown into gaseous decomposition products, whereas the perchlorate forms its gaseous decomposition products without melting. Undoubtedly this fundamental difference accounts for the great difference in combustion behavior generally observed between these two classes of propellants. We have selected ammonium perchlorate propellants as a starting point because, technologically, these propellants are of greater interest at the present time than are ammonium nitrate propellants, especially in view of such missile developments as Polaris and the many "second generation" solid propellant missiles now under development.

Our approach to the development of a physical model for the ammonium perchlorate propellant flame zone was described in some detail in the semi-annual report of October 1, 1957. Visual, photographic, thermometric, and spectroscopic techniques were employed to clarify our understanding of the structure of the flame zone. The experimental evidence compiled led to the formulation of a model for the combustion process which has been described as a granular diffusion flame.

The essential features of the model are these: Solid phase reaction is not a significant feature of the process. Therefore reaction is essentially gas phase, following thermal gasification ("sublimation"),

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of the solid phase. Unreacted fuel and oxidizer gases enter the flame zone initially unmixed. Oxidizer gases exist as pockets of gas within a sea of fuel gases. The size of each pocket of oxidizer gas is proportional to the size of the oxidizer crystal from which it comes. The reaction zone thickness is dependent upon the time required for two consecutive processes to occur: first, diffusional mixing of fuel and oxidizer gases; then chemical reaction between the mixed gases. The burning rate is proportional to rate of feedback of energy and therefore inversely proportional to the reaction zone thickness. The flame thickness required for diffusional mixing alone is proportional to $1/p^{1/3}$. If the logical assumption is made that the chemical reaction is second order, the flame thickness required for reaction of the mixed gases is proportional to $1/p$. At very low pressures chemical reaction controls, and at very high pressures diffusional mixing controls. The simplest possible mathematical relationship which will have such asymptotic forms at the two extremes of the pressure spectrum is:

$$\frac{1}{r} = \frac{a}{p} + \frac{b}{p^{1/3}} \quad (A)$$

(where a and b are proportionality constants).

Evidence to support this model at the time it was proposed included the following: The flame zone is very thin. Reaction is essentially complete within 0.1 mm of the propellant surface. Experimental burning rate data obtained by Sutherland on several different composite propellants made in our laboratories when plotted in the form $\left(\frac{p}{r} = a + bp^{2/3}\right)$ on a graph having values of $\frac{p}{r}$ along the y axis, and values of $p^{2/3}$

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along the x axis, grouped nicely about a straight line.

During the past period additional burning rate data accumulated on several different propellant compositions by Webb and Taback were tested graphically for conformance to this equation. For all compositions which contained oxidizers having a relatively narrow particle size distribution, the fit was quite satisfactory.

Experimental evidence of a different sort which supports the concept of a gaseous flame zone that controls the burning rate by feedback of energy to the solid surface derives from the research of Reid into solid propellant flame extinguishment. It was found that extinguishment occurred only in well-defined ranges of pressure, and that the process of extinguishment always started at the periphery of the burning surface. Dilution of the gaseous flame by the surrounding atmosphere seems to be the cause. Furthermore, Reid observed, and Taback (during the past six-month period) confirmed under more precise conditions, that even when a propellant strand extinguished after burning for only a portion of its length, the rate at which it burns prior to extinguishment is essentially the same as that observed for a larger strand which burns without extinguishment at the same pressure. This confirms the hypothesis that the process that leads to extinguishment is confined to the periphery of the flame zone, that the central portion of the flame is unaffected, and that therefore the burning rate is not affected by the dilution process.

The most attractive feature of our burning rate law arises from the fact that the parameters a and b may be considered to relate,

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respectively, to the chemical kinetic reaction time and to the inter-diffusion time of the flame gases. Data obtained independently by both Sutherland and Webb did indeed show that the experimentally determined value of b varied in the predicted direction with changes in the oxidizer particle size. However, whereas Sutherland's results showed the expected dependence of a on mixture ratio (the hotter the mixture, the smaller the reaction time), Webb's data seemed to show that a was more affected by particle size than mixture ratio. The most recent data of Taback on the effect of different amounts of Cu CrO_2 catalyst (0, 1/2, 2 1/2%) showed a reduction of both a and b as a result of catalyst addition. In all cases, it should be stressed, the burning rate data were found to fit the theoretical burning rate equation. It is our belief that the unexplained variations of a and b are partly a result of lack of information on the particle size distributions, and partly the result of imperfect propellant processing. Both of these defects can be overcome with certain equipment, which we hope to acquire in the next contract period.

This project is being carried out by Mr. H. J. Taback as an MSE thesis. Dr. K. P. Hall, is helping to guide the research in its laboratory phases.

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THEORY OF DETONATIONS AND FLAME PROPAGATION IN GASES

University of Wisconsin - Phase I

J. O. Hirschfelder, Phase Leader
C. F. Curtiss, Associate Phase Leader

Introduction and Discussion

Our group has been working on the detailed structure and mechanism of detonations in gases considering the one-dimensional steady state systems involving idealized reaction kinetics. This work will continue for a long time.

Work on the system $A \rightarrow s^B$ will be credited to our Squid contract.

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Notes and References

During the past year the following publications resulting from our SQUID research have appeared:

A Contribution to Flame Theory, by G. Klein, Phil. Trans. Royal Soc. London, 249, 389-415

The Properties of Flames Supported by Chain-Branching Reactions, by J. Calvin Giddings and Joseph O. Hirschfelder, J. Phys. Chem. 61, 738-743

Flame Properties and the Kinetics of Chain-Branching Reactions, by J. Calvin Giddings and J. O. Hirschfelder, Sixth International Symposium on Combustion (Reinhold (1957), Structure and Propagation of Laminar Flames (25), 199-212)

Relaxation-Time Model for Free-Radical Concentration, by J. Calvin Giddings, J. Chem. Phys. 26, 1201-1215

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TECHNICAL REPORTS
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Number	Title and Author	Microcard Distr. Date	Other Presentation () Indicates Plans (Jet Propulsion 1958)
BUM-24-P	The Ignition of Combustible Mixtures by Hot Gases, H. G. Wolfhard and A. Strasser	2/58	
CAL-74-P	Shock Wave and Flame Interactions, G. Rudinger	2/58	AGARD Colloquium, Palermo, Sicily, 1958
DEL-7-R	Heat Transfer by Free Convection with Natural Counter-Flow Between Liquid and the Inside Walls of Vertical Passages, S. A. Guerrieri, C. V. Foster, and L. L. Saphier	1/58	Final Report
DEL-8-P	The Study of Flow and Reaction Rates in Turbulent Flames, R. P. Barbor, J. D. Larkin, H. E. von Rosenberg, and C. W. Shipman	2/58	Not known
EXP-6-P	Mechanisms for the Formation of Ions in Flames, H. F. Calocote	1/58	(Combustion and Flame) 1958
JHU-17-P	Optical Auto-Correlation Measurement of Two-Dimensional Random Patterns, L. S. G. Kovaszny and A. Arman	1/58	Review of Scientific Instruments, 28, 793 (1957)
PR-74-R	Experimental Verification of Nozzle Admittance Theory in a Simulated Rocket Chamber, S. Lambiris	1/58	Thesis
PR-75-P	Flame Kinetics as Determined from Flame Speeds, W. H. Clingman and R. N. Pease	-	J. Am. Chem. Soc., 78, 1775 (1956)
PR-76-R	Experimental Studies of Energy Release Rates in Rocket Motor Combustion Chambers, J. V. Charyk and G. B. Matthews	2/58	None

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