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October 1965

AD-473565

PROJECT SQUID

SEMI-ANNUAL PROGRESS REPORT

1 OCTOBER 1965

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UNIVERSITY OF VIRGINIA

Project SQUID is a cooperative program of basic research relating to Jet Propulsion. It is sponsored by the Office of Naval Research and is administered by the University of Virginia through Contract Nonr 3623(00), NR-098-038.

SEMI-ANNUAL PROGRESS REPORT

PROJECT SQUID

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

This report covers the work accomplished
during the period 1 April 1965 to 30 September 1965
by prime and subcontractors under Contract Nonr 3623(00), NR-098-038.

1 October 1965

PROJECT SQUID HEADQUARTERS
DEPARTMENT OF AEROSPACE ENGINEERING
SCHOOL OF ENGINEERING AND APPLIED SCIENCE
UNIVERSITY OF VIRGINIA
CHARLOTTESVILLE, VIRGINIA

FOREWORD

Project SQUID is supported under Contract Nonr 3623(00) by the Power Branch (Code 429) of the Office of Naval Research. The project officers are Mr. James R. Patton, Jr. and Mr. Roland Jackel, Office of Naval Research, Code 429, Department of the Navy, Washington, D. C. 20360. (Tel.: 696-3505).

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FUNDAMENTAL INVESTIGATION OF NONSTEADY AND NONEQUILIBRIUM FLOW

Cornell Aeronautical Laboratory, Inc. - Phase 1

G. Rudinger, Phase Leader

Introduction

This study deals with the extension of theoretical and experimental methods for the analysis of problems involving nonsteady and nonequilibrium flows. At present, two-phase flows are being investigated in which a gas carries along a large number of small particles that are evenly distributed over the cross section of a duct. The temperature and velocity of the particles cannot follow rapid changes of the conditions in the gas, and if the particles represent an appreciable mass fraction of the mixture, their response to the flow changes, in turn, affects the carrier gas. Considerable deviation from equilibrium may occur, and there exists a need to investigate such systems both theoretically and experimentally.

Discussion

The shock-tube experiments to determine the effective drag coefficient under the conditions of two-phase flow have been continued. A small glass shock tube of about 1 cm diameter, as described previously,[1] was completed. Particles were injected near the diaphragm section by means of a syringe injector. The injection rate was measured by recording the time in which the piston of the syringe travels a known distance, and the rate of airflow was measured by means of a sonic orifice, so that the initial composition of the gas-particle mixture in the tube could be determined. Instantaneous particle concentration was recorded by means of light scattering, and the pressure was measured with a conventional transducer. A second, upstream, light-scattering measurement served to check the uniformity of the particle distribution before passage of the shock wave. A second pressure transducer allowed the average shock speed to be measured with a microsecond counter.

Preliminary experiments indicated reasonably uniform particle concentrations for periods of several tens of milliseconds; superposed, high-frequency random fluctuations, produced by the statistical distribution of the particles across and along the duct, could be reduced on the records by a low-pass filter.

The experiments were carried out with spherical glass beads of about 30 μ diameter which were injected at a rate of about 0.7 grams/sec.

Air was introduced into the shock tube at a rate of several grams per second. The resulting initial flow velocity in the shock tube was of the order of 30 m/sec and was high enough to prevent particles from sticking to the wall. The particle-to-gas mass ratio was varied between about 0.16 and 0.24, and the shock pressure ratio between about 1.1 and 1.3.

A number of records were obtained and the relationship between the effective particle drag coefficient and particle Reynolds number evaluated. The resultant correlation differs markedly from both the classical Stokes drag and from the customarily used drag coefficient for single spheres in steady flow, but agreed quite well with preliminary data obtained previously by a somewhat different shock-tube technique.[2]

Although this agreement is gratifying, there are some aspects of the present method that should be clarified before the results can be accepted as correct. From the shock velocity and the initial composition of the gas-particle mixture, it is possible to compute the equilibrium concentration of the particles. This value was found to be consistently lower than that obtained from the light scattering records. Such an effect might be produced by the shock-tube boundary layer, but since its mechanism is not clear at this time, a correction cannot readily be made. For the stronger shocks, the pressure was corrected for boundary-layer effects by subtracting from the recorded pressure rise the rise obtained for the same shock strength but without particles. Because of the uncertainty of these needed corrections, only the early part of the relaxation zone was evaluated where they are likely to be small. Rather than trying to obtain better estimates for the corrections, it seemed preferable to reduce the boundary-layer effects by increasing the size of the shock tube to a diameter of about 2.5 cm. At this size, the required gas and particle flow rates would still not be excessive. Since the developed experimental techniques have proved to be satisfactory for the small tube, no difficulties on this account are expected with the larger one. Such a shock tube is currently being set up.

In connection with the injection of particles into a compressible flow, it appeared interesting to analyze this probelm in a more general form. The analysis is similar to that for heat addition to a gas.[3] As the particles are added to an initially subsonic flow, the flow is modified both upstream and downstream of the region of mass addition in a manner which depends on the gas supply system. A number of relationships for such flows have been obtained, but their significance, for example for pneumatic conveying of small particles, is not yet clear.

A paper on the effect of finite particle volume on the dynamics of gas-particle mixtures, which had previously been submitted to a journal, has been published.[4]

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INVESTIGATION OF TURBULENCE

The Johns Hopkins University - Phase I

Leslie S. G. Kovasznay

Introduction

Following the decision by Project SQUID to terminate the contract by September 30, 1965, we have concentrated on obtaining the maximum results out of the equipment. One problem (A) has terminated and the other (B) will continue on a "no-cost" extension.

Discussion

(A) Instability and transition due to solitary disturbance. The successful series of experiments which were reported during the last progress report were analyzed and very interesting results were obtained.

A laminar boundary layer on a flat plate under zero pressure gradient was excited by a three-dimensional disturbance. The disturbance was small enough so that the boundary layer would not become turbulent at the point of generation of disturbance. The growth of the disturbance was studied.

The experimental results clearly showed a systematic variation of the flow pattern from the distance of the plate. This indicated a gradual phase lag between layers with increasing distance from the wall.

The contours of maximum amplitude ever attained clearly showed the saddle point predicted by theory (Criminale and Kovasznay (1)).

The results were submitted as a part of a Ph.D. dissertation by B. R. Vasudeva. A SQUID Technical Report is in the final stages of preparation.

(B) Plasma turbulence measurement. As already stated in the preceding progress report, rather extensive performance tests of the new, 6-inch I.D. shock tube were conducted using nitrogen as working fluid.

In April, similar though less extensive, tests were made with three other gases--argon, helium, and nitrogen. In these tests the streak camera was again used. Briefly, the speed measurement results were as follows: the wave velocity in hydrogen was the highest (reaching nearly 90 mm/μ sec momentarily at a pressure of 50 μ Hg) followed by helium (about 40 mm/μ sec at 50 μ Hg). Wave velocities in nitrogen and argon were much lower and approximately equal (about 20 mm/μ sec, maximum at 50 μ Hg). As far as Mach numbers were concerned, hydrogen gave the highest, followed by helium, then nitrogen and lastly, argon. E. G., at a pressure of 200 μ Hg, and at a location seven inches downstream of the discharge section, the Mach numbers were approximately: hydrogen 25, helium 18, nitrogen 15, and argon 13.

Streak camera photographs using a transverse slit configuration provide a visual record of the time history of the plasma. Nitrogen only was used in this series. Essentially these pictures show that in the range of variables of most interest the luminous front is immediately followed by a very non-uniform region with a length of the order of half the tube diameter. Following this region is a much more uniform slug of highly luminous plasma of the order of one tube diameter long. Behind this slug the luminosity drops off gradually.

After the foregoing tests it was discovered that five of the eight Pyrex pipe sections in the discharge section of the shock tube were severely cracked. All the Pyrex pieces in the discharge section were then removed so that the walls were now composed of the plastic rings which formerly enclosed the Pyrex pieces. New streak camera tests were made to see if there were any changes in the shock speed and general properties. There were no striking differences although there were some changes greater than the experimental uncertainty.

Magnetic probe tests were made using all four gases. The primary purpose of this series of tests was to select the most suitable gas for all subsequent work. An external magnetic field was provided by a permanent magnet of approximately 350 gauss. The tests showed that helium and hydrogen gave decidedly larger probe signals than argon or nitrogen. Because of its generally better probe signal-to-noise ratio and safer handling properties, helium was chosen as the gas to be used.

A field coil was designed and constructed to replace the permanent magnet in providing the external magnetic field. This coil consists of two independent halves, each of 52 turns, would on a twelve-inch core. One can be placed above the expansion section of the shock tube and the other below it to provide a transverse magnetic field. On the other hand, the two halves can be joined together and placed coaxially over the expansion section to provide a longitudinal field. The larger coil diameter, of course, provides a more nearly uniform magnetic field over a large region of the expansion section.

Current for the coils is provided by four 7.5 microfarad capacitors in parallel. When these capacitors are charged to 10 k.v., the coil produces a transverse magnetic field of approximately 2,000 gauss or a longitudinal field of about 3,000 gauss.

A variable time delay unit was inserted into the triggering circuit so that the field coil capacitors would be triggered first. The shock tube itself is then fired at such a time when the plasma would be moving already through the magnetic field region when the field is at its peak and is almost steady. The ringing frequency of the magnetic field circuit is low enough that the field strength is virtually constant during the passage of the plasma slug. A brief series of tests with helium showed that a transverse magnetic field of approximately 2,000 gauss reduced the luminous front velocity by about 20% at an initial gas pressure of 200 μHg. At 1,000 gauss the effect was much smaller. At a pressure of 500 μHg the effect was below the experimental scatter.

Up to this time, all magnetic probe signals obtained under identical conditions in the shock tube contained some rather reproducible fluctuations that could not be regarded as true turbulence. Therefore, a turbulence-generating grid was built and inserted into the shock tube immediately downstream of the last electrode. The grid was constructed of brass strips set at an angle of attack of 15° with respect to mean flow direction in order to generate vorticity more effectively than by a wire mesh screen.

Luminous front speed measurements were then made with the grid in place, with and without the external magnetic field. The screen, of course, tended to reduce the luminous front velocity and also made it more nearly constant along the tube. The effect is less pronounced at higher pressures and at higher magnetic fields.

Preliminary magnetic probe tests were then made with the grid in place, using helium as the test gas. The resulting probe signals display a larger random component superimposed on repeatable waveform.

Lately, a conductivity probe of the plasma was developed. The method was originally developed by Dr. Gross in his Ph. D. thesis at Harvard University, and it is based on the detuning of an RF oscillator due to conductivity outside the core. A 30 mc oscillator has been built and a 30 mc F. M. discriminator purchased and calibrated. A probe which should be suitable for the conductivity measurement has been built inside a Pyrex tube having an electrostatic shield for the probe. In the immediate future, the conductivity probe will be calibrated and then the conductivity measurements will be made in the shock tube.

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SHOCK WAVE SEPARATION IN GAS MIXTURES

Princeton University - Phase XIII

J. B. Fenn, D. G. H. Marsden, J. H. Chang, A. L. Cooper,
J. B. Anderson, G. Maise

Introduction

This program comprises an investigation of the species separation in small supersonic jets which was reported ten years ago by Becker and his associates in the first of a continuing series of papers (1). The effect, confirmed by Waterman and Stern (2) and by Chow (3) shows up as an increase in the concentration of heavy species, relative to the nozzle gas composition, in the gas withdrawn through a sampling probe immersed in the jet issuing from the nozzle. The generally accepted mechanism for explaining the separation has consisted in the idea that the lighter species migrated from the jet axis at a greater rate than the heavy species resulting in a relative depletion of light species. Early results in our laboratory indicated that at least under some conditions the separation was due to the presence of the probe and could not be accounted for by species migration in the undisturbed jet. We found that when the shock wave caused by the probe was attached to or "swallowed" by the probe inlet the sampled gas had the same composition as the original gas (4). When the shock wave was detached the sampled gas was richer in heavy species than the original gas. Recently, Sherman has examined theoretically the extent to which diffusion processes within the jet can affect the composition of the jet gas (5). He arrived at an equation for center line composition equivalent to the results of an earlier analysis by Zigan (6) and shows that at least on the jet axis the enrichment of heavy species which has been observed experimentally is many times greater than can be accounted for by diffusion in the jet.

Discussion

We are attempting to examine the probe-induced separation effect under conditions which are more tractable analytically than those obtaining with the conical sampling probes first used. We have chosen a hemispherical shape with a very small orifice at the stagnation point. The composition of the gas in the probe is determined by simultaneous pressure measurements with an Alphatron which is composition sensitive and a McLeod gauge which is not. We have established that we can determine a steady state composition of gas in the sampling probe which corresponds to a zero sampling rate. Therefore, we are reasonably confident that we are measuring the composition of the undisturbed stagnation region.

Measurements with a range of helium argon mixtures have shown a pattern of probe-induced separation effects which is very similar to those reported by Reis and Fenn. The concentration of argon in the stagnation region gradually increases with increasing nozzle-probe distances to a maximum value and then falls off to zero. At very large distances we have observed under some conditions so-called negative separation, i. e., an excess concentration of helium instead of argon in the probe gas. These experiments have been done with a range of probe sizes and nozzle sizes as well as gas compositions. We are accumulating a catalog of data from which we will try to extract some general correlations which will hopefully lead to a suitable theoretical analysis.

More recently we have been making measurements with the probe off the axis of the jet. These measurements are interesting and important because they should help establish whether and to what extent there may be diffusive separation in the jet, a question which is still not settled to everyone's satisfaction. By total pressure measurements with pure gases we have found that the Mach number distribution in the jet flow field corresponds very closely to the theory along stream lines as far as 45 degrees from the jet axis. Moreover, the preliminary separation results indicate that for a given Mach number the stagnation zone composition is the same on all streamlines. It would seem, therefore, that the free stream composition is uniform throughout that portion of the flow field which we have so far examined. Of course, we cannot detect nonuniformities less than about one per cent of argon.

We have also continued our study of the anomalously high stagnation thermal recovery factors which we believe are associated with the species separation effect (7). We have found that the maximum recovery factor for a particular probe Knudsen number always occurs when the nozzle gas comprises 12 per cent argon and 88 per cent helium. Results with nitrogen-hydrogen mixtures show a similar maximum at 93 per cent hydrogen and 7 per cent nitrogen. At comparable probe Knudsen numbers the maximum value of the recovery factor with nitrogen-hydrogen mixtures is greater than with argon-helium mixtures, e. g., 1.55 vs. 1.25.

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INELASTIC MOLECULAR COLLISIONS

The University of Virginia - Task Order 1

John E. Scott, Jr., Chief Investigator
John F. Moonan
Harold S. Morton, Jr.
John A. Phipps

Introduction

This research program makes use of molecular beam techniques enabling the examination of individual molecular collisions leading to the transfer of momentum and energy and to chemical reaction. The collision phenomena which can be effected in molecular beam experiments are closely related to those involved in chemical reactions and to those occurring in high speed flight in rarefied atmospheres. The use of an aerodynamic, or nozzle, beam source provides intense beams with attractive properties. In addition, the nozzle beam system provides unique capabilities for the examination of relevant problems in fluid mechanics; e. g., the transition between collision dominated (hydrodynamic) and collisionless (free molecular) channel flows.

Discussion

As indicated previously (1) the distribution of speeds in beams of Argon from a nozzle source have been measured with the mechanical velocity selector as a function of the nozzle source density and the nozzle-skimmer separation distance. Data were taken over the entire range of nozzle-skimmer separation (very small to very large) for each source density. Unfortunately, the bearings on the mechanical velocity selector failed after tests with only three values of the source density had been completed. However, reduction of these data yielded the following results: At a given source density, the transmitted differential intensity distribution (number of atoms per second per unit speed interval entering the detector) becomes more narrow as nozzle-skimmer separation distance increases. At small nozzle-skimmer separation, "skimmer interference" effects result in a rather broad differential intensity distribution. At large nozzle-skimmer separation, translational "freezing" in the freely expanding jet is observed beyond a critical distance which increases with increasing source density.

During the report period, emphasis has been placed on determining the relationship between the transmitted differential intensity and that incident on the mechanical velocity selector. This effort, which is purely analytical in nature, involves the evaluation of the integral of the product of the velocity selector admittance function (determined by selector geometry) and the incident differential intensity over the speed interval transmitted by the selector. If the thermal spread in the incident beam is large, this integral is easily evaluated and has been checked experimentally (2). On the other hand, if the thermal spread is of the same order as the transmitted speed interval, evaluation of the integral is very cumbersome. Such evaluations have been made, however, over a wide range of values of thermal spread in the incident beam. Furthermore, a series expansion approximation of this integral has been shown to agree satisfactorily with the "exact" evaluation. In general, the effect of selector admittance is to broaden the transmitted differential intensity distribution by an amount which increases markedly with decreasing thermal spread in the incident beam. Beam divergence;

i. e., imperfect beam collimation, results in the same effect. Calculations of the influence of beam divergence on the transmitted differential intensity distribution have been made under the assumption that the beam intensity is uniform over the detector aperture. Application of the corrections to the transmitted differential intensity distribution for selector admittance and for beam divergence result in values of the thermal spread in the incident beam which are in reasonable agreement with results obtained in Princeton and in Karlsruhe. Experimental verification of the beam divergence correction is currently under way using more highly collimated beams than have been examined heretofore.

As indicated in the last report (1), Morton has developed a method for computing a more complete set of the properties of the free-molecular orifice flow field as functions of position. These properties include not only the density, streaming velocity and temperature, but also the several elements of the pressure tensor and the components of the heat flow vector as well. This will provide a more complete, once-and-for-all, characterization of the flow field than is presently available. These results will be used to obtain (through numerical integration) Knudsen-number-dependent corrections to the distribution function at points downstream of the orifice through the use of an improved Krook-type collision term, the so-called ellipsoidal statistical model (3), which specifically requires a knowledge of the pressure anisotropy and which permits the Prandtl number to have a value different from unity. Although the machine programming is under way, no numerical results have been obtained as yet. However, preliminary calculations indicate that this somewhat more complicated collision term will provide appreciably better agreement between the theoretically-predicted and experimentally-observed effusion-type beam speed distributions. Experimental data of this type has already been obtained(2

Such comparisons, to be completed in the near future, should be useful in establishing the limits of validity of the Boltzmann-like kinetic equation approach to a wide variety of problems in gas dynamics.

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FUNDAMENTAL STUDY OF DYNAMICS OF GASES AND PLASMAS

Aeronautical Research Associates of Princeton, Inc. - Phase 1

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Introduction

The general purpose of our program is to give a solid theoretical handle on the flows of the multicomponent, chemically reacting gases and plasmas that are of central interest to power generation and propulsion, high-altitude-high-speed flow and space physics.

Kinetic relaxation model equations are constructed and shown to be an approximate form of the lowest order equation of the BBGKY hierarchy (1) (an equation derived without approximation from the Liouville equation). The model equations are also an approximate form of the Boltzmann kinetic equation (an equation which is completely valid only for dilute hard spheres). Generally, in the study of transport properties the approach is to introduce as few approximations as possible in establishing the kinetic equations but then, because of the nonlinearity of the kinetic equations, many approximations are required in the mathematical solution.

Because these approximations tend to be of a mathematical rather than physical nature, the validity and applicability of the deduced transport coefficients are difficult to evaluate. The deduction of transport properties from the relaxation model for the kinetic equation requires most of the assumptions at the stage of obtaining the kinetic equation and not in the mathematical solution which is relatively simple. Consequently, the assumptions are mostly physical rather than mathematical and, as a result, are easier to understand.

Discussion

The kinetic equation employed in this study (2)-(7)

$$\frac{\partial f_i}{\partial t} = \frac{M_i - f_i}{\tau_i} \qquad \text{(no inhomogeneities)}$$

$$M_i = \frac{n_i}{(2\pi R_i T)^{3/2}} \exp\left\{- \frac{(\vec{v} - \vec{u})^2}{2R_i T}\right\}$$

(where u and T are determined by the conservation of momentum and energy laws), requires that the gas be close to equilibrium. The transport coefficients are obtained for an inhomogeneous gas (in steady state) by studying the solutions for times of the order of the size of the inhomogeneity divided by the thermal velocity (L/v_{th}). This is the time required for the weak inhomogeneities to be smoothed out by viscous, conductive, and diffusive dissipation. The assumptions involved in employing the relaxation model are discussed.

The kinetic equations employed require parameters which can be related to physical parameters such as the collision frequency, ratio of specific heats, and chemical reaction rates. The kinetic equation parameters are expressed in terms of the experimental observables, mutual and thermal diffusion, viscosity, and thermal conductivity. For gaseous binary mixtures (either inert or reacting), only three kinetic parameters are needed, so that required relationships between the four experimental observables must be satisfied.

For inert mixtures we have used three kinetic parameters, τ_1 , τ_2 and Γ . The results are summarized as follows:

viscosity $\eta = \tau_1 p_1 + \tau_2 p_2 = kT(\tau_1 n_1 + \tau_2 n_2)$

mutual diffusion $D_{12} = \frac{kTn_1 n_2}{n}\left(\frac{\tau_1}{\rho_1} + \frac{\tau_2}{\rho_2}\right)$

thermal diffusion $D_T = \Gamma kT \left\{\frac{\tau_2}{m_2} - \frac{\tau_1}{m_1}\right\} \frac{n_1 n_2}{n^2}$

thermal conductivity $\lambda = \left(\frac{5}{2} - 2\Gamma\right)k^2 T\left(\frac{\tau_1 n_1}{m_1} + \frac{\tau_2 n_2}{m_2}\right) - \frac{n^3 k D_T^2}{n_1 n_2 D_{12}}$

The temperature T is defined by

$$T = \frac{\frac{n_1}{\tau_1} T_1 + \frac{n_2}{\tau_2} T_2}{\frac{n_1}{\tau_1} + \frac{n_2}{\tau_2}}$$

Thus we have a description of transport phenomena when the temperatures of the two constituents differ. The equation for the viscosity and mutual diffusion are used to obtain $\tau_1(\eta, D_{12})$ and $\tau_2(\eta, D_{12})$. These are used in the equation for D_T to obtain [illegible](η, D_{12}, D_T). Substituting the results in the expression for λ, we obtain $\lambda(\eta, D_{12}, D_T)$. The validity of this relationship has been investigated numerically (8)-(9).

Reacting gaseous mixtures are considered in which either excitation or dissociation-recombination are occuring. The right side kinetic equations, the collision terms, employed for a mixture of O_2 and O are

$$\frac{M_1 - f_1}{\tau_1} + \frac{2K_2 n_2}{n_1} M_1 - 2K_1 n_1 f_1$$

and

$$\frac{M_2 - f_2}{\tau_2} + \frac{K_1 n_1^2}{n_2} M_2 - K_2 f_2$$

where the subscripts 1 and 2 refer to O and O_2 respectively. This description of the chemically reacting gas yields expressions for the observable transport coefficients which have the same form as those for the inert gas mixture but with τ replaced by τ' where

$$\frac{1}{\tau'_1} = \frac{1}{\tau_1} + 2K_1 n_1 \qquad \frac{1}{\tau'_2} = \frac{1}{\tau_2} + K_2$$

Since the temperature dependence of τ differs from that of τ', the validity of the kinetic relaxation model for gaseous reacting mixtures can be checked.

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RESEARCH ON THERMODYNAMIC AND TRANSPORT PROPERTIES OF GASES AT HIGH TEMPERATURES AND PRESSURES

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Dr. J. H. Whitelaw
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Introduction

The research program is concerned with the precise determination of the transport properties of gases and with their utilization for the improvement of statistical-mechanical theories for the calculation of these properties from a small number of molecular constants. The project is co-sponsored by the National Science Foundation.

Discussion

A. First torsional viscometer. This instrument has been reactivated for a short period of time in order to investigate the possibility of the existence of a relaxation effect in liquid water. It has been reported by J. R. Moszynski (Trans. ASME C, vol. 83, 1961, p. 111) that the viscosity of liquid water at atmospheric pressure and 20°C appears to decrease by 2% when measurements are made after a pressure cycle. More precisely, when measurements were made after the instrument had just been filled with water, the value

1.005 cpoise or 0.9840

was obtained. The sample was subsequently subjected to a pressure cycle, consisting in pressurizing it to 340 atm for a day or so and in releasing the pressure to atmospheric. Measurement after that cycle yielded a value of

0.989 cpoise ,

showing a decrease of at least 1.5%.

The preceding observation led to speculations about the possible existence of a slow relaxation process produced in liquid water by pressure cycles. Simultaneously, the explanation was advanced that the effect might be due to an increase in the amount of air dissolved in water caused by the pressure cycle.

We have now repeated the measurements under carefully controlled conditions and ascertained that no such relaxation effects could be detected. We have also ascertained that the viscosity of liquid water is insensitive to the amount of air dissolved in it.

The preceding observations are of importance for the general understanding of the structure of liquids and for the assessment of the suitability of liquid water to serve as a recognized standard of viscosity.

B. Second torsional viscometer. The instrument continues to be used for the determination of the viscosity of binary mixtures at 20°C and 30°C and at pressures of 1 to 30 atm. During the present run we have completed the work on the mixtures

$He\text{-}N_2$; $N_2\text{-}CO_2$; $Ar\text{-}CO_2$; He-Kr.

At present, work continues on the mixture: $Ne\text{-}CO_2$.

C. Third torsional viscometer. The instrument has been brought to full operational conditions and the first series of measurements has now been satisfactorily completed. Several minor difficulties have been encountered and removed, and it can be asserted that the instrument has so far fulfilled all our expectations.

Any one series of measurements must be performed with a fixed spacing between the two plates. This means that the range of values of viscosity which can be determined with a single setting is restricted, because gases of a viscosity higher than a certain flexible upper limit lead to very high damping. Consequently, the number of oscillations per cycle decreases, and the precision declines. The first series was performed with the smallest spacing, because the viscosity of any gas is lowest at room temperature, increasing with an increase in temperature. Thus the full precision can be maintained up to a maximum temperature which is different for each gas. With the present spacing we covered the following isotherms:

CO_2: 25, 30, 50, 75, 100, 150, 180, 200, 210, 250, 300, 400, 500°C

N_2: 25, 30, 50, 75, 100, 150, 180, 210, 250, 300, 400, 500°C

Dry air: 25, 50, 75, 100, 150, 180, 210, 250, 300, 400, 500°C

He: 25, 30, 50, 75, 100, 150, 180, 210, 250, 300, 400°C

Ar: 25, 30, 50, 75, 100, 150, 250, 300°C

Kr: 30, 50, 75, 100, 150, 180, 200°C

Ne: 25, 30, 50, 75, 100, 150, 180°C.

The instrument will now be dismantled, inspected, and re-assembled with the next wider spacing. This will enable us to proceed to temperatures in excess of 500°C, hopefully to 800°C.

A statistical-mechanical analysis of the preceding body of data is now in progress. It can, however, be reported in a preliminary way that the constants σ and ε for a Lennard-Jones potential derived from the preceding data on viscosity do not reproduce the best measurements on second virial coefficients. This confirms that the Lennard-Jones potential is not universally valid. Nevertheless, its use for interpolation purposes seems to be justified.

D. Capillary flow viscometer. Preliminary measurements have been made on the viscosity of nitrogen at -50°C in the new low-temperature thermostat. These measurements extend over a range of pressure up to 170 atm and agree very well with previous measurements made under these conditions. Measurements on this gas and others will be made at lower temperatures.

E. Theory of the thermal conductivity of a moderately dense gas. The work on the subject has been described previously. An article has been prepared and submitted for publication to the J. of Chem. Physics and is being prepared as a Project Squid Technical Report.

F. Non-equilibrium effects in chemical kinetics. In collaboration with Dr. N. Snider of Cornell University a study has been made of the relation between various possible definitions of rate coefficients. A rate equation derived from the Boltzmann equation leads to theoretical rate coefficients which are statistical averages of reactive cross-sections. The distribution functions used in these averages may contain non-equilibrium contributions. The ratio of the forward to the reverse theoretical rate coefficient does not in general equal the equilibrium constant. However, it is possible to re-arrange the rate equation and to obtain rate coefficients which do obey this relation at all times. It is the latter coefficient which the chemist usually measures. These re-arranged rate coefficients depend not only on relative cross-sections but also on inelastic cross-sections. It is believed that account must be taken of these effects in fast reactions.

An article has been prepared on the subject and submitted to the J. of Chem. Phys. The article has also been prepared as a Project Squid Technical Report BRN-14-P, July 1965.

G. Publications. The following papers have been written and submitted for publication:

(1) J. Kestin, Y. Kobayashi and R. T. Wood, The viscosity of four binary, gaseous mixtures at 20 and 30°C. (To be published in Physica).

(2) R. DiPippo, J. Kestin and J. H. Whitelaw, A high-temperature oscillating-disk viscometer. (To be published in Physica).

(3) K. P. Lowley and J. Ross, A Semi-classical theory of rotational excitation of a diatomic molecule by an atom, J. Chem. Phys. Nov. 1965.

(4) K. P. Lowley and J. Ross, A semi-classical calculation of rotational excitation, J. Chem. Phys. Nov. 1965.

(5) N. S. Snider and J. Ross, Non-equilibrium effects in the kinetics of gas phase reactions, submitted to J. Chem. Phys., Project Squid Technical Report BRN-14-P, July 1965.

(6) E. F. Greene, A. L. Moursund and J. Ross, Elastic scattering in chemically reactive systems, an article in "Advances in Chemical Physics", vol. X, ed. J. Ross, John Wiley and Sons, New York, 1965.

(7) S. K. Kim, G. P. Flynn, and J. Ross, Thermal conductivity of moderately dense gases, submitted to J. Chem. Phys., Project Squid Technical Report.

H. Lectures. Professor J. Kestin has been invited to present lectures at Southern Methodist University, the University of Aix-Marseille, the AVA in Göttingen, and the Technische Hochschule in Braunschweig. The latter three will coincide with his sabbatic leave (Feb. 1966 to Aug. 1966) in France; they are in addition to those already announced previously.

Professor J. Ross presented a lecture on molecular beam research at the California Institute of Technology and a lecture on transport properties at the University of Southern California. He also presented lectures at the Gordon Conference on molecular beams and on the physics and chemistry of liquids. He has been invited to spend one semester in 1966 as Visiting Van der Waals Professor at the University of Amsterdam.

K. Move to new premises. The instruments which operate under the direction of Professor J. Kestin will be relocated to the new Physics and Engineering Building (Barus-Holley) of Brown University. Dr. J. H. Whitelaw prepared lay-outs for the new space together with the required specifications. The move will be effected in a way to minimize interference with measurements, and should be completed by the end of the year.

During Professor J. Kestin's absence the work will proceed uninterruptedly under the direction of Mr. R. DiPippo.

MAGNETOHYDRODYNAMICS OF PARTIALLY IONIZED GASES

Massachusetts Institute of Technology - Phase 3

James A. Fay, Phase Leader
W. C. Moffatt
F. W. Fraim
J. B. Workman
F. C. Karins
P. A. Croce

Introduction

The purpose of this research is to study both experimentally and theoretically the important gas dynamic phenomena associated with magnetohydrodynamic propulsion or power generation. The principal experimental apparatus is a gas-driven shock tube which generates a partially ionized gas whose velocity, density, temperature and electrical conductivity duplicates those which might prevail in an actual device. The motion of this gas sample under the influence of magnetic forces is studied. The emphasis of the study is placed on the motion of the plasma rather than on its physical state.

Discussion

The Faraday accelerator, operating as a shock tunnel (as described in

Ref. 1), has been tested at peak field strengths of 28 kilogauss and maximum drive current of 59 kiloamperes. The magnetic field distribution with axial distance in the flow direction is one having a rapid increase to a maximum value followed by a gradual decrease to zero over a distance of about eight tube diameters. Three pairs of electrodes, each about two tube diameters in axial extent, could be connected separately or in parallel to the drive current capacitor bank.

The gas velocity into and out of the accelerator section was measured with an electromagnetic flowmeter (Ref. 2). The inlet velocity was found to agree reasonably well with that calculated in accordance with one-dimensional gas dynamic considerations. For low field strengths and drive currents, the exit velocity was about equal to its theoretically predicted value, but at higher field strengths and drive currents no appreciable increase in velocity was observed. A measurement of the magnetic field induced by the drive current showed that, at high current levels, the current flowed through regions of small magnetic field, giving low thrust.

It was observed that the maximum exit velocity did not exceed the so-called "ionization velocity," which is the velocity of an atom having a kinetic energy equal to its ionization energy. Whether this is a coincidence or a fundamental limit on the operation of such an accelerator is not presently known.

A preliminary investigation of an experiment to study non-linear Alfvén waves in liquid mercury has led to abandoning the proposed experiment.

Although it was found that a probe using a solid-state Hall field element could be used to measure the magnetic field fluctuations caused by fluid motion in a steady applied magnetic field, the "noise" of the applied magnetic field was too great compared with the signal to be measured, even for several field magnets available in the National Magnet Laboratory at M.I.T.

The theoretical study of wall ablation in a magnetic shock tube has been completed and published as a Squid Report (Ref. 3). In addition two other Squid Technical reports on MHD boundary layer problems have been issued (Refs. 4 and 5) as well as a report on measurements in a turbulent MHD flow (Ref. 6) partially sponsored by Project Squid.

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3. J. B. Workman, "Insulator Ablation in Magnetic Piston Shock Tubes," Project Squid Technical Report MIT-39-P, July 1965 (also to be published in Phys. Fluids).
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CHEMI-IONIZATION

AeroChem Research Laboratories Inc. - Task Order 1

A. Fontijn, Chief Investigator
A. D. Freda

Introduction

The main objectives of this program are to establish whether chemi-ionization is a common phenomenon in the reactions of such species as oxygen and nitrogen atoms with a second reactant and to study the mechanism [illegible] such reactions. During the reporting period chemi-ionization was found to occur in a number of reactions not previously studied in this regard. A detailed investigation of some of the "new" chemi-ionization reactions will commence shortly.

Our work on the mechanism of formation of the Vaidya hydrocarbon flame bands emitter has been completed, and a discussion of this work submitted.[1] Interesting incidental observations on CN and NH emission have been investigated in some further detail. These results have now also been reported.[2]

Discussion

During our work on the Vaidya bands[1, 3] it was observed that the CN red, CN violet and NH 3360 Å band systems appeared in emission when NO was added to the O atom-acetylene reaction. In a more thorough investigation of this phenomenon, it was found that if the N atoms in the N-C_2H_2 reaction--which was known to produce these same emissions--were partially replaced by O atoms, a severalfold increase in the intensity of the emissions resulted. These results have been discussed in detail in Ref. 2. They are explained by postulating that O atoms, in their reaction with C_2H_2, more efficiently produce precursors of the CN and NH emitters than do N atoms. It was considered of interest to establish whether a similar enhancement phenomenon occurs for chemi-ion formation in the N-O-C_2H_2 reaction; a study of this system showed no such enhancement. Instead, a gradual decrease in chemi-ion concentration was observed in going from an O-C_2H_2 system to an N-C_2H_2 system.

In our [illegible]arch for further chemi-ion producing reactions, we have now found that such ions are produced in the reaction between active nitrogen (N[illegible]toms) and C_2F_4 to an extent comparable to that found previously[4] in the O-C_2H_2 reaction. Thus, for an N atom concentration of [illegible]0^{14} cc^{-1} an ion concentration of ≈ 10^{10} cc^{-1} was observed. Oxygen atoms also produce ions with this reactant, however, in smaller concentrations, i.e., for an O atom concentration of ≈ 10^{15} cc^{-1}, an ion concentration of ≈ 10^8 cc^{-1} was measured. Evidence of chemi-ion formation in the oxygen atom-diborane reaction has also been obtained, but no quantitative measurements have yet been made on this system. The apparatus used in this study was the Langmuir probe/Wood-Bonhoeffer system described previously,[4] which has now been modified by the inclusion of a light trap (Wood's horn) between the discharge and the reaction tube.

Dr. A. Fontijn presented lectures to the Chemistry Department of the University of Delaware (May, 11, 1965) and the Department of Aerospace and Mechanical Sciences of Princeton University, (June 1, 1965). A talk based on Ref. 1 was given at the September 1965 meeting of the American Chemical Society in Atlantic City, N. J.

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INVESTIGATION OF REACTION KINETICS IN HIGH-TEMPERATURE GASES

Cornell Aeronautical Laboratory, Inc. - Phase 2

G. Markstein, Phase Leader

Introduction

This study is concerned with kinetics and mechanisms of reactions in high-temperature gases. The work has recently concentrated on reactions of metal vapors with oxygen. Specifically, the heterogeneous reaction of magnesium vapor and oxygen on the surface of growing magnesium oxide deposits is currently being investigated. Electronic excitation processes at the surface are studied by measuring electron emission currents and luminescence intensity. Work on the application of both mass spectrometry and an electron beam probe to the investigation of these reactions has been started.

Discussion

Measurements of electron current and of luminescence emitted from magnesium oxide deposits growing by heterogeneous reaction of magnesium vapor and oxygen on the deposit surface have been continued. The work has concentrated on the effects of two variables, oxygen concentration and deposit temperature, on emission current and luminescence. As discussed in preceding progress reports, the deposits were grown on a stainless-steel capillary that could be cooled by passing a flow of nitrogen through it. In this way, the deposit temperature was varied between a maximum of about 450°C without cooling and minimum values slightly above room temperature. The technique of introducing magnesium vapor into the reaction zone has been described previously (1). The pressure of the argon-oxygen mixture was maintained at about 0.5 torr. A conical Lucite condenser (2) was used for collecting the luminescence radiation and transmitting it onto a 1P21 photomultiplier. A shield surrounding the vaporizer prevented thermal and luminescence radiation originating at the vaporizer from reaching the photomultiplier, and served simultaneously as an electrostatic shield against AC pickup in the emission current measurement.

The preliminary observation of closely parallel dependence of emission current and luminescence on oxygen concentration, which was discussed in the preceding progress report, was confirmed by the subsequent measurements. Both variables vanished in the absence of oxygen, rose to a maximum at a low oxygen concentration, and decreased gradually upon further increase of oxygen flow.

However, the maximum of the luminescence occurred at a slightly higher oxygen percentage than that of the current. This result does not necessarily imply basically different mechanisms for the two effects, since the present method of measurement gives average values over a region of the deposit exposed to varying concentration of magnesium vapor. The oxygen-magnesium concentration ratio, rather than absolute oxygen concentration, is presumably the significant independent variable. Thus, the shift of the luminescence maximum to slightly higher oxygen concentration could have been caused by differences in the averaging process for the luminescence and the current measurements, with the former giving greater influence to the central region of the deposit, where the magnesium concentration has its largest value. Modifications of the technique which will allow measurements restricted to a smaller region of essentially constant magnesium concentration are planned for future work.

A complication encountered in these measurements was the occurrence of relaxation effects: the instantaneous responses of emission current and luminescence to any sudden change of oxygen concentration were always larger than their ultimate variations; after the initial jumps, constant values were approached by a relaxation process that lasted several minutes. Moreover, both current and luminescence also changed gradually under constant conditions, due to the growth of thickness of the deposit. Nevertheless, it was possible to obtain meaningful results by selecting in each run a standard condition corresponding to a particular oxygen concentration and the deposit temperature attained without cooling. This condition was reestablished frequently, so that the values corresponding to other oxygen concentrations and temperatures could be referred to interpolated standard values.

The present measurements confirmed earlier results, discussed in the preceding progress report, which had shown that the emission current depended on deposit temperature by an Arrhenius law. The activation energy of about 0.44eV did not vary noticeably with oxygen concentration. The luminescence intensity was found to be much less temperature-dependent, and, moreover, an increase of luminescence level with decreasing temperature was observed under some conditions. The results are as yet somewhat inconclusive, but the observed trends seem to favor a negative temperature coefficient of luminescence for low oxygen concentration and a positive coefficient for high oxygen concentration.

One of the most important independent variables that characterize the heterogeneous reaction process investigated in the present work is the magnesium concentration. However, no satisfactory method for measuring this variable has yet been developed. Work on the use of a mass spectrometer for measuring magnesium concentration has been continued, but has thus far been unsuccessful. Sampling through a heated orifice did not appreciably increase the magnitude of the magnesium peak. Moreover, in the course of attempts to sample gases containing magnesium vapor and oxygen severe irreversible contamination of the ion source was encountered, possible due to formation of magnesium oxide deposits on source electrodes.

While the mass spectrometer, after replacement of the ion source, has continued to be of great value for determining the oxygen concentration in the measurements of emission current and luminescence, the efforts to adapt it for measuring magnesium concentration have been temporarily abandoned.

As an alternative, work has been started on the use of an electron-beam probe, combined with optical spectrometry, for determining the composition of the reacting low-density gas mixture. The electron-beam technique has been used successfully in studies of low-density gas flows (3, 4) and its application for the present investigation seems attractive. Preliminary work has been carried out with a commercial oxide-cathode electron gun that was mounted in the low-pressure chamber of the differential pumping system earlier used for mass-spectrometer sampling. Visual observation of the beam showed that the presence of magnesium vapor could be detected by the emission of green ratiation, presumably due to the triplet at 5167, 5173 and 5183 Å.

Thus, the measurement of magnesium concentration relative to that of argon should be possible by the electron-beam method. A problem encountered in the preliminary tests was deflection of the beam by the AC magnetic field of the vaporizer heating current. Magnetic shielding and modification of the geometry of the electric leads to the vaporizer tube will be used for suppressing this effect. Another difficulty was greatly reduced emission of the oxide cathode when oxygen was admitted to the reaction chamber. Injection of a portion of the diluent argon (or helium) gas into the orifice through which the beam enters the reaction chamber will be tried is a means for preventing oxygen from reaching the cathode.

To complement the experimental work, a theoretical study aimed at formulating detailed models of heterogeneous metal oxidation reactions is being started. Past work in this area has dealt almost exclusively with low-temperature corrosion problems (5, 6), while the extension to high temperature oxidation and combustion of metals is in its infancy. Moreover, the heterogeneous reaction of metal vapor and oxygen on the oxide surface, which is the subject of the present experimental work and constitutes an important mode of metal oxidation, differs fundamentally from the oxidation mechanisms treated in refs. (5, 6). The latter mechanisms concern the reaction of an oxidizing atmosphere with metal covered by an oxide layer. Nevertheless, some of the participating elementary reaction steps, such as adsorption on the oxide surface and ionic transport within the oxide, are common to the two otherwise dissimilar reaction processes, so that their consideration under a unifying viewpoint may be profitable.

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REACTIONS OF IONS AND ELECTRONICALLY EXCITED SPECIES WITH ATOMS AND MOLECULES IN THE GAS PHASE

Esso Research and Engineering Company

M. S. B. Munson and F. H. Field

The research effort in these laboratories supported by Project SQUID was expended in the first half of the fiscal year, and no work has been done since the last semi-annual progress report (dated 1 April 1965).

Since the last progress report, two project reports have been issued: "Reactions of Gaseous Ions XVI. Effects of Additives on Ionic Reactions in Methane" and "Reactions of Gaseous Brønsted Acids".

RESEARCH ON CHEMI-IONIZATION AND ION-MOLECULE REACTIONS IN ELECTRIC DISCHARGES

Rice University - NONR 3623 S-21

Dr. J. L. Franklin, Chief Investigator
Dr. P. K. Ghosh

Introduction

The purpose of this research is to study ion-molecule reactions and chemi-ionization reactions at pressures beyond those ordinarily attainable in a mass spectrometer. By this means we hope to be able to carry out reactions of much higher order than those ordinarily studied and therefore to find products of a quite different nature than those obtained by mass spectrometry. With rare exceptions, mass spectrometers can seldom operate at source pressures above about 100 microns, and in almost all instances the reaction time is limited to a few micro-seconds. By employing an electric discharge, ionic reactions should be observable at pressures up to 100 millimeters and the retention time in the reaction zone increased to the millisecond range. In this way very extensive reactions can be carried out and probably in some systems an equilibrium state attained. In addition to ion-molecule reactions, various chemi-ionization processes will be investigated and especially those brought about by the recombination energy of very active atoms or free radicals. By varying the reactants and the conditions of reaction we expect to be able to determine the rates of such chemi-ionization processes and eventually perhaps to develop an understanding of the rules governing them.

Discussion

In order to carry out this program we will employ micro-wave, glow, and perhaps brush type discharges. At this time we have on hand a microwave generator and have constructed a power supply for the generation of glow discharges. A quadrupole mass spectrometer has been built and is now operable. Preliminary testing has been completed and the instrument appears to be operating according to design. The quadrupole mass filter consists of 4 stainless steel tubes 1" in diameter and 20" long. There is no auxiliary ion source at this time, the instrument employing the discharge as a source of ions. However, the instrument is so designed that an auxiliary ion source can be installed later if it is needed. At present a conical gold plated aluminum sampling cone having a .03" aperture at the apex is used for sampling the ions from the discharge. These are focused by means of an electrostatic lens on the entrance port into the analyzer section. The lens and quadrupole sections are pumped separately. Upon leaving the analyzer section the intensity of the focused ion beam is measured either by means of a Faraday cup and electrometer or by an electron multiplier and electrometer. With this arrangement, the instrument should be capable of handling masses up to 300, with a resolution of 1 part in 100. Preliminary tests show at least a resolving power of 1 in 86. At this time the heaviest molecule that has been employed with the instrument is krypton, the highest of whose isotopes has a mass of 86. Thus the upper limit to the mass observable has not been tested. It should be mentioned that the resolution could be increased to about 1 part in 500 by employing a smaller orifice with, of course, some loss in sensitivity.

The instrument can employ either strip chart recording or it can display the spectrum on an oscilloscope screen and this can be recorded photographically. Scan rates up to one complete mass spectrum per second have been employed satisfactorily with the photographic recorder. A more rapid scan can be obtained by using an electric programmer in place of the present mechanical scanner. At this time such a change does not appear necessary.

In the preliminary studies designed primarily to test the instrument, air has been passed through a micro-wave discharge centered about 6 mm. from the sampling orifice. When pressures of 20 microns were employed the following mass spectrum was obtained:

m/e	Probable Ion	Relative Intensity
14	N^+	40.1
16	O^+	15.0
18	H_2O^+	5.0
28	N_2^+	100.0
30	NO^+	61.4
32	O_2^+	15.7
38+	? perhaps a metastable	3.7
42	N_3^+	19.4
44	CO_2^+ or N_2O^+	5.6
48	O_3^+	1.5
56	N_4^+	1.5
64	O_4^+	1.3

We are at a loss to know how to identify the peak at mass 39 unless it represents a metastable ion or some impurity. All of these peaks are well resolved to the base line. We have started a study of the effect of variables such as power input, pressure, and flow rate upon the various products, but we are unable to report results at this time.

A very cursory study shows a reduction in the intensity of all the ions when pressure is increased. This is probably to be attributed to a reduction in the volume of the discharge zone causing it to retreat from the sampling orifice. The sampling nozzle will have to be re-located in order to correct this difficulty.

CHEMICAL KINETICS AND GAS DYNAMICS OF ATOM AND FREE-RADICAL REACTIONS

Stanford Research Institute - Phase I

Henry Wise - Phase Leader
Y. Rajapakse
K. M. Sancier
B. J. Wood

Introduction

Our studies on the kinematics and kinetics of gases undergoing chemical reaction are related to processes encountered in propulsion systems of advanced design. Some of the problems of importance to gas dynamics include: reactive collisions of atomic species with solid surfaces, gas-phase reactions of uncharged and charged particles, and transport properties of reacting gases. The progress made on some aspects of this program is summarized in this report.

Discussion

Interaction of atoms with solid surfaces. The role of solid-state properties on the reactivity of solid surfaces with gaseous species represents an important aspect of the ablation problem. In order to explore the relationship between bulk electronic properties and surface kinetics, we have extended our measurements from graphite[1] and germanium[2] to silicon. The reaction studied is the formation of a diatomic molecule of hydrogen by the catalytic recombination of atoms. Similar to the observations for germanium, the catalytic efficiency of several etched silicon crystals was found to be independent of electronic carrier type and carrier density over a range of doping levels extending from p-type (10^{20} holes/cm^3) to n-type (10^{20} electrons/cm^3).

Some progress has been made in developing a pulse-technique for the study of surface-reaction kinetics. The principle of this technique is based on a diffusion model in which the source of gaseous reactant is located at one end of a cylinder and the reactive solid at some distance from the source. After establishment of steady-state conditions within the system, the supply of reactant is cut off. In a theoretical analysis of the non-steady-state diffusion equation, the rate of disappearance of reactant is shown to be a measure of the reactivity of the solid. Application of this pulse technique might employ ESR (electron-spin resonance) to follow the decay in reactant density as a function of time for such species as atoms and radicals which possess an unpaired electron. The principle of the method may also find application in the measurement of diffusion coefficients of atoms through complex multicomponent mixtures.

Homogeneous, gas-phase kinetics involving atoms. The kinetics of atom recombination by three-body gas-phase reaction have been measured in recent years by shock-tube experiments. As a result, the available data apply primarily to high temperatures needed for the production of the atoms in the shock tube. At lower temperatures, on the other hand, little information is available on the kinetics of such reaction in the presence of different third bodies. We have completed some experiments of the rate of hydrogen atom recombination at room temperature and total gas pressures up to 10 torr. As pointed out in a previous publication,[3] the atom flux to a catalytic probe approaches in the high-pressure limit a value which is independent of the probe's catalytic activity but inversely proportional to the reaction rate constant k_1 for the homogeneous recombination process. At the present time, the experimental results are being analyzed and the third-body efficiency determined.

Transport properties of reacting gases. As reported[2] the effective thermal conductivity has been determined for gas mixtures containing atomic and molecular oxygen in the presence of an enthalpy flux due to surface reaction. The temperature-jump analysis associated with the interpretation of the experimental data has led to an evaluation of the thermal accommodation coefficient α of oxygen molecules and atoms colliding with a surface composed of a silicon-monoxide coating on a tungsten filament. These results are summarized in Table 1. It will be noted that α tends to decrease with increasing atom density, an effect undoubtedly associated with the loss of the internal degrees of freedom of the molecule. Also as a consequence, the ratio of temperature-jump distance to mean-free path increases from a value of about 15 for molecular oxygen to 130 for atomic oxygen. A manuscript describing these studies has been prepared.[4]

Table 1

TEMPERATURE-JUMP FUNCTION AND THERMAL ACCOMMODATION COEFFICIENT OF O/O_2 GAS MIXTURES

Mole Fraction of Atoms	Temperature-Jump Function* $g' \times 10^{-2}$ ($g.\ sec^{-2}$)	Accommodation Coefficient α
0	1.16	0.17
0.05	1.55	0.15
0.10	2.28	0.13
0.15	2.82	0.13
0.20	3.44	0.12
0.30	4.38	0.12
1.00	(11.5)**	(0.01)**

* Temp.-jump distance $= g = g'/P = \dfrac{2-\alpha}{\alpha} \; \dfrac{(2\pi M RT)^{\frac{1}{2}} \lambda}{2 C_v + R}$

(cf. E. H. Kennard, <u>Kinetic Theory of Gases</u>, McGraw-Hill Book Co., New York, 1938).

** By extrapolation of experimental results.

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SOLID-PROPELLANT FLAME MECHANISMS

Atlantic Research Corporation - Phase 4

R. Friedman, Phase Leader
A. Maček
J. M. Semple

Introduction

The objective of this program is to gain basic information pertinent to solid-propellant combustion mechanisms by studying combustion of single metal particles (aluminum and beryllium) injected into flame gases of known temperature and composition.

Discussion

The study of combustion of pure spherical beryllium particles, 25 to 35 μ in diameter, in high-temperature gases, generated by the gas burner described in previous reports, has continued.

The primary emphasis has been on observation of various combustion phases by means of two optical techniques, specially developed for studies of details of particle combustion mechanisms. The hot gases, into which single metal particle are being injected are mostly dry, generated by combustion of CO in O_2, containing relatively large (10-40%) amounts of excess O_2, and having temperatures which range from 2750° to 2950°K. An attempt has also been made at a study of beryllium particles burning in the presence of water, but moist gas temperatures attainable by the available equipment were somewhat too low to allow a detailed study. Modifications of the burner necessary for such a study may become desirable in the future.

The first optical technique, employing magnified photography previously developed for the study of fine details of aluminum particle combustion (1), has now been applied to a study of burning beryllium particles, and it has revealed many interesting features of the process. The ignition time is not nearly so sharply defined as in the case of aluminum. While in the case of aluminum the time necessary for the full development of a flame is usually 0.1 msec or less, in the case of beryllium particles of comparable sizes the corresponding time varies from 0.2 to 0.5 msec. Tracks of brightly burning particles (fully developed flame) are about 40 microns wide, while the typical width of the glowing particles both before ignition and after burnout is about 30 microns, indicating that the metal flame stands rather close to the surface of the particle. On the other hand, the diffuse luminosity which surrounds the particle during its burning time (usually 1.5 to 3 msec), which presumably comes from clouds of freshly formed finely dispersed beryllium oxide, measures up to 400 microns in diameter. Quantitative data of this sort -- burning time, particle diameter, flame diameter, BeO cloud size -- have been obtained over a range of ambient gas compositions and temperatures. These results support our previous conclusion that beryllium burns in a vapor-phase flame, part of the oxide condensing from the gas phase as a fine "spray" (diameter of the order of 1 μ), and part on the original particle. The magnified photography, however, has also revealed that combustion is not strictly spherically symmetrical, because high-resolution photographs of burning particles in flight, as a rule, do show a slight periodic variation in light intensity at frequencies of the order of 10^4 rps, which is the result of particle rotation. This asymmetry is analogous to, but very much less pronounced than, the one observed in the case of aluminum. Even at very high oxygen contents in the ambient gas (30% or more), there is little evidence of sudden direction changes in the path of the particles, and no spectacular fragmentation characteristic of combustion of aluminum in oxygen-rich atmospheres.

The second optical technique, aimed toward obtaining time-resolved spectra of single burning metal particles is now under development. The principle behind this technique is that the straight narrow track of the burning particle, obtained by photographic time-exposure, both eliminates the need of a slit and provides for time-resolution. For this purpose a newly acquired optically fast (f/4.5) Hilger-Watts Raman prism spectrograph with quartz optics, covering the spectral range from 2000 to 8000 Å, has been modified in two ways. First, its lens system has been arranged so as to allow focusing on the burning metal particle. Second, an arrangement of mirrors has been constructed which allows one to obtain the direct (undispersed) photograph of the particle on the spectrogram simultaneously with the dispersed spectrum, a feature which should greatly facilitate interpretation of particle spectra. A few attempts have been made to apply this system to combustion of aluminum particles, which are appreciably more luminous in the visible than beryllium particles. The preliminary results of this study are encouraging, because the aluminum vapor lines, 3944 and 3961 Å, are visible in some single-particle spectrograms. The main purpose of this avenue of approach is to follow the appearance and disappearance of various pertinent species (Be, Be^+, BeO) during combustion of beryllium particles, because such information would greatly increase our knowledge of their combustion mechanism. Be and Be^+ have strong lines in the ultraviolet, at 3321 and 3130 Å respectively, and BeO has a prominent band system in the blue-green.

The immediate future plans, besides further development and application of the spectroscopic technique, include theoretical calculations of beryllium particle combustion based on the assumption of vapor-phase burning of the metal. Such a calculation appears appropriate at the present time because of the availability of newly acquired data on beryllium particle burning times and approximate particle and flame radii. Also, all our results so far indicate that beryllium particles do indeed burn by a vapor-phase mechanism and in a fairly uniform fashion (no violent bursts of vapor expulsion, fragmentation, etc.).

We have been invited to submit a paper for presentation at the Eleventh International Symposium on Combustion, and we plan to do so. The subject of the invited paper will be combustion of beryllium and aluminum particles.

Reference

1. A. Maček, R. Friedman, and J. M. Semple in Heterogeneous Combustion (Progress in Astronautics and Aeronautics, Vol. 15), pp. 3-16 Academic Press, 1964.

V. INDEX BY CONTRACTOR

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APPENDIX A

TECHNICAL REPORTS

1 April 1965 - 31 September 1965

Semi-Annual Progress Report

REPORTS SINCE 1 APRIL 1965

Number	Title and Author	Report Dist. Date	Other Presentation ( ) Indicates Plans
AC-2-P	Mechanism of Chemiluminescence of Atomic Oxygen-Hydrocarbon Reactions. Formation of the Vaidya Hydrocarbon Flame Bands Emitter - Arthur Fontijn	6/65	J. Chem. Phys., Vol. 43, No. 5, pp. 1829-1830 Sept. 1965
AC-3-P	Mechaninism of CN and NH Chemiluminescence in the N-O-C_2H_2 and O-NO-C_2H_2 Reactions - A. Fontijn	6/65	(J. Chem. Phys.)
BRN-14-P	Non-equilibrium Effects in the Kinetics of Gas Phase Reactions - Neil S. Snider and John Ross	8/65	(J. Chem. Phys.)
BRN-15-P	Thermal Conductivity of Moderately Dense Gases - S. K. Kim, G. P. Flynn and J. Ross	10/65	(J. Chem. Phys.)
HUM-12-P	Reactions of Gaseous Ions XVI. Effects of Additives on Ionic Reactions in Methane - M. S. B. Munson and F. H. Field	6/65	(J. of Amer. Chem. Soc.)
HUM-13-P	Reactions of Gaseous Brønsted Acids - M. S. B. Munson	8/65	(J. of Amer. Chem. Soc.)
MIT-36-P	Approximate Solutions for Skin Friction and Heat Transfer in MHD Channel Flows - W. Craig Moffatt	7/65	ASME-AIChE Heat Transfer Conf. & Exhibit, Los Angeles, 8-11 Aug. 1965
MIT-37-P	The Validity of Integral Methods in MHD Boundary Layer Analyses - J. B. Heywood and W. Craig Moffatt	7/65	AIAA Journal, Vol. 3, No. 8, pp. 1565 - 1567, Aug. 1965
MIT-38-P	Experimental Measurement of the Growth of a Turbulent Mercury Jet in a Coaxial Magnetic Field - Miklos Sajben and James A. Fay	8/65	(J. Fluid Mech.)
MIT-39-P	Insulator Ablation in Magnetic Piston Shock Tubes- J. B. Workman	8/65	(Physics of Fluids)
UVA-7-P	Mixing and Combustion of a Supersonic Fuel Jet and and a Subsonic, Coaxial Gas Stream - J. E. Scott, Jr.	8/65	2nd Annual Mtg. of AIAA 26-29 July 1965, San Francisco

UNCLASSIFIED

Security Classification

DOCUMENT CONTROL DATA - R&D

(Security classification of title, body of abstract and indexing annotation must be entered when the overall report is classified)

1. ORIGINATING ACTIVITY *(Corporate author)*

Project SQUID
Department of Aerospace Engineering
School of Engineering and Applied Science
University of Virginia, Charlottesville, Va. 22901

2a. REPORT SECURITY CLASSIFICATION
UNCLASSIFIED

2b. GROUP
N/A

3. REPORT TITLE

PROJECT SQUID SEMI-ANNUAL PROGRESS REPORT - 1 October 1965

4. DESCRIPTIVE NOTES *(Type of report and inclusive dates)*
N. A

5. AUTHOR(S) *(Last name, first name, initial)*

Fay, J. A.	Franklin, J. L.	Markstein, G.	Sandri, G.
Fenn, J.	Friedman, R.	Munson, M. S. B.	Scott, J. E., Jr.
Field, F. H.	Kestin, J.	Ross, J.	Wise, Henry
Fontijn, A.	Kovasznay, L. S. G.	Rudinger, G.	

6. REPORT DATE
October 1965

7a. TOTAL NO. OF PAGES
74

7b. NO. OF REFS
54

8a. CONTRACT OR GRANT NO.
Nonr 3623(00)

b. PROJECT NO.
NR-098-038

c.

d.

9a. ORIGINATOR'S REPORT NUMBER(S)
Project SQUID Semi-Annual Progress Report 1 October 1965

9b. OTHER REPORT NO(S) *(Any other numbers that may be assigned this report)*
N/A

10. AVAILABILITY/LIMITATION NOTICES

Qualified requesters may obtain copies of this report from DDC

11. SUPPLEMENTARY NOTES
N/A

12. SPONSORING MILITARY ACTIVITY

Office of Naval Research
Power Branch, Code 429
Department of the Navy
Washington, D. C. 20360

13. ABSTRACT

Reports of progress during the past 6 months on 13 research programs comprising Project SQUID are presented. The research programs fall into the areas of Fluid Mechanics, Transport and Transfer Processes, Chemical Kinetics, and Combustion Phenomena. Project SQUID is a cooperative program of basic research relating to Jet Propulsion, administered by the University of Virginia and sponsored by the Office of Naval Research.

14. KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
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Fluid Mechanics						
Transport and Transfer Processes						
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