# PART 1. AN INVESTIGATION OF RELAXATION PROCESSES

# PART 2. STUDIES IN COMBUSTION

Thesis by

Theodore A. Jacobs

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To the Memory of M. B. J.

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# ABSTRACT

## Part 1

I The rate of the homogeneous thermal decomposition of $NH_3$ in $NH_3$-Ar mixtures has been measured in a shock tube by monitoring the radiation emitted by the $NH_3$ in the 3 micron wavelength region. For the temperature range 2000-3000°K an apparent activation energy of about 52 Kcal was found.

II The vibrational relaxation of isothermal, dilute gas mixtures after excitation by an external radiation field has been investigated, leading to a proposed experiment for the measurement of collision transition probabilities.

## Part 2

I A review of recent papers in the field of combustion has been prepared for the 1960 Edition of Annual Reviews of Physical Chemistry.

II An approximate theoretical performance evaluation for a diverging rocket has been performed. A paper describing the evaluation has been published in Astronautica Acta.

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# PART 1. AN INVESTIGATION OF RELAXATION PROCESSES

The process by which a physical system adjusts itself upon disturbance so as to approach a state of equilibrium is termed relaxation. In Section I we report on our investigation of a particular chemical relaxation process; ammonia, initially at room temperature, is suddenly heated to a temperature of 2000-3000°K and proceeds to decompose, approaching an equilibrium state in which it has reverted to its elemental constituents. In Section II the vibrational relaxation of an absorbing gas, when suddenly immersed or removed from a radiation field is considered.

## I. SHOCK TUBE MEASUREMENTS OF THE RATE OF HOMOGENEOUS DECOMPOSITION OF $NH_3$ in $NH_3$-Ar MIXTURES

### A. Introduction

The kinetics of the heterogeneous thermal decomposition of $NH_3$ have been studied in great detail and a voluminous literature is available on this subject.(1) Little information is available, however, concerning the homogeneous reaction rates. In an early paper, Hinshelwood and Burk(2) investigated the homogeneous decomposition and noted that no measurable reaction occurred up to temperatures of about 1500°K. More recently Sage,(3) using a ballistic piston, has observed the reaction to proceed at temperatures between 1500 and 4500°K although no rate data were derived from these measurements.

The advent of the shock tube and "fast" infrared detectors has now made possible a method for the measurement of the homogeneous decomposition rate. In this paper we report the results of preliminary activation energy measurements for the homogeneous decomposition of $NH_3$.

The use of the shock tube for emission measurements has been described by several authors.(4-8) The present investigations are probably the first published data on reaction-rate measurements using infrared emission. Many shock tube rate measurements have, however, been made by monitoring light intensities in the visible and ultraviolet regions of the spectrum.(9-14) If it is assumed that radiative equilibrium is attained in times short compared with the chemical decomposition times after the passage of the shock wave and, furthermore, that the $NH_3$ behaves as a transparent gas, then it is possible to measure the change in $NH_3$ concentration directly by following the infrared emission intensity as a function of time. Radiation of intermediates may be minimized by measuring only the initial concentration changes.

Rough calculations, based on the absolute intensity data of McKean and Schatz(15) indicate that the most advantageous band for a shock tube study, considering available detectors and window materials, is the one centered at 3 microns. For judiciously chosen optical depths, the assumption of transparency may then be shown to be quite reasonable.

Because of the low specific heat ratio of $NH_3$, it is impossible to achieve sufficiently high temperatures for initiation of the decomposition by shock-wave heating of the pure gas. For our rate studies 1% $NH_3$ - 99% Ar and 8% $NH_3$ - 92% Ar mixtures were used.

## B. Experimental Equipment

### 1. The shock tube and gas-manifolding systems

The basic features of the shock tube used for experimental measurements are indicated in Figs. 1 and 2.

The low pressure end of the tube was constructed of commercial square tubing (3-1/4 inches on a side internally and 5/8 inch thick). The length from the plane of the diaphragm to the end plate was originally 114 inches but this was later increased to 142 inches in an effort to extend the testing time. The interior of the tube was sand blasted but no further effort was expended in obtaining a smooth surface. However, shock velocity measurements made using four thin-film heat gages showed that shock wave attenuation in the range of Mach numbers from 5 to 6 was only about 3% over a distance of approximately 70 cm.

The high-pressure section of the shock tube was constructed from commercial thick-walled, round tubing of 4-1/2 inches inside diameter. The length of this section was 74 inches. In a transition section approximately 2 inches long, the round cross section was tapered to a square cross section that matched the low pressure end of the shock tube. This section of the shock tube was hydraulically tested to 3000 psi.

The individual component sections of the shock tube were flanged at both ends; sealing between mating flanges was accomplished by means of O-rings lubricated with Apiezon type M vacuum grease. The entire exterior surface of the shock tube was painted with red lead primer paint to minimize rust accumulation.

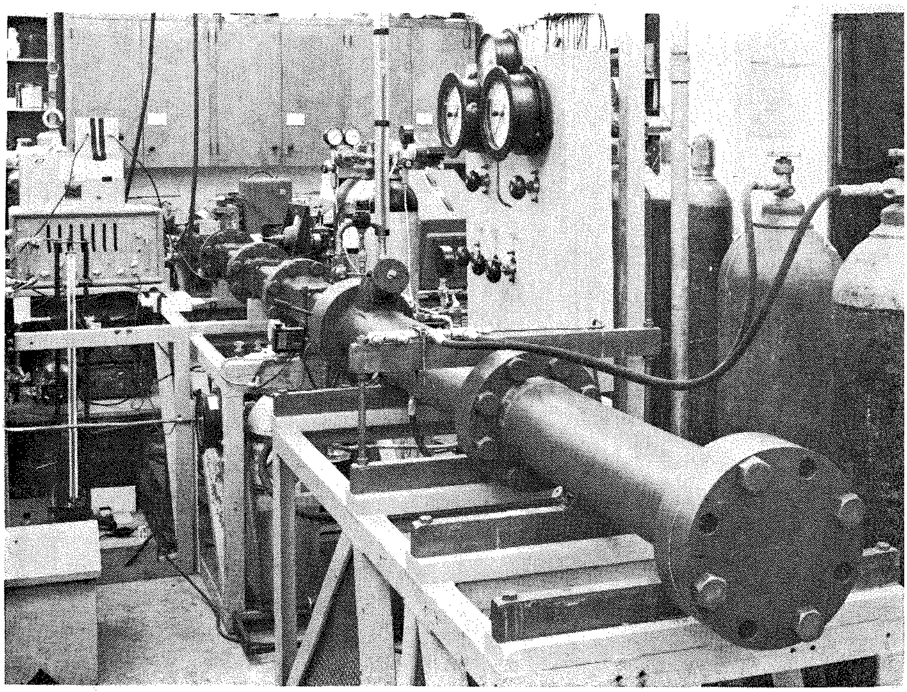


Fig. 1. The shock tube and associated equipment.

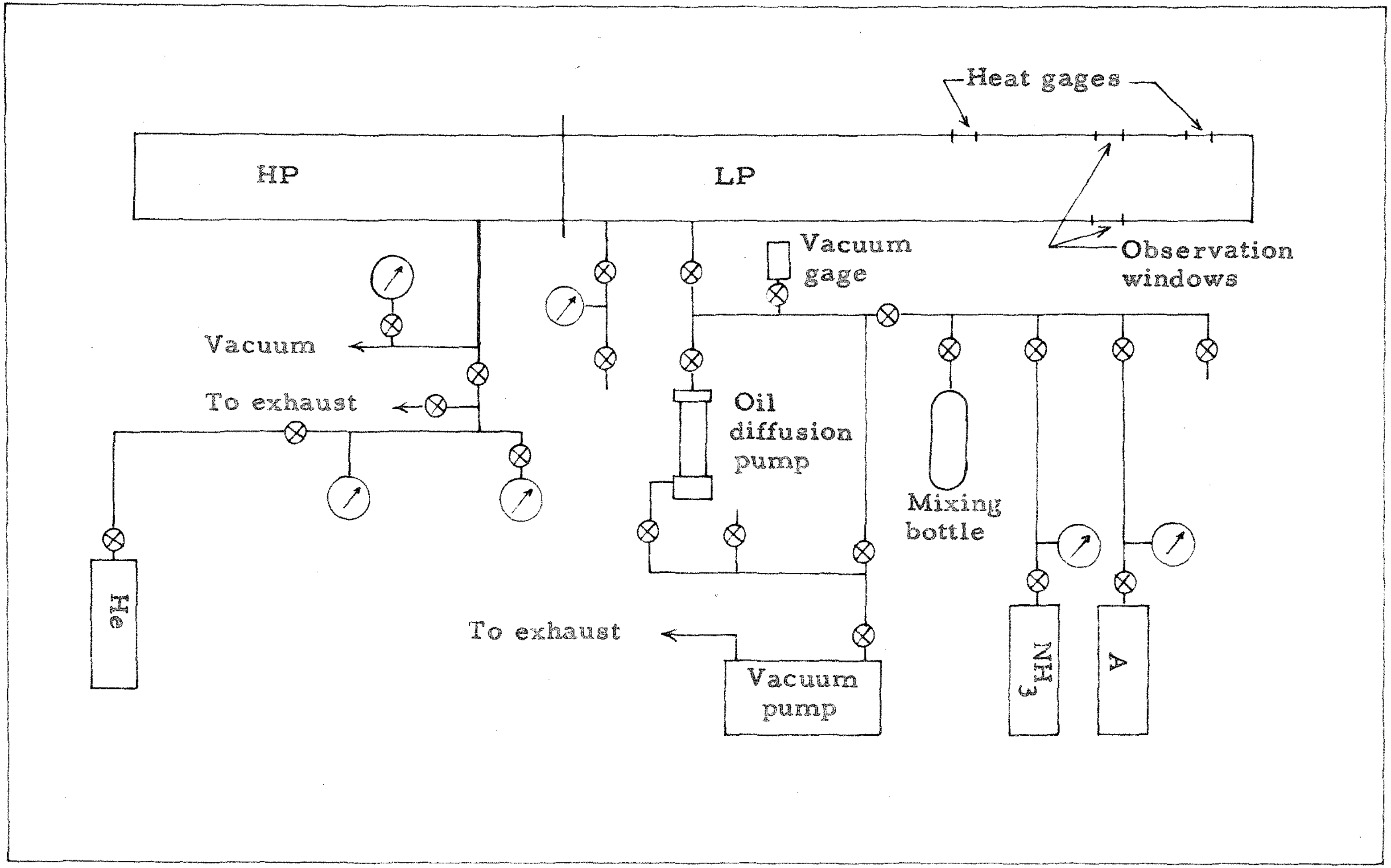


Fig. 2. Block diagram of the shock tube and the associated manifold system.

Accommodations for observation windows and thin-film heat gages were provided at several positions along the low-pressure end of the tube. Fig. 3 is illustrative of a typical window mount. Windows were constructed from synthetic sapphire ($A\ell_2O_3$) and periclase (MgO). These materials were selected for their good transmission characteristics throughout a wide range of the spectrum. An end plate was constructed with a sapphire window for axial observation in the shock tube. Epibond No. 104 furane resin was used to cement the windows to the mounts.

Provision was made in the high-pressure section for the mechanical piercing of diaphragms; however, this method of shock initiation, which was intended to be used with copper diaphragms, was not employed. After considerable experimentation it was decided to abandon copper in favor of some material that would not require careful scribing for consistent results and that would produce less scratching and abrasion of observation windows. The material finally selected was DuPont Mylar which was available in thicknesses ranging from .001 to .010 inch and which could be stacked to obtain any desired thickness and strength. Mylar diaphragms were not scribed, and bursting was accomplished simply by raising the driver pressure. Shock velocity measurements showed that Mylar gave results that could be reproduced with a precision of better than 1/2%.

The gas manifold for the low pressure end of the tube was designed for handling of test gases and evacuation of the system. It was fabricated from Mueller Brass Company solder fittings and copper tubing. A saturated aqueous solution of $ZnC\ell_2$ was used as a solder flux with no

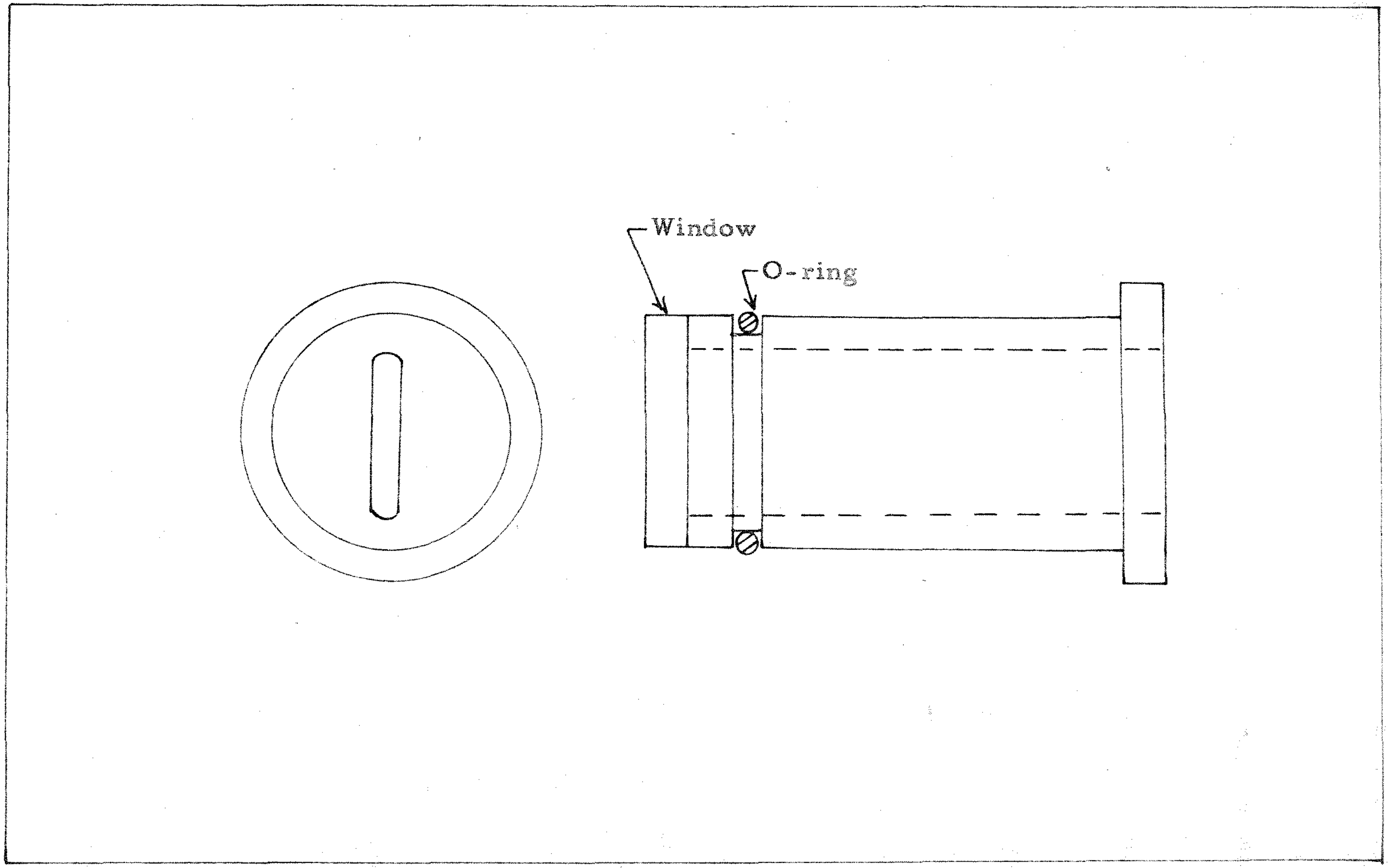


Fig. 3. Typical window mount construction.

adverse effects being experienced at high vacua. Circle Seal plug valves were used throughout the manifold. A Norris-Thermador $CO_2$ cylinder served as a gas mixing bottle and a Marshalltown Manufacturing Company vacuum gage was used as a guide to the quantity of a gas introduced into the bottle. A direct outlet from the shock tube was provided for taking samples of mixed gases for chemical analysis.

The vacuum pumping system centered about a Consolidated Vacuum Corporation type MCF-60 oil diffusion pump using Dow Corning 703 silicone oil, which was attached, by means of 3/4 inch o.d. copper line, to the top of the shock tube. The diffusion pump was backed by a Kinney type KC-8 double-stage mechanical vacuum pump. A piping system conveyed the Kinney pump discharge and test gases to a chemical hood.

The pressure in the manifold was measured by means of a Consolidated Vacuum Corporation Phillips gage, type PHG-09. The calibration of this gage was checked against a McLeod gage. Test gas pressures for an experimental run were measured with a Wallace and Tiernan 0 to 50 mm absolute pressure gage which was connected directly to the shock tube. Wallace and Tiernan absolute pressure gages are individually calibrated at the factory; however, as a precaution against any possible change in calibration during shipment this gage was checked against a precision mercury manometer. The ultimate vacuum in the gas manifold system was $5 \times 10^{-5}$ mm of Hg, while the shock tube could be pumped to $10^{-4}$ mm of Hg. The measured leak rate for the entire system was of the order of 0.1 micron of Hg per minute.

The high pressure manifold was assembled using 1/4 inch o.d. copper tubing and Parker high pressure flare fittings. Grove O-ring seat needle-valves were used throughout. The manifold was connected to the shock tube by Parker high-pressure flexible hose. A connection was provided for evacuating the high pressure section. Ashcroft-15 to 400 and 0 to 2000 psi gages were used for pressure measurements.

## 2. Shock velocity measurement

Thin-film platinum heat gages similar to those described by Rabinowicz(16) were employed for shock velocity measurements. Figs. 4 and 5 are illustrative of the heat gage construction and associated electronic circuitry. A great deal of effort was expended in arriving at this system which functioned reliably and gave reproducible results.

The heat gages were stationed 67.5 cm apart. The voltage output from each gage was fed through a Technology Instrument Co. Type 500A, 1000-gain wide-band amplifier to a Berkeley Model 7360 counter. The first heat gage served both to start the counter and also to trigger the oscilloscope sweep. The trigger circuit of the Tektronix oscilloscope functioned erratically for the low voltage output of the gages (approximately 1-10 mv). A study of this problem culminated in the construction of the extremely high-gain transistorized trigger amplifier depicted in Fig. 6. This amplifier was balanced to give a sharp spike for square wave input as indicated in Fig. 7. By setting the oscilloscope to trigger at 5v, a level at which its performance was quite consistent, the sweep was delayed not more than 2 microseconds as a result of the trigger amplifier.

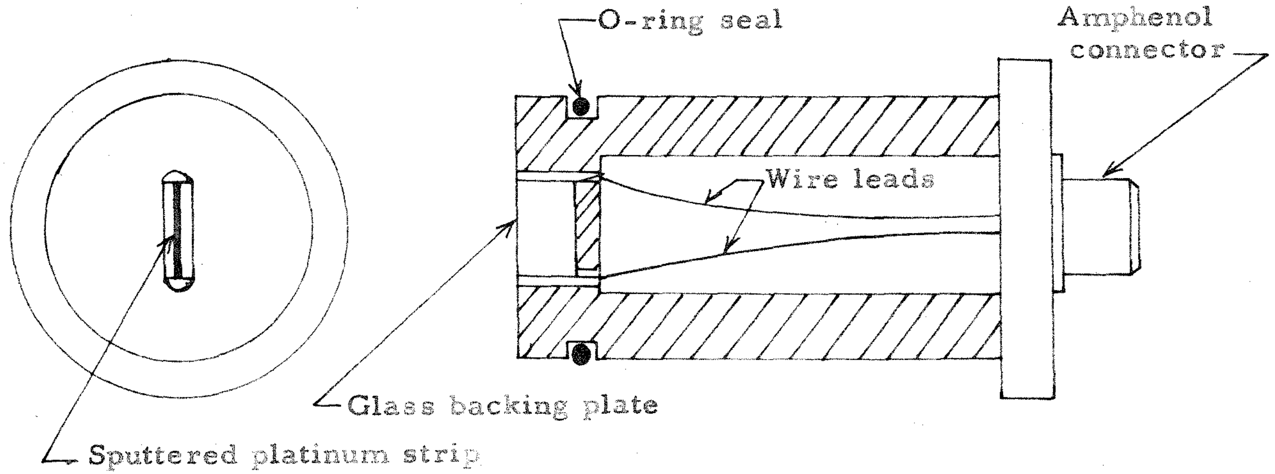


Fig. 4. Schematic drawing of heat gage construction.

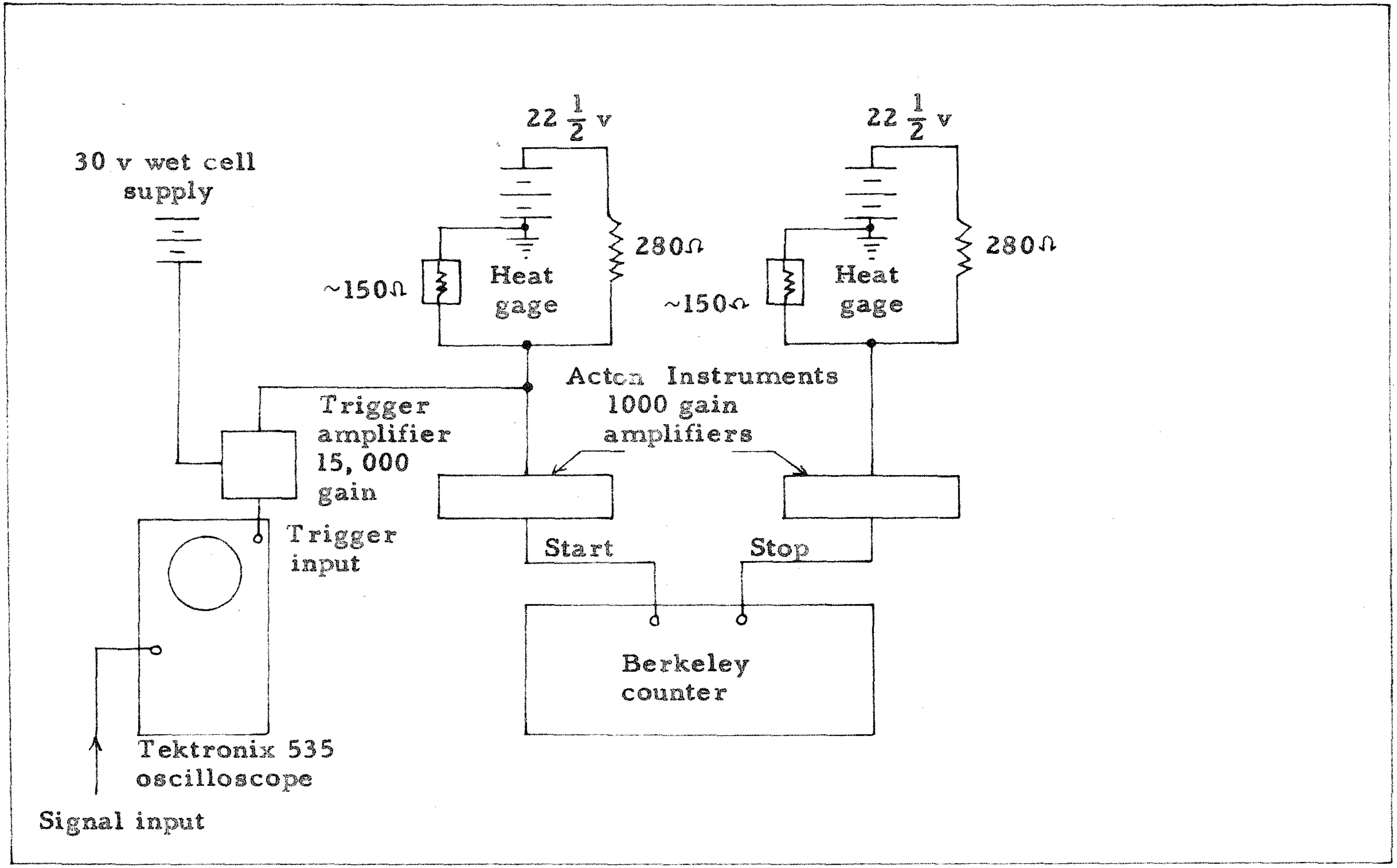


Fig. 5. Block diagram of the shock tube electronic instrumentation.

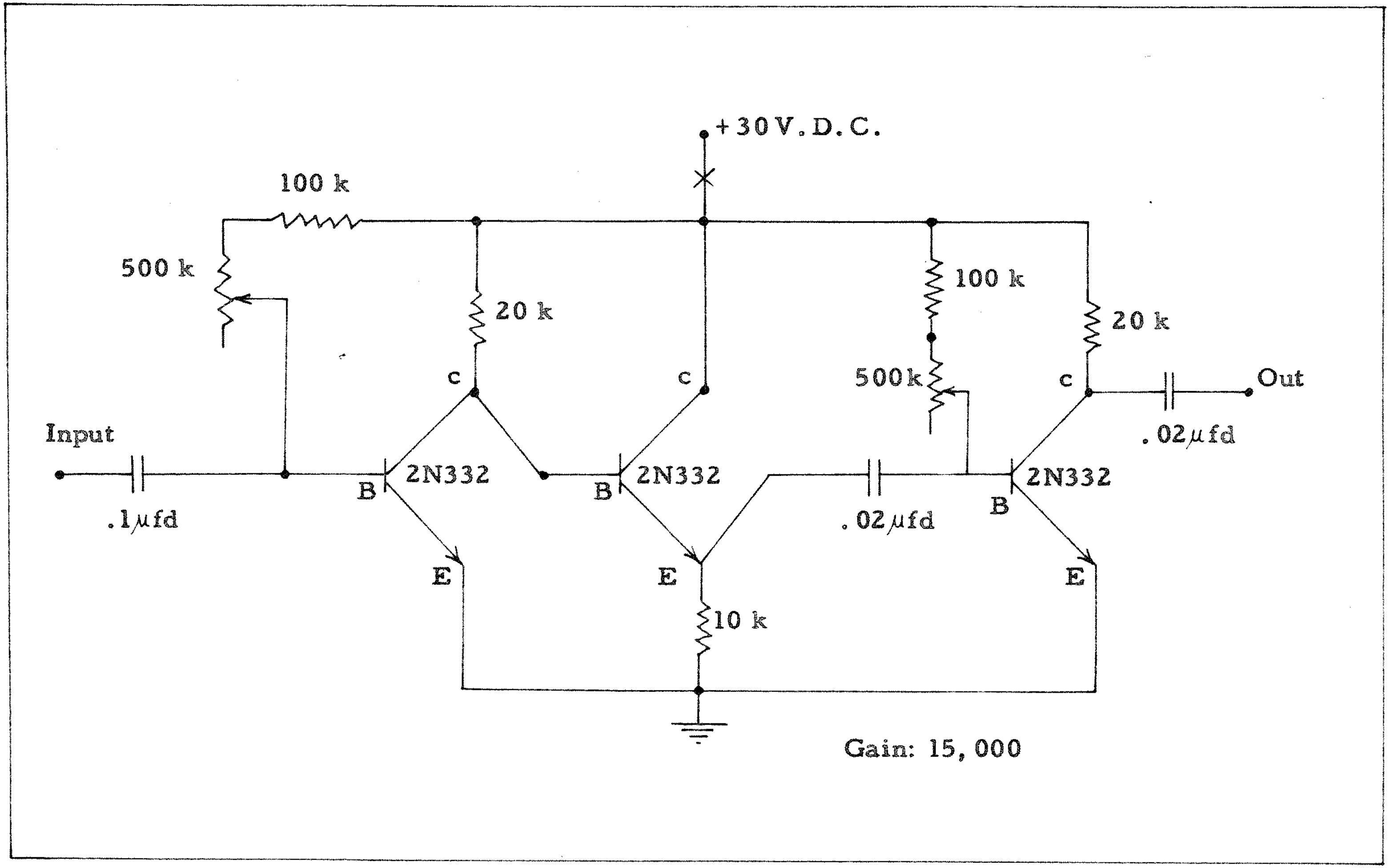
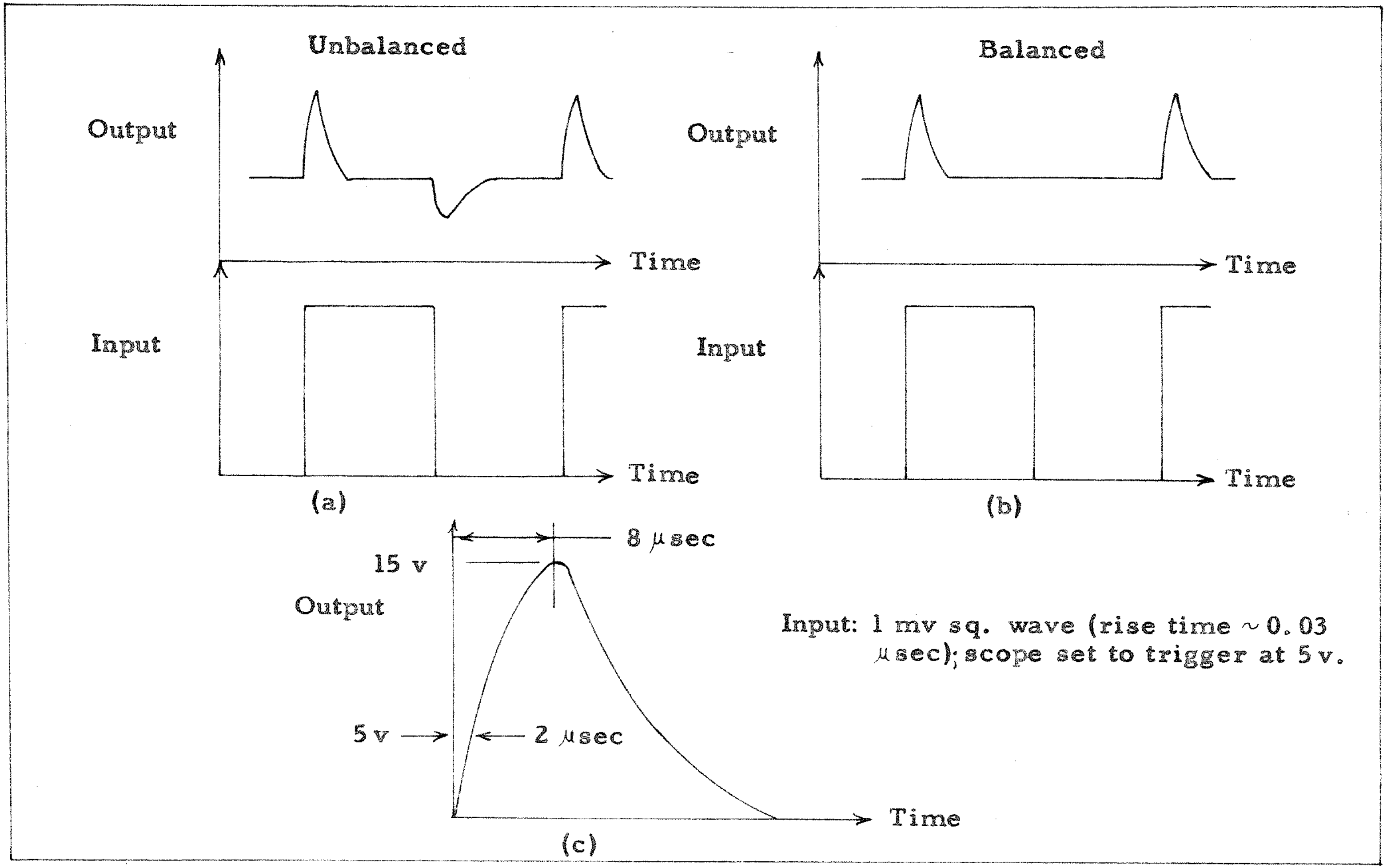


Fig. 6. Transistorized trigger amplifier.



Input: 1 mv sq. wave (rise time ~ 0.03 μsec); scope set to trigger at 5 v.

Fig. 7. Output wave forms of trigger amplifier.

The minimum count of the Berkeley counter was 1 microsecond. An average transit time of the shock wave across the face of a heat gage was about 1 microsecond. Thus, for typical shock velocity measurements, which were of the order of 400 microseconds, the uncertainty was less than 1/2%.

### 3. Chemical analysis of test-gas mixtures

In order to observe the homogeneous thermal decomposition of $NH_3$ temperatures in excess of 2000°K were required. Because of the low specific heat ratio of $NH_3$, temperatures of this order could not be achieved in our tube by shock wave heating of the pure gas. It was therefore necessary to dilute the $NH_3$ with a more suitable gas and argon was the logical selection. In order to make certain that the decomposition proceeds in a nearly isothermal manner, a large excess of argon was employed. Mixtures of 1 to 10% $NH_3$ in Ar were used during the experimental program.

In order to determine the exact composition of the test-gas mixture and minimize uncertainties resulting from surface adsorption in the gas manifold and mixing bottle, a sample of gas for chemical analysis was taken directly from the low-pressure section of the shock tube prior to each experimental run. Spectroscopic analysis directly in the shock tube was not feasible because of the extremely low optical path lengths of the $NH_3$. The gas sample was collected in the large bulb of the container shown schematically in Fig. 8. This bulb, which had an accurately known volume, was pumped down along with the shock tube and was filled with test gas while the tube was being filled. The pressure in the bulb was

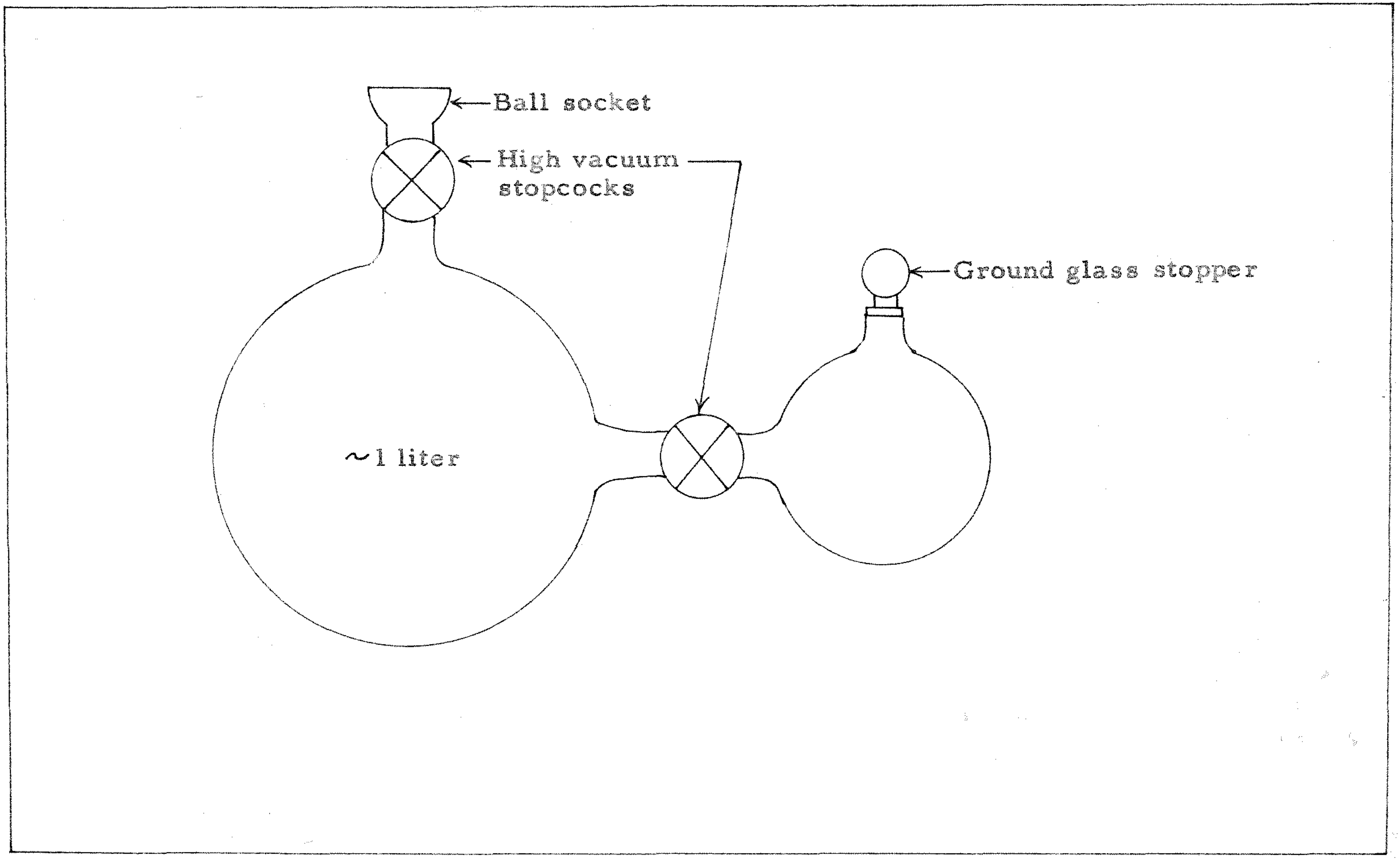


Fig. 8. Schematic drawing of gas sampling container.

thus the same as that measured in the shock tube. Just prior to an experimental run, the bulb was closed off and the gas thus trapped was analyzed at the conclusion of the run.

Because the quantity of $NH_3$ in the sample container was so small, titration of the gas (suitably absorbed in a liquid vehicle) with a standard acid solution could not serve as a means of analysis. Instead, a colormetric analysis was performed using a Fisher electrophotometer. The method used is essentially the Folin and Wu(17) technique for determination of non-protein nitrogen.

To absorb the $NH_3$, 50 ml of 5% aqueous solution of $HC\ell$ were introduced into the small bulb of the sample container with a volumetric pipette. By means of the stopcock separating the two bulbs, the $HC\ell$ solution was brought into contact with the gas mixture and the container was agitated for 4 or 5 minutes. An accurate volume of this mixture was then drawn off and Folin-Nessler's solution was added rendering the mixture a yellow color. The percentage of light transmission was compared to distilled water and an identical quantity of Nessler's solution, using the electrophotometer. This measurement yielded the mass of $NH_3$ in the sample container.

Calibration of the electrophotometer was accomplished by means of a standard solution of $NH_4C\ell$. A calibration curve was prepared showing the percentage of light transmission as a function of the number of milligrams of nitrogen. With a reading from the electrophotometer and the knowledge of the pressure, temperature and volume of the gas mixture, the fraction of $NH_3$ present could be determined. Repeated experiments indicated a precision of approximately 3% for this analytical procedure.

Anhydrous grade $NH_3$, minimum purity 99.99%, and standard grade Ar, minimum purity 99.998%, supplied by the Matheson Co. were used to prepare the test gas mixtures. No attempt was made to perform an exact analysis of the impurities; however, from the supplier's literature it would appear that the principal impurities in the gases used were oxygen, hydrogen and nitrogen.

### 4. Infrared detectors

Since the shock tube program undertaken required radiation measurements in the near infrared portion of the spectrum, it was necessary to investigate in some detail the characteristics of detectors available for this wavelength region.

In recent years the U.S. Government has sponsored a significant research effort in infrared detection, primarily in connection with missile detection systems, and as a result of this effort there are now available on the commercial market a number of infrared detectors of high sensitivity and very short time response suitable for shock tube research. The principles and practices of these devices have been discussed in considerable detail by Smith et al(18), Moss(19), Jones(20), and others(21).

In spite of the abundance of literature on the subject, the adaptation of particular detectors for the shock tube program required a good deal of experimentation. Of paramount importance was the elimination of spurious atmospheric electrical disturbances, and the minimization of stray capacitance in the electronic circuits so that the ultimate time response could be achieved with a given detector.

During the course of our experimental work, two photoconductive infrared cells were used. In the early survey work, a Santa Barbara PbSe cell with a useful range of wavelengths from 1 to 5 microns and with a cell time constant of about 20 microseconds was employed. Later in our program, when actual quantitative runs were undertaken, a Westinghouse gold-doped germanium cell became available. This cell covered the wavelength region from about 2 to 9 microns with a cell time constant of 0.2 microseconds.

Since photoconductive cells operate by a change in resistance when irradiated, a load resistor-biasing arrangement was called for. The simplest biasing scheme that could be employed is illustrated in Fig. 9a. Examination of this figure reveals that the circuit time constant, irrespective of the detector time constant, is the product of the load resistance and the stray plus amplifier imput capacitances, presuming, of course, that the load resistance is small compared to the detector resistance. In order to achieve the ultimate time response of the detector, the circuit time constant must be made small compared with the detector time constant. This can be accomplished simply by decreasing the load resistance. There is, however, a lower limit to this decrease. Although the detector signal-to-detector noise is independent of the value of the load resistance, the detector signal-to-amplifier noise increases with a decreasing load. Our broad band amplifiers had an output noise level of 5 mv for a gain of 100. This, then, represented the limiting signal voltage

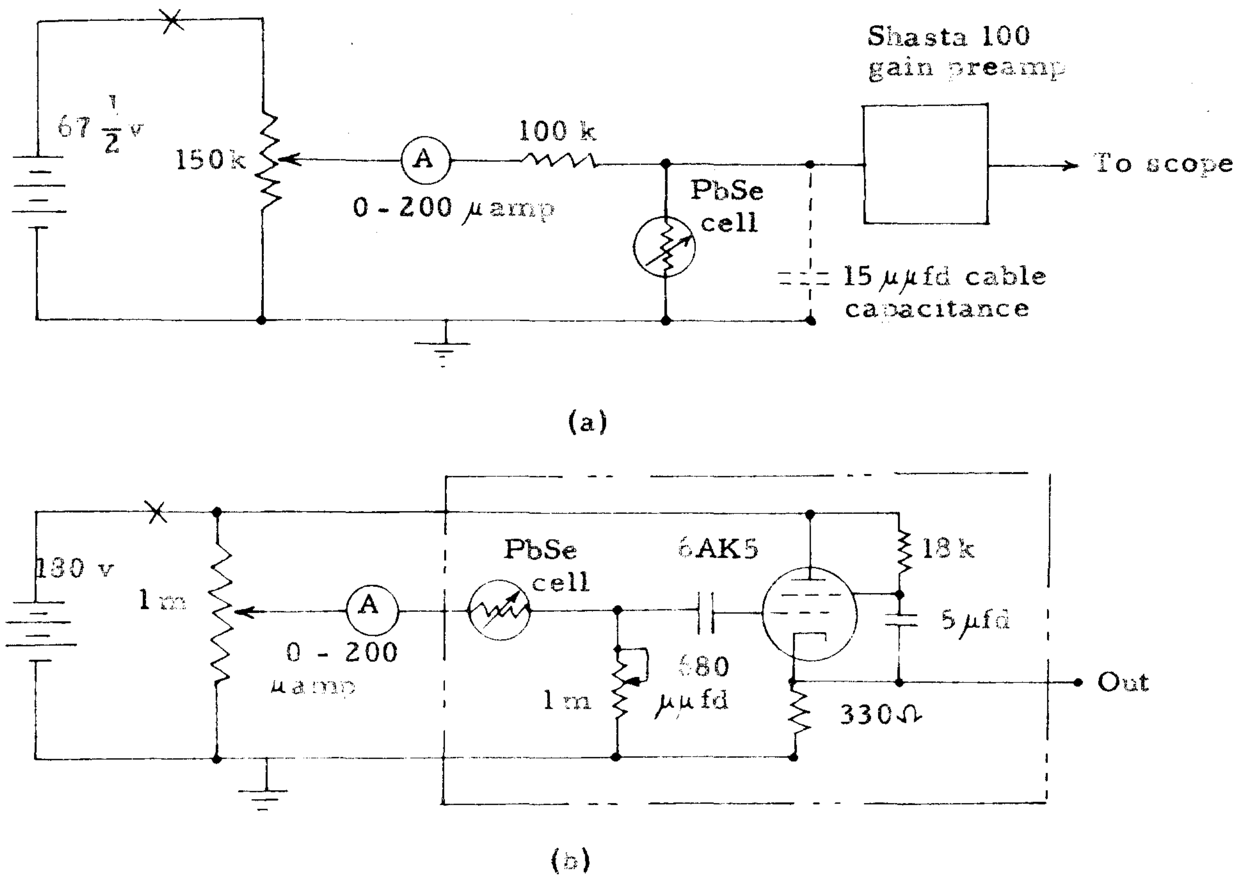


Fig. 9. Bias circuits for the Santa Barbara PbSe cell.

for detection. Experiments indicated that $NH_3$ radiation behind the shock front was not of sufficient intensity to be measured unequivocally with this arrangement with the load resistance set low enough to attain the minimum required time constant. It should be pointed out that the 5 mv figure quoted above was further aggravated by the stray pickup of this relatively high-impedance system.

The alternative avenue of approach involved decreasing the value of ground-shunted capacitance and using a cathode follower circuit. In Fig. 9b we have indicated the circuit used for the PbSe cell; for the gold-doped germanium cell we used the same circuit except for the introduction of a separate 30 v battery for the cell bias supply. The measured input capacitance to this cathode follower was 5 micro-microfarads. Thus, for the full 1 megohm load, this portion of the circuit had a maximum time constant of 5 microseconds. This circuit represented a factor of five or six gain over the simple circuit, with the added advantage that the low output impedance of the cathode follower minimized stray pickup. Radiation emitted from $NH_3$ was successfully detected with this system.

The photoconductive cells were mounted in the same chassis box as the vacuum tube and located as close as possible to the tube input grid. The components that were housed together are indicated by phantom lines in Fig. 9b.

Two methods were employed to measure the time response of a detector assembly. In Fig. 10 we have illustrated what may be called the oscilloscope method in which the detector "looked at" the face of one

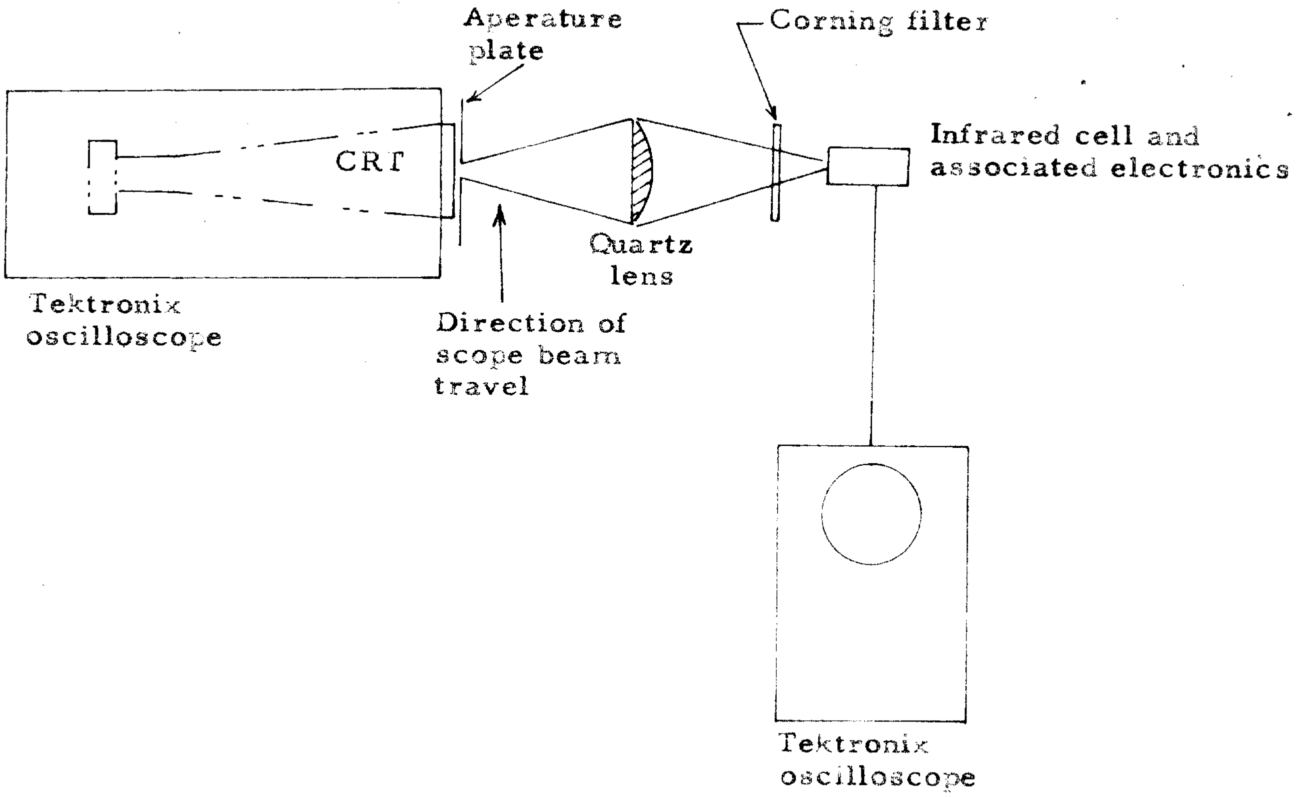


Fig. 10. Arrangement for measuring detector time constant.

oscilloscope (CRT) while its output was measured on a second oscilloscope. By masking the face of the CRT which the detector observed, it was possible to obtain a step input of light with extremely fast rise time. The CRT face does not emit infrared radiation, as was determined by inserting a series of Corning Glass filters in the optical path, but rather radiation at wavelengths shorter than about 0.55 microns. A measurement could be attempted then only in the visible region of the spectrum where, unfortunately, the detector sensitivity was extremely low. With the PbSe cell a measurement was possible since with its high time constant a fairly large load resistance could be used with the cathode follower. The measured value was about 20 microseconds. For the gold-doped Ge cell, an overall time constant of about 1 microsecond was sought and for this value the load had to be reduced below the point where visible radiation could be detected.

The shock tube itself was employed in our other method for time constant measurements. By using a gas with a fast vibrational relaxation time, a "step of light" could be produced by the passage of the shock wave. Pure $NH_3$ was employed for this purpose. With the load resistance set at about $10^5 \Omega$, the measured overall time constant of the gold-doped Ge assembly was approximately 0.7 microseconds.

Both of the aforementioned cells were operated at the temperature of liquid nitrogen. The Santa Barbara cell employed a miniature cryostat which manufactured its own liquid nitrogen from a high pressure bottle of $N_2$ gas. The Westinghouse cell had a reservoir into which liquid nitrogen could be poured.

## 5. Optical systems for measurement of radiation behind shock fronts

Our studies indicated that the spectral region most easily accessible for an investigation of the decomposition of $NH_3$ centered about a wavelength of 3 microns. To isolate this region, a monochromator was required. A prerequisite for the radiation measurements was an optical system with adequate light-gathering power which would focus the light on the monochromator slits.

The first optical bench constructed used quartz optics, since the manufacturers' literature indicated that the spectral transmission of quartz extended beyond 3 microns. Fig. 11 contains a schematic diagram of the arrangement. The light source was used to focus the lenses accurately on the center line of the tube. Although measurements showed that light transmission for this system extended to about 3.4 microns, the fairly sharp decrease in intensity beyond 2.8 microns was felt to be too limiting for our purposes.

In Fig. 12 is depicted the system actually used for the experiments. With MgO windows in the tube, spectral transmission was flat to about 6 microns, being limited here by the absorption of the LiF lens. By use of an aperture plate, the f-number of the system was adjusted to f/12, a value which matched the f-number of the monochromator used and still gave a calculated time resolution of about 2 microseconds at the window of the shock tube.

The monochromator from a Beckman IR-2 spectrograph was employed for spectral resolution. The dispersing element was rock salt. The monochromator with the infrared detector assembly in place is shown in Fig. 13. Accuracy of the wavelength scale was tested by

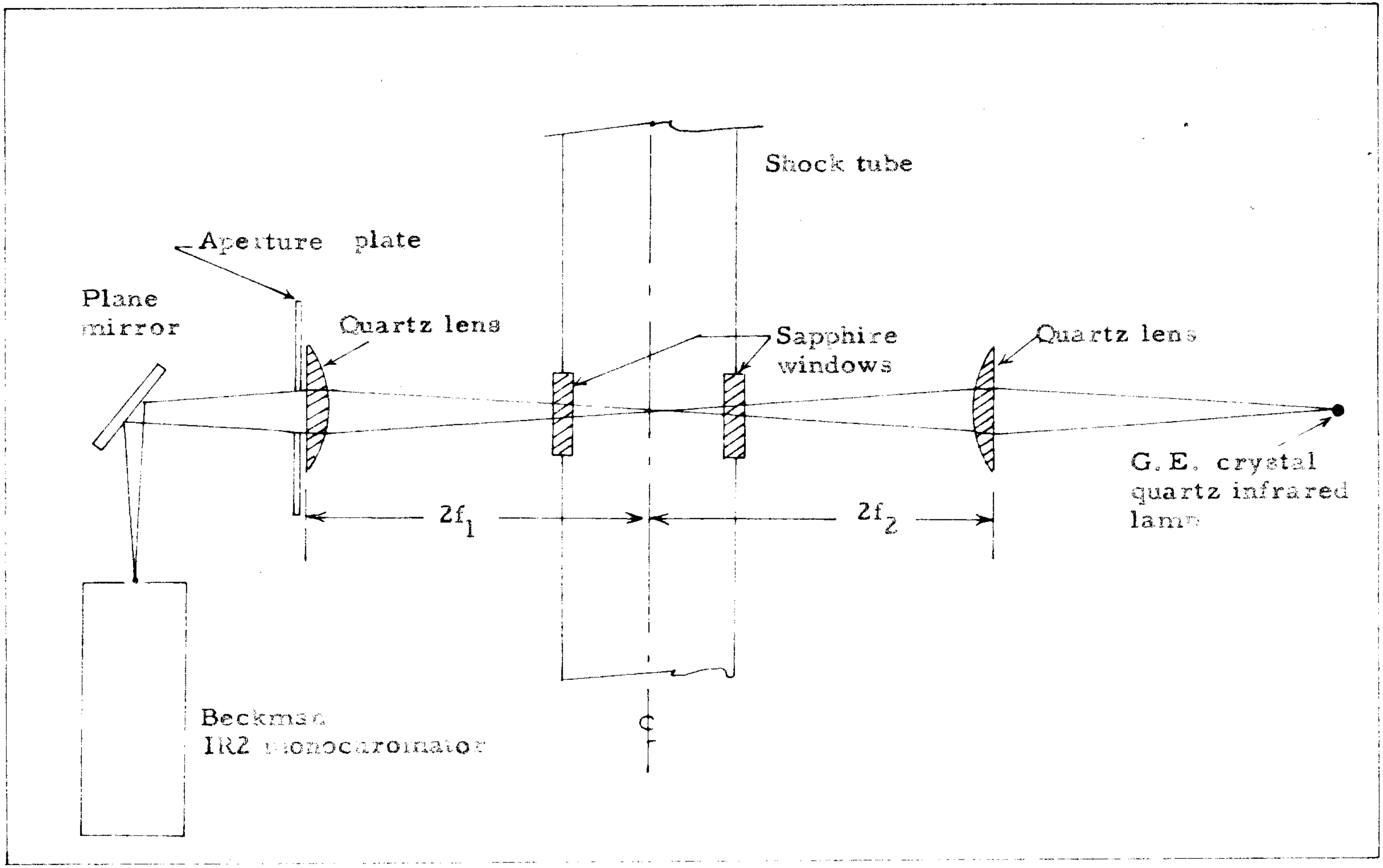


Fig. 11. Diagram of quartz limited optical system.

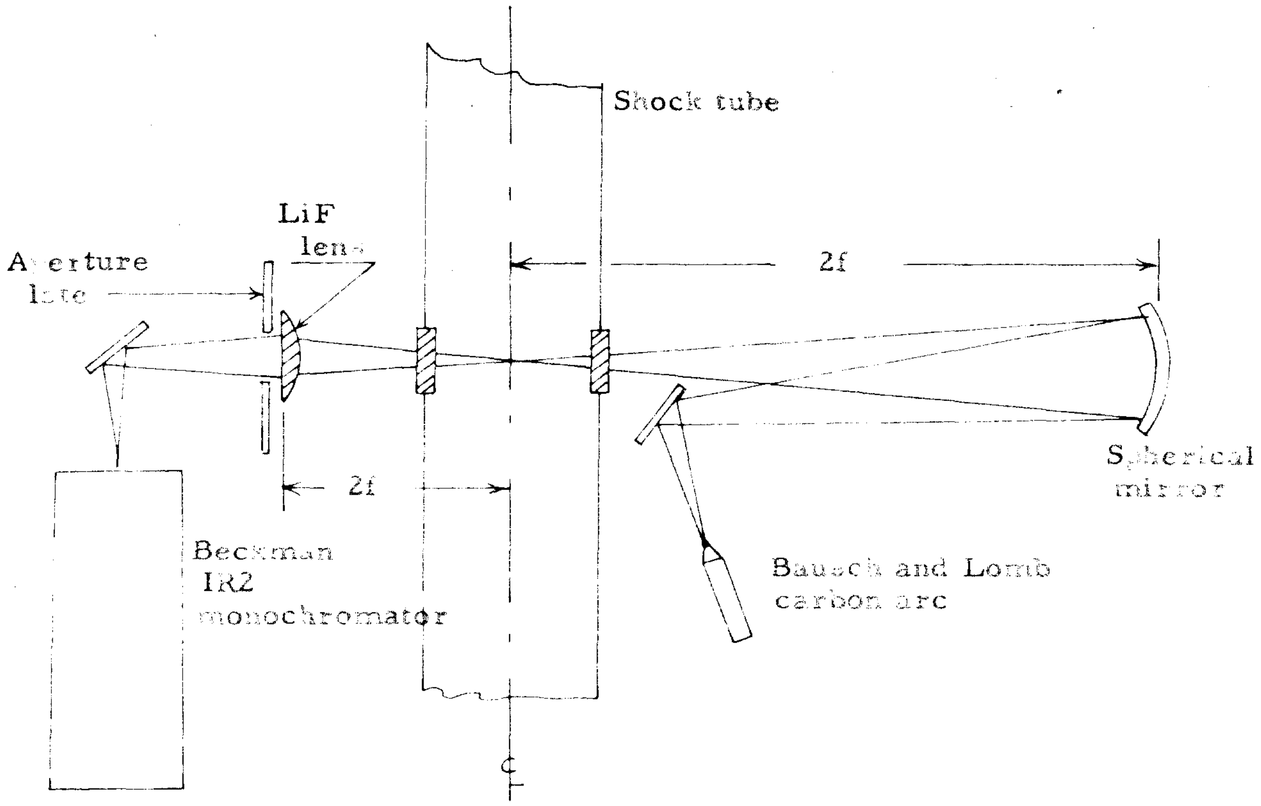


Fig. 12. Diagram of LiF limited optical system.

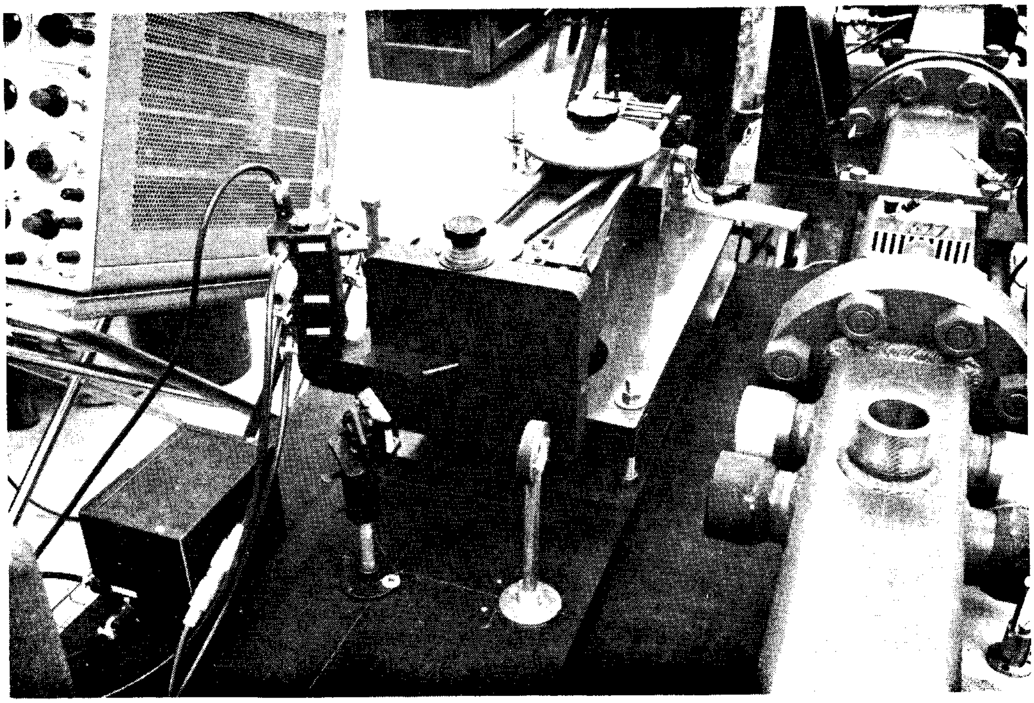


Fig. 13. View of the monochromator and associated optical equipment. The Santa Barbara PbSe detector assembly is mounted just to the left of the monochromator.

means of a calibrated strip of polystyrene and the presence of short wavelength scattered light was checked by inserting a germanium interference filter with a sharp 2 micron rise in the aligning light beam. In the spectral region of interest, the scattered light intensity was found to be negligibly small.

## C. Experimental Results

The initial rate of decomposition of $NH_3$ in Ar has been measured between 2000 and 3000°K by following the rate of decrease of emission intensity in the 2.7 to 3.2 micron wavelength region. A typical experimental record is shown in Fig. 14. As was pointed out earlier, the intensity of the emission is assumed proportional to the concentration of $NH_3$. From the record it may be seen that the emission intensity jumps very rapidly to a maximum value after passage of the shock wave and then decays, approaching the zero level asymptotically.

In order to study our records it was first necessary to determine the state of the gas mixture after the passage of the shock. The required thermodynamic parameters were calculated from the measured initial conditions and shock velocity using the well known conservation equations. Since the kinetic studies were to be restricted to initial rate measurements, only properties immediately behind the shock front were required. For the mixture containing 1% $NH_3$, the calculations were performed neglecting the presence of the $NH_3$. Calculations for the 8% mixture were carried out by assuming equilibrium before and after the shock wave with respect to the internal degrees of freedom but not with respect to chemical composition. Enthalpies for $NH_3$ were computed in

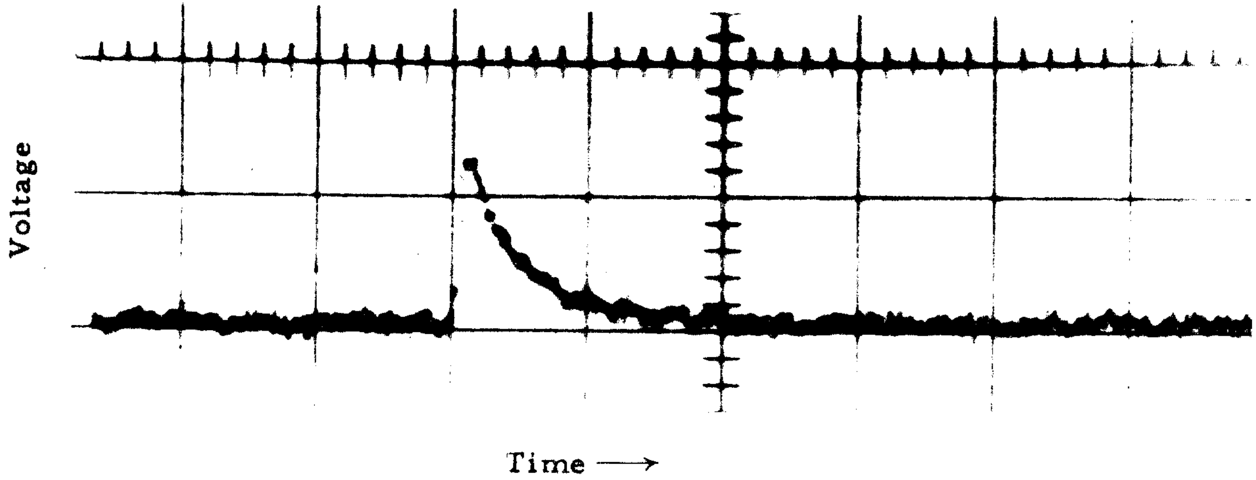


Fig. 14. Typical experimental record. Vertical lines are at 20 microsecond intervals. $X_{NH_3} = 0.08$, $T = 2720^{\circ}K$.

the 2000-3000°K range using standard methods.(22)

For reduction of the kinetic data it was assumed that

$$-\frac{d(NH_3)}{dt} = k(NH_3)(M) \tag{1}$$

where (M) represents either Ar or $NH_3$.

In terms of the $NH_3$ partial pressure $p_{NH_3}$, and mole fractions $X_M$ and $X_{NH_3}$, Eq. (1) may be written as

$$\frac{-RT}{X_{NH_3} p_T^2} \frac{dp_{NH_3}}{dt} = k\, X_M \,. \tag{2}$$

Here $p_T$ is the total pressure and T the temperature after the passage of the shock; t represents the actual time for the decomposition reaction and may be obtained from the "oscilloscope time" by multiplying by an appropriate density ratio. For transparent gases, $p_{NH_3}$ is directly proportional to the emission intensity and, with properly designed electronic circuits, directly proportional to the oscilloscope voltage V registered by the detector. Hence,

$$V = \text{const.}\ p_{NH_3} \tag{3}$$

or

$$\frac{dV}{dt} = \text{const.}\ \frac{dp_{NH_3}}{dt} \,.$$

The constant of proportionality may be evaluated at t = 0 from the oscilloscope trace and the known partial pressure of $NH_3$ immediately behind the shock front. Thus in terms of the initial voltage $V^o$ and mole fraction $X^o_{NH_3}$, and with an assumed Arrhenius temperature dependence, Eq. (2) becomes

$$\frac{-RT}{X_{NH_3} p_T^{\,2}} \frac{dp_{NH_3}}{dt} = \frac{-X^o_{NH_3}}{X_{NH_3}} \frac{RT}{p_T} \frac{d\,\frac{V}{V^o}}{dt} = B\,e^{-E/RT} . \tag{4}$$

For the initial stages of the reaction, T and $p_T$ are approximately constant and $X^o_{NH_3} \simeq X_{NH_3}$. On this basis, an activation energy has been determined from Eq. (4). The logarithm of the left-hand side of Eq. (4) has been plotted against 1/T for our measurements and the resulting graph is shown in Fig. 15. Least square straight line fits of these data yield apparent activation energies of 51 Kcal/mole for the mixture containing 1% $NH_3$ and 53 Kcal/mole for the mixture containing 8% $NH_3$. The pre-exponential factor B of the Arrhenius function was found to be of the order $10^{12}$ liter/mole-sec.

## D. Conclusions

It is natural to assume that the initial step in the homogeneous decomposition of $NH_3$ is

$$NH_3 + M \longrightarrow NH_2 + H + M \tag{5}$$

where M is either Ar or $NH_3$. Comparing our measured activation energy of about 52 Kcal/mole with the experimental value of about 105 Kcal/mole for the $NH_2$-H bond strength, (23), (24) it is clear that our data do not represent the initial decomposition rate. No doubt we are measuring the early rate and a chain mechanism is a reasonable explanation of our low activation energy.* We shall not attempt to guess the details of the actual mechanism but shall simply note that a chain with

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* The author is indebted to Dr. Norman Davidson for a discussion of this point.

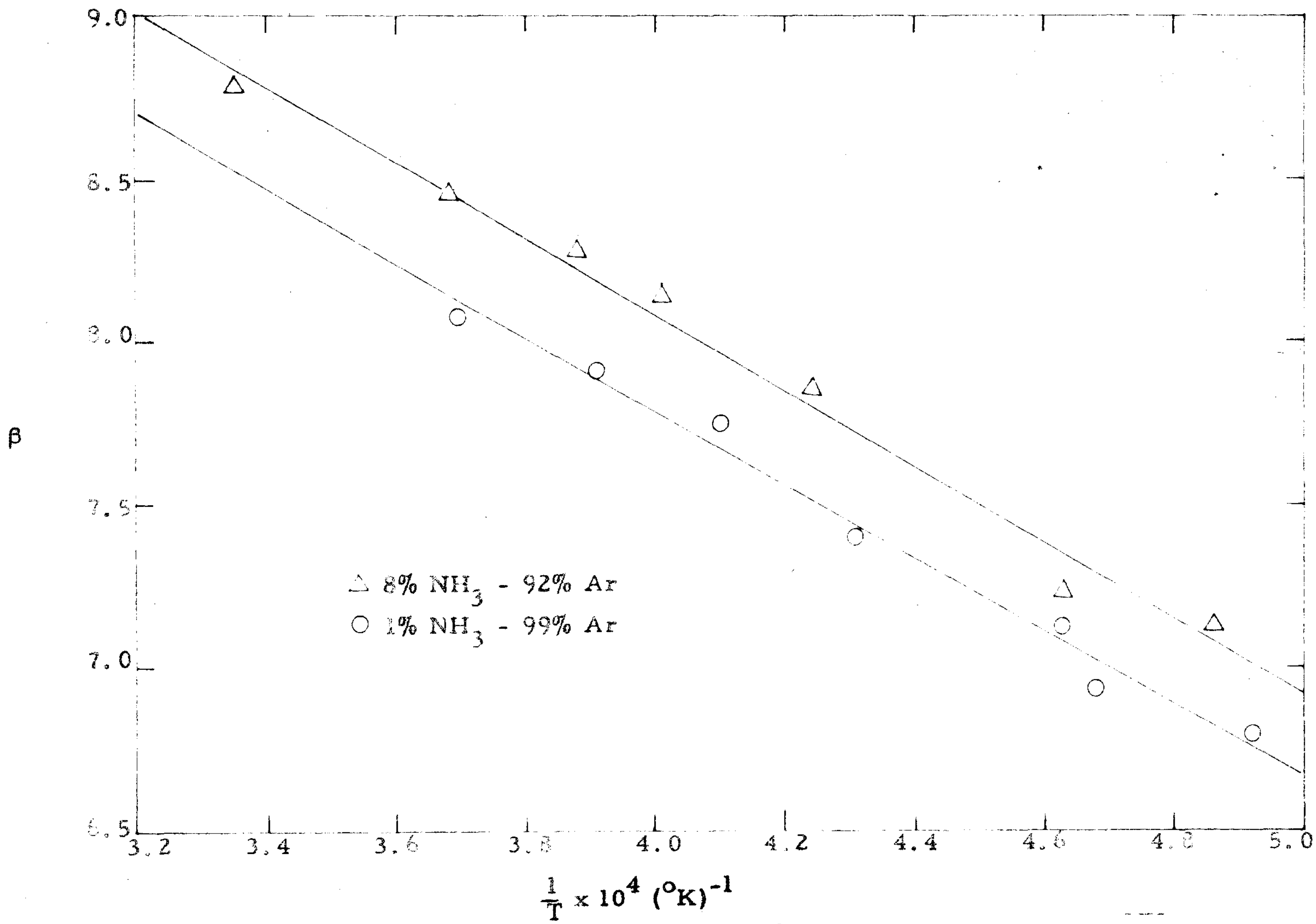

Fig. 15. The quantity $\beta = \log_{10}\left[(RT/X_{NH_3}p_T^{\,2})(dp_{NH_3}/dt)\right]$ vs. (1/T) The term $dp_{NH_3}/dt$ has been evaluated for the initial decrease in $NH_3$ emission.

bimolecular termination would involve the square root of the initial rate constant, indicating an initial activation energy of about twice our measured value. This result follows, at least qualitatively, from the assumption that the reaction rate may be written(25)

$$\text{rate of reaction} \propto r_p \left(\frac{r_i}{r_b}\right)^{1/2} \tag{6}$$

where $r_p$, $r_i$ and $r_b$ are the rates of chain propagation, initiation and breaking, respectively. For simple Arrhenius temperature dependence the apparent activation energy of Eq. (6) would be

$$E = E_p + \frac{1}{2}(E_i - E_b) \tag{7}$$

where the subscripts have the same meaning as for the rates in Eq. (6). For $E_p$ and $E_b$ small, we have $E_i \simeq 2E$ in accord with our experimental findings.

## II. VIBRATIONAL RELAXATION IN CYLINDRICAL CHAMBERS OF ISOTHERMAL, DILUTE MIXTURES

### A. Introduction

We consider vibrational excitation in the presence of an external radiation field and deexcitation in the absence of the field for stationary, dilute systems in cylindrical containers in which surface deactivation of excited species is so effective as to reduce the concentration of vibrationally excited molecules to zero at the bounding surfaces. The mathematical problem is similar to that encountered in the study of isothermal explosion limits with catalytic surfaces.(26) We presume that the maximum fraction of vibrationally excited molecules is sufficiently small to permit the approximation that the system remains isothermal at the temperature T and at constant pressure p and density $\rho$. In the following analysis we examine the rate of excitation in an external radiation field and the subsequent rate of deexcitation when the external radiation field is removed. The external radiation field is assumed to be of such high intensity compared with thermal radiation in the system that the latter may be considered to be negligibly small. Internal reflection and scattering are neglected.

## B. Derivation of the Governing Equation

### 1. The basic equation

Since we deal with isothermal and constant pressure systems at constant composition, the integrated energy, momentum and continuity equations are satisfied automatically. Only the species conservation equations with zero mass average velocity need to be considered. Furthermore, we restrict our considerations to pure gases (e.g., CO, CO2, NO, etc.) and small number densities of vibrationally excited molecules. Hence only the continuity equation for the molecules in the first excited vibrational level needs to be considered. Using a binary mixture approximation, we find(27) that

$$\frac{\partial n_1}{\partial t} - D \frac{\partial^2 n_1}{\partial x_\ell \partial x_\ell} = - \dot{w}_1 + \dot{w}_2 \tag{8}$$

where $n_1$ represents the number of molecules per cm$^3$ in the first vibrationally excited level, t denotes the time, D is the binary diffusion coefficient for diffusion of vibrationally excited molecules through molecules in the ground state, $\partial^2/\partial x_\ell \, \partial x_\ell$ denotes the Laplacian operator in cartesian tensor notation, $-\dot{w}_1$ is the rate of removal of vibrationally excited molecules by gas-phase collisions and radiative transitions, and $\dot{w}_2$ is the rate of production of vibrationally excited molecules in the presence of an external radiation field. We must now specify the functional forms of $\dot{w}_1$ and of $\dot{w}_2$.

## 2. Excitation in an external radiation field

The sum of the rates of deexcitation $-\dot{w}_1$ and of excitation $\dot{w}_2$ consists of contributions made by gas-phase collisions and by radiative transitions. Rubin and Shuler(28) have noted that the collisional transitions, to the Landau-Teller(29) approximation, obey the same selection rules as radiative transitions, viz., collisional energy exchange occurs only between adjacent vibrational levels. Thus, considering molecules in the ith vibrational level,

$$-(\dot{w}_1)_c + (\dot{w}_2)_c = k_{1\to 0}\left[ie^{-\Theta}n_{i-1} - in_i - (i+1)e^{-\Theta}n_i + (i+1)n_{i+1}\right] \quad \text{for } i=1,2,\ldots\,\infty \tag{9}$$

and

$$-(\dot{w}_1)_c + (\dot{w}_2)_c = k_{1\to 0}(n_1 - e^{-\Theta}n_0) \; . \tag{10}$$

Here $k_{1\to 0}$ is the transition probability per second from the first excited vibrational level to the ground level and

$$\Theta = \frac{h\nu_{1,0}}{kT} \tag{11}$$

represents the reduced vibrational temperature if $\nu_{1\to 0}$ is the characteristic normal vibration frequency, h denotes Planck's constant, and k is the Boltzmann constant. The transition probability $k_{1\rightarrow 0}$ may be written in the form

$$k_{1\rightarrow 0} = \eta Z_c \tag{12}$$

if $Z_c$ is the mean collision frequency of excited molecules in the gas phase and $\eta$ represents the collision efficiency (i.e., the probability of deexcitation on collision).

The radiative contribution to $-\dot{w}_1 + \dot{w}_2$ will be denoted by $-(\dot{w}_1)_r + (\dot{w}_2)_r$ and may be evaluated by considering a radiation field with volume density of radiant energy $\rho_{\nu_{1\rightarrow 0}}$. It follows then, to the harmonic oscillator approximation, that

$$-(\dot{w}_1)_r + (\dot{w}_2)_r = \rho_{\nu_{1\rightarrow 0}} B_{i-1\rightarrow i} n_{i-1} - \left[\rho_{\nu_{1\rightarrow 0}} (B_{i\rightarrow i+1} + B_{i\rightarrow i-1}) + A_{i\rightarrow i-1}\right] n_i + (\rho_{\nu_{1\rightarrow 0}} B_{i+1\rightarrow i} + A_{i+1\rightarrow i}) n_{i+1} \quad \text{for } i=1, 2, \ldots \infty \tag{13}$$

and

$$-(\dot{w}_1)_r + (\dot{w}_2)_r = (\rho_{\nu_{1\rightarrow 0}} B_{1\rightarrow 0} + A_{1\rightarrow 0}) n_1 - \rho_{\nu_{1\rightarrow 0}} B_{0\rightarrow 1} n_0 \,. \tag{14}$$

In Eqs. (13) and (14) the $B_{i\rightarrow i'}$ and $A_{i\rightarrow i'}$ identify the Einstein coefficients for induced and spontaneous emission, respectively. We now use the equality

$$A_{i\rightarrow i'} = \frac{8\pi h \nu_{1,0}^3}{c^3} B_{i\rightarrow i'}$$

and the harmonic oscillator approximations $A_{i\rightarrow i-1} = i A_{1\rightarrow 0}$ and $B_{i\rightarrow i'} = B_{i'\rightarrow i}$; next we note that

$$\rho_{\nu_{1\to 0}} = \frac{8\pi h\nu_{1\to 0}^3}{c^3} \left( \frac{1}{e^{\theta}-1} + \frac{1}{e^{\theta'}-1} \right)$$

if the effective blackbody temperature for the external radiation field is T' corresponding to

$$\theta' = \frac{h\nu_{1\to 0}}{kT'} .$$

However, under normal experimental conditions,

$$T' \gg T \text{ and } \frac{1}{e^{\theta'}-1} \gg \frac{1}{e^{\theta}-1} .$$

Using this last approximation, it is readily shown that

$$-(\dot{w}_1)_r + (\dot{w}_2)_r = A_{1\to 0}(1-e^{-\theta'})^{-1} \left[ ie^{-\theta'} n_{i-1} - in_i - (i+1)e^{-\theta'} n_i + (i+1)n_{i+1} \right]$$

$$\text{for } i = 1, 2, \ldots \infty \qquad (15)$$

and

$$-(\dot{w}_1)_r + (\dot{w}_2)_r = A_{1\to 0}(1-e^{-\theta'})^{-1} (n_1 - e^{\theta'} n_0). \qquad (16)$$

In the absence of the external radiation field, the term $e^{-\theta'}$ in Eq. (15) is to be replaced everywhere by $e^{-\theta}$ except that all of the terms involving products of Einstein coefficients for spontaneous emission with $e^{-\theta}$ are assumed to be negligibly small compared with the dominant terms.

Combination of Eqs. (9) and (15) leads to the result

$$-\dot{w}_1 + \dot{w}_2 = -\left[(\dot{w}_1)_c + (\dot{w}_1)_r\right] + \left[(\dot{w}_2)_c + (\dot{w}_2)_r\right]$$

$$= \left[iA_{1\rightarrow 0}(1-e^{-\theta'})^{-1} e^{-\theta'} + ik_{1\rightarrow 0}\, e^{-\theta}\right] n_{i-1}$$

$$-\left\{A_{1\rightarrow 0}(1-e^{-\theta'})^{-1}\left[i+(i+1)e^{-\theta'}\right] + k_{1\rightarrow 0}\left[i+(i+1)e^{-\theta}\right]\right\} n_1$$

$$+\left[A_{1\rightarrow 0}(1-e^{-\theta'})^{-1} + k_{1\rightarrow 0}\right](i+1)n_{i+1} \ . \qquad (17)$$

Specializing Eq. (17) to i=1, assuming that $n_2 \ll n_1$ and $n_0$, and neglecting $e^{-\theta}$ and $e^{-\theta'}$ in comparison with unity, we find that

$$-\dot{w}_1 + \dot{w}_2 = -(A_{1\rightarrow 0}+k_{1\rightarrow 0})n_1 + (A_{1\rightarrow 0}\, e^{-\theta'} + k_{1\rightarrow 0}e^{-\theta})n_0 . \qquad (18)$$

Hence we obtain the following identifications:

$$\dot{w}_1 = (A_{1\rightarrow 0} + k_{1\rightarrow 0})n_1 \qquad (19)$$

and

$$\dot{w}_2 = (A_{1\rightarrow 0}\, e^{-\theta'} + k_{1\rightarrow 0}e^{-\theta})n_0 \qquad (20)$$

where $n_0$ may be equated to $n_T$ ($n_T$ equals the total number of molecules per unit volume) under the specified experimental conditions.

The mathematical problem for the rate of excitation in an external radiation field has now been reduced to the use of Eq. (8) with $\dot{w}_1$ defined by Eq. (19) and with $\dot{w}_2$ determined from Eq. (20). Thus

$$\left.\begin{aligned} &\frac{\partial n_1}{\partial t} - D\frac{\partial^2 n_1}{\partial x_\ell \partial x_\ell} = -\gamma n_1 + \dot{w}_2 \\ &\gamma = (A_{1\rightarrow 0} + k_{1\rightarrow 0}), \\ &\dot{w}_2 = (A_{1\rightarrow 0}\, e^{-\theta'} + k_{1\rightarrow 0}\, e^{-\theta})n_T \ ; \end{aligned}\right\} \qquad (21)$$

the boundary conditions are

$$\left.\begin{aligned} &n_1(t, x_\ell \text{ at the wall}) = 0 \\ \text{and}\quad & \\ &n_1(0, x_\ell) \simeq 0 \end{aligned}\right\} \tag{21}$$

if the steady-state concentration of $n_1$ is unobservably small prior to illumination. In terms of the reduced variables

$$\left.\begin{aligned} &t' = t/\tau \ , \\ &\tau = L^2/D, \text{ and} \\ &x_\ell' = x_\ell /L, \end{aligned}\right\} \tag{22}$$

we find

$$\left.\begin{aligned} &\frac{\partial n_1}{\partial t'} - \frac{\partial^2 n_1}{\partial x_\ell' \partial x_\ell'} = -\tau\gamma n_1 + \tau \mathring{w}_2 \ , \\ &n_1(t', x_\ell' \text{ at the wall} = 0), \ n_1(0, x_\ell') = 0. \end{aligned}\right\} \tag{23}$$

Here L denotes a characteristic chamber length.

The time-dependent contribution to $n_1$ is the solution of the homogeneous differential equation

$$\frac{\partial n_{1,t'}}{\partial t'} - \frac{\partial^2 n_{1,t'}}{\partial x_\ell' \partial x_\ell'} + \tau\gamma n_{1,t'} = 0. \tag{24}$$

The general solution to Eq. (24) may be written in the form

$$n_{1,t'} = \sum_j A_j e^{-(\tau\gamma+\omega_j)t'} f_j(x_\ell'). \tag{25}$$

Introduction of Eq. (25) into Eq. (24) shows that the functions $f_j(x_\ell')$

and the eigenvalues $\omega_j$ are solutions of the set of differential equations

$$\frac{\partial^2 f_j(x_\ell')}{\partial x_\ell' \, \partial x_\ell'} + \omega_j f_j(x_\ell') = 0. \tag{26}$$

where, in accord with the first boundary condition specified in Eq. (23),

$$f_j(x_\ell' = \text{values at the wall}) = 0. \tag{27}$$

We assume that the functions $f_j(x_\ell')$ form a complete and orthonormal set.

The steady-state value of $n_1 = n_{1,\,s.s.}$ is a solution of the time-independent inhomogeneous differential equation

$$\frac{\partial^2 n_{1,\,s.s.}}{\partial x_\ell' \, \partial x_\ell'} - \tau\gamma \, n_{1,\,s.s.} + \tau \dot{w}_2 = 0 \;. \tag{28}$$

The functions $n_{1,\,s.s.}$ may be expressed in the form

$$n_{1,\,s.s.} = \sum_j B_j f_j(x_\ell') \tag{29}$$

where the coefficients $B_j$ are obtained by introducing Eq. (29) into Eq. (28) and then making use of Eq. (26). In this manner it is found that

$$\sum_j B_j(\tau\gamma + \omega_j) f_j(x_\ell') = \tau \dot{w}_2 \;. \tag{30}$$

Since the $f_j(x_\ell')$ form a complete and orthonormal set, Eq. (30) may be used to derive the expression

$$B_j = \frac{\tau \dot{w}_2}{\tau\gamma + \omega_j} \int_a^b f_j(x_\ell') \, p(x_\ell') \, dx_\ell' \tag{31}$$

where $p(x_\ell')$ is the appropriate weighting function with respect to which the $f_j(x_\ell')$ are orthonormal on the interval $a \leq x_\ell' \leq b$.

The general solution of Eq. (23) may now be written as

$$n_1(t', x_\ell') = n_{1,t'} + n_{1,s.s.} = \sum_j \left[ A_j e^{-(\tau\gamma + \omega_j)t'} + B_j \right] f_j(x_\ell'). \tag{32}$$

Use of the boundary condition

$$n_1(0, x_\ell') = 0$$

shows that

$$A_j = -B_j$$

whence

$$n_1(t', x_\ell') = \tau \dot{w}_2 \sum_j \frac{1 - e^{-(\tau\gamma + \omega_j)t'}}{\tau\gamma + \omega_j} f_j(x_\ell') \int_a^b f_j(x_\ell') p(x_\ell') dx_\ell' \ . \tag{33}$$

Consider now an infinite cylinder of radius L in which we may neglect edge effects. Then Eq. (26) becomes

$$r'^2 \frac{d^2 f_j(r')}{dr'^2} + r' \frac{df_j(r')}{dr'} + r'^2 \omega_j f_j(r') = 0$$

whence the orthonormal functions are

$$f_j(x_\ell') = f_j(r') = \frac{\sqrt{2}}{J_1(\sqrt{\omega_j})} J_0(\sqrt{\omega_j}\, r')$$

with the weighting function

$$p(x_\ell') = r'$$

on the interval $0 \leq r' \leq 1$. Hence

$$n_1(t', x_\ell') = n_1(t', r') = \tau \dot{w}_2 \sum_j \frac{1-e^{-(\tau\gamma+\omega_j)t'}}{\tau\gamma+\omega_j} \frac{\sqrt{2}}{J_1(\sqrt{\omega_j})} J_0(\sqrt{\omega_j}\, r') \frac{\sqrt{2}}{\sqrt{\omega_j}} \tag{34}$$

since

$$\frac{\sqrt{2}}{J_1(\sqrt{\omega_j})} \int_0^1 J_0(\sqrt{\omega_j}\, r') r' dr' = \frac{\sqrt{2}}{\sqrt{\omega_j}} .$$

Furthermore, the total concentration of $n_1$ per unit length of cylinder becomes

$$\iiint_{V_\ell} n_1(t, r) d\tau = 2\pi L^2 \int_0^1 n_1(t', r') r' dr'$$

whence

$$n_1^{T,\ell}(t') \equiv \iiint_{V_\ell} n_1(t, r) d\tau = \tau \dot{w}_2 4\pi L^2 \sum_j \frac{1-e^{-(\tau\gamma+\omega_j)t'}}{(\tau\gamma+\omega_j)\omega_j} \tag{35}$$

where the boundary condition specified in Eq. (27) shows that

$$J_0(\sqrt{\omega_j}) = 0, \text{ i.e., } \omega_j = (J_{0j})^2 \tag{36}$$

if $J_{0j}$ denotes the roots of

$$J_0(x) = 0.$$

The steady state value of $n_1^T(t')$ is evidently

$$n_{1,\, s.s.}^{T,\ell} = \tau \dot{w}_2 4\pi L^2 \sum_j \frac{1}{J_{0j}^2(\tau\gamma + J_{0j}^2)} \tag{37}$$

whence

$$\frac{n_1^{T,\ell}(t')}{n_{1,s.s}^{T,\ell}} = \frac{\sum_j \frac{1-e^{-(\tau\gamma+J_{0j}^2)t'}}{J_{0j}^2(\tau\gamma+J_{0j}^2)}}{\sum_j \frac{1}{J_{0j}^2(\tau\gamma+J_{0j}^2)}} \quad . \tag{38}$$

Reference to Eq. (38) shows that the excitation process is dominated by the term

$$e^{-\tau\gamma t'} = e^{-(A_{1\to 0}+k_{1\to 0})t} ,$$

i.e., by the time constant

$$t_{exc} \sim \frac{1}{A_{1\to 0}+k_{1\to 0}} \quad .$$

On the other hand, $n_{1,s.s.}^{T,\ell}$ is directly proportional to $\tau$ . In other words, the characteristic diffusion time $L^2/D$ must not be too small since, otherwise, wall deexcitation reduces the prevailing steady-state concentration. Thus an experimental measurement of the rate of excitation cannot be performed at too low pressures.

### 3. Relaxation after the light source is turned off

After the steady-state has been reached and the external light source has been turned off, the primary process is that of deexcitation and the term $\dot{w}_2$ in Eq. (8) disappears. Furthermore, $n_1(0, x_\ell') = \left[n_1(t', r')\right]_{s.s.}$ where the steady-state value is determined from Eq. (34). Proceeding as before, it is now readily shown for an infinite cylinder that

$$\frac{n_1^{T,\ell}(t')}{n_{1,s.s.}^{T,\ell}} = \frac{\sum\limits_j \frac{e^{-(\tau\gamma + J_{0j}^2)t'}}{J_{0j}^2(\tau\gamma + J_{0j}^2)}}{\sum\limits_j \frac{1}{J_{0j}^2(\tau\gamma + J_{0j}^2)}} \tag{39}$$

## C. A Representative Calculation for CO

The infinite sums appearing in the equations for the number densities may be evaluated as follows:

$$\frac{1}{\sum\limits_j J_{0j}^2(\tau\gamma + J_{0j}^2)} \simeq \frac{1}{J_{01}^4} + \frac{1}{J_{02}^4}$$

$$= \frac{1}{(2.4)^4} + \frac{1}{(5.5)^4}$$

$$= 0.033 + 0.0019 \text{ for } \tau\gamma \ll J_{01}^2 \text{ and } J_{02}^2$$

where the roots of $J_0(x) = 0$ have been taken from Jahnke and Emde.(30) Also

$$\sum_j \frac{1}{J_{0j}^2(\tau\gamma + J_{0j}^2)} \simeq \frac{1}{J_{01}^2\tau\gamma} + \frac{1}{J_{02}^2\tau\gamma}$$

$$= \frac{1}{(2.4)^2\tau\gamma} + \frac{1}{(5.5)^2\tau\gamma}$$

$$= \frac{0.17}{\tau\gamma} + \frac{0.033}{\tau\gamma} \text{ for } \tau\gamma \gg J_{01}^2,\ J_{02}^2, \ldots .$$

Thus it may be seen that a reasonable approximation is obtained if only the first term of the series is retained, either for very small values of $\tau\gamma$ or for very large values of $\tau\gamma$.

In order to obtain upper limits for the radiant energy output, we confine our attention to the case in which wall deexcitation is unimportant, i.e.,

$$\tau\gamma >> J_{01}^{2} . \tag{40}$$

Equation (37) for the steady-state number density of molecules in the first level becomes now

$$n_{1,\,s.s.}^{T,\ell} = \tau \dot{w}_2 4\pi L^2 \frac{1}{J_{01}^{2}\,\tau\gamma} \simeq 0.7\pi L^2 \frac{\dot{w}_2}{\gamma}$$

or

$$\frac{C n_{1,\,s.s.}^{T,\ell}}{n_T} = 0.7\pi L^2\, C\, \frac{(A_{1\rightarrow 0} e^{-\theta'} + k_{1\rightarrow 0}{}^{-\theta})}{A_{1\rightarrow 0} + k_{1\rightarrow 0}} \tag{41}$$

where C is the length of the cylindrical chamber. For CO we have$^{(31)}$ $A_{1\rightarrow 0} = 33 \text{ sec}^{-1}$ and $\nu_{1,\,0} = 2143 \text{ cm}^{-1}$. At a temperature of 300°K; from the kinetic theory and from sound dispersion experiments,$^{(32),\,(33)}$

$$k_{1\rightarrow 0} = \eta Z_c \cong (10^{-4})(5 \times 10^{9} p) \text{ sec}^{-1}$$

and

$$D \simeq 10^{-2}\; p^{-1}\; \text{cm}^2/\text{sec}$$

where p is the pressure in atmospheres. Thus, in order to satisfy the assumed inequality given in Eq. (40), we must have

$$\frac{L^2}{D} (A_{1\rightarrow 0} + k_{1\rightarrow 0}) = \frac{L^2}{10^{-2}\; p^{-1}}\; (33 + 5 \times 10^{5} p) >> J_{01}^{2} \cong 5$$

which yields $p \gg 10^{-4}$ atmos for a characteristic length of about 1.5 cm. Setting $p = 10^{-3}$, we find that

$$k_{1\rightarrow 0} = 5 \times 10^{2}\ \mathrm{sec}^{-1}.$$

Since collisional deexcitation is of dominant importance for the relaxation processes, it is apparent that currently available infrared detectors (time constants $\simeq 10^{-6}$ sec) possess sufficiently high time resolution for observation of the decay period.

We must now compute the magnitude of the emitted radiation in order to determine whether detection with available infrared cells is, in fact, possible. The maximum intensity of radiation, $I_{\mathrm{max}}$, reaching the detector will be

$$I_{\mathrm{max}} = B\, Cn_{1,\,s.s.}^{T,\ell}\ A_{1\rightarrow 0}\ h\nu_{1,\,0} \tag{42}$$

where B is the fraction of the total emitted radiation reaching the detector, and includes collimation, lens and geometrical losses. With the use of Eq. (41), $I_{\mathrm{max}}$ becomes

$$I_{\mathrm{max}} = 0.7\pi L^{2}\, Cn_{T}\, \frac{A_{1\rightarrow 0}\, e^{-\theta'} + k_{1\rightarrow 0}\, e^{-\theta}}{A_{1\rightarrow 0} + k_{1\rightarrow 0}}\ h\nu_{1,\,0}B \tag{43}$$

whence for CO with $T' = 900^{\circ}$K, $B = 0.1$, $CL^{2} = 10\ \mathrm{cm}^{3}$, and $p = 10^{-3}$ atmos,

$$I_{\mathrm{max}} \cong 2 \times 10^{-6}\ \mathrm{watt}.$$

The NEP (noise-equivalent power) of a detector is defined as the incident power required on a detector to generate a signal equal to its rms noise level in a 1 cps band width. For larger band widths, the NEP increases linearly with the square root of the band width.(34) In the wavelength region of interest, a typical modern detector will possess an NEP of about $10^{-10}$. Considering a 10 kc bandpass as suitable for adequate time resolution in a CO relaxation measurement, and allowing a factor of 10 in excess of the detector noise level as a minimum for unequivocal observation, a signal level of about $10^{-7}$ watts should be detectable. Since this estimate is smaller by a factor of 10 than the calculated signal level, it appears that an experimental measurement of relaxation time is feasible from a study of the rate of decay of infrared radiation.

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## PART 2. STUDIES IN COMBUSTION

I. COMBUSTION AND FLAMES; A PAPER, REPRODUCED HERE FROM PROOF, TO APPEAR IN THE 1960 EDITION OF *ANNUAL REVIEWS OF PHYSICAL CHEMISTRY* (ANNUAL REVIEWS, INC., PALO ALTO).

# COMBUSTION AND FLAMES

By S. S. Penner and T. A. Jacobs

*Daniel and Florence Guggenheim Jet Propulsion Center, California Institute of Technology, Pasadena, California*

## Introduction

In combustion research, as in other fields of applied science, it is often helpful to differentiate between three essentially distinct categories of endeavor, namely (*a*) fundamental research designed to clarify basic principles involved in flame processes, (*b*) applied research that is motivated by the urgent need to solve a practically important problem, and (*c*) research of an intermediate character that is not likely to aid in the solution of a practically important problem and also does not provide new basic insight into combustion mechanisms. In combustion research, as perhaps in no other field of science, the investigator must continuously guard himself against the ever present temptation to invent a problem that requires extensive studies for proper comprehension but is ultimately neither illuminating nor useful.

## Basic Theoretical Research in Combustion

All combustion processes involve chemical changes in flow systems. The fundamental ingredients of the science are therefore composed of (*a*) the conservation equations for multicomponent, reacting gas mixtures; (*b*) explicit introduction of appropriate sets of rate laws for gas-phase and surface-catalyzed reaction rates; (*c*) imposition of suitable initial or boundary conditions; and (*d*), what is perhaps most difficult to accomplish in a meaningful manner, the mathematical formulation of a tractable problem that contains the essential features of the physical processes under study.

Satisfactory kinetic theory formulations for the conservation equations in reacting gas mixtures have been given by Chapman & Cowling (1) and by Hirschfelder and his collaborators (2). The continuum theory approach is less transparent (3, 4) although it has recently been shown by Nachbar, Williams & Penner (5) to yield results equivalent to those derived from the kinetic theory of gases.

Formally, the problem of estimating transport properties in reacting gas mixtures is well understood, although significant uncertainties remain in any given case in so far as appropriate estimates for interaction potentials and effective collision cross sections are concerned. This last statement is particularly true for free radicals and excited atoms or molecules of the type that is likely to occur in regions of active combustion.

Combustion processes involve all of the uncertainties that are imposed by incomplete knowledge of chemical reaction rates. The numerous publications in this field will be mentioned in the following discussion only if they have a direct bearing on the flame processes considered by us in detail. Nevertheless, it is important to note that some specialists in combustion favor the opinion that basic research in combustion is essentially synonymous with studies on the elucidation of fundamental reaction mechanisms and rates.

*Steady laminar flames in premixed gases.*—Perhaps the simplest and most fundamental problem in flame theory concerns the theoretical prediction of the steady laminar flame velocity in combustible gas mixtures. The studies of Zeldovich (6), Jost (7), Lewis & von Elbe (8), Hirschfelder *et al.* (9), von Kármán, Penner & Millán (10 to 12), Eyring *et al.* (13), Spalding (14), Emmons (15), and others (16 to 20) have clarified the basic problems to such an extent that general agreement may be said to exist now among active workers in this field concerning proper methods for formulating the differential equations, associated boundary conditions, and efficient procedures for solving the basic set of differential equations either numerically or by approximate (semi-) analytical techniques. The steady-state assumptions for the chain carriers (10) may often be used to advantage in deriving first approximations to the flame speed (10 to 12) although detailed composition profiles are not usually predicted correctly (21 to 23). The principal errors in laminar flame theory result from the lack of knowledge concerning chemical reaction mechanisms and rates and, to a lesser extent, from errors in the estimates of the transport parameters. In spite of observed large deviations for selected chemical species in excited states, it must be concluded from the apparent successes of laminar flame theory that the use of local average properties (e.g., temperature, velocity distribution, etc.) constitutes an acceptable approximation.

Detailed analytical studies by Montroll & Shuler and their collaborators (24 to 27) of relaxation processes for selected emitters in excited states provide some insight into the nature of the persistence of anomalous rotational and vibrational temperatures (28 to 31). This fascinating subject is, however, beset by experimental and analytical difficulties in practically important flames. It is unrealistic to expect that early advances in this field will lead to a proper foundation for a truly molecular theory of combustion in which significant differentiation is introduced not only between chemical species but also between specified chemical reactants with either different translational energies or effective population temperatures or both.

*Homogeneous and heterogeneous diffusion flames.*—A significant number of flame problems can be understood, in good approximation, on the assumption that the chemical reaction rates occur rapidly as compared with the transport of mass and energy. This concept has been used with good success in homogeneous systems and also in heterogeneous (e.g., two-phase) systems (32 to 37). The demonstration (38 to 41) of the practical utility of the diffusion-flame approximation in some liquid-fuel rocket engines suggests the possibility of developing rational scaling procedures for these devices (42, 43). Of considerable fundamental importance is the development of a statistical theory of spray combustion by Williams (44 to 47) using the diffusion-flame approximation.

The detailed description of diffusion flames is far more advanced for laminar processes than for the practically important turbulent reactions. Nevertheless, useful progress (48) has also been made in the latter field, particularly because of the utilization of appropriate dimensionless groups for correlating and extrapolating available experimental data.

A simplifying approximation that has been employed extensively in recent theoretical studies on flames, particularly diffusion flames, is the Shvab-Zeldovich procedure (49 to 51) in which the kinetic theory estimate of unity is introduced for the dimensionless ratio (i.e., the W. K. Lewis or Lewis number) measuring the relative energy transport by thermal conduction and by diffusion. With this assumption, the local energy in a reacting gas mixture becomes independent of the occurrence of diffusion and heat conduction. Furthermore, the equations for the conservation of the individual chemical species become similar with each other and with the energy equation in such a way that (partial) solutions may be found that are independent of the generally poorly-understood specific reaction rate parameters. Applications have been made of this procedure in the solution of such diverse combustion problems as the burning of single fuel droplets (51) or of statistical distributions of droplets in an oxidizing medium (44).

ignition and combustion in a laminar boundary layer (52 to 55), constant-volume explosions (56), laminar flame propagation (10), etc.

*Burning of monopropellant droplets.*—The burning mechanism of monopropellant droplets involves over-all rates that are controlled by both chemical reaction rates and by transport processes. Significant theoretical solutions to this important problem have been obtained by Williams (44, 47) and by Millán & Sanz (57). A numerical solution for the burning of single monopropellant droplets was obtained earlier by Lorell & Wise (58).

*Ignition of premixed gases.*—A very useful empirical correlation formula has been developed for minimum ignition energies in premixed gaseous systems. Early interpretation by Lewis & von Elbe (59) of the empirical results in terms of an "excess enthalpy principle" must be revised since the "excess" enthalpy has been shown to be either positive, negative, or zero depending only on the numerical value of the effective Lewis number (60 to 62).

Ignition processes seem to involve the requirement that the minimum energy supply is equivalent to the energy required for steady propagation of the flame (62, 63). This fundamental idea is in accord with results observed in many homogeneous and heterogeneous systems. A more elaborate theory of ignition has been discussed by Rosen (64). Some interesting recent experimental studies on ignition have been performed by Wolfhard (65).

*Flammability limits.*—Following the introduction by Spalding (66) of the idea that flammability limits are determined by heat losses from a combustion zone, a more transparent analytical treatment has been worked out by von Kármán (67). Mayer (68) has succeeded in presenting this approach in a form which is really useful for the correlation of experimental data.

*Turbulent flames.*—In view of the enormous difficulties involved in the quantitative description of turbulent processes without combustion, it is not surprising to find that progress in our understanding of turbulent combustion flames has been very slow. The early work of Scurlock & Grover (69) and Karlovitz (70) appears to be beset with conceptual and interpretive difficulties that include even experimental uncertainties (71) concerning the existence and magnitude of flame-generated turbulence. However, Kovaszny (72) has recently proposed a simple and useful approach, at least to the phenomenological description of turbulent flame processes, which appears to find immediate applications in the interpretation of measured turbulent flame velocities. Extensive studies on turbulent flames have been described at a recent international symposium (73). Translations of representative Russian papers in this field have also become available (74). Spectroscopic studies on turbulent flames and their proper interpretations are still a somewhat controversial problem (75, 76).

*Chemical reactions in supersonic flow.*—With the current interest in the development of high-Mach number ramjets, as well as with long-standing studies on rocket nozzle and exhaust flows, there has recently been considerable interest and activity relating to chemical changes in supersonic flow. Clever experimental arrangements have been devised by Behrens & Rössler, (77), Nichols *et al.* (78, 79), Gross *et al.* (80, 81), and others (82 to 85). However, little progress has been reported on the quantitative interpretation of results although there is no basic uncertainty about the proper utilization of characteristics calculations in supersonic flows with heat release.

*Detonation phenomena.*—There is probably no part of combustion research in which more careful measurements or more careful interpretive work has been done than on detonation phenomena. This work covers the entire spectrum of activity: steady propagation velocity measurements in order to verify or disprove the existence of Chapman-Jouguet detonations by Kistiakowsky *et al.* (86 to 89), related theoretical studies by Kirkwood & Wood (90, 91), Hirschfelder *et al.* (89, 92 to 94), and others (89, 95 to 102); measurements of detonation induction distance (89, 103); two-dimensional phenomena by Fay (104 to 106); gas-dynamic or phenomenological interpretations by Oppenheim (102, 107); spinning detonations by Chu (108); transitions from deflagration to detonation (89, 103); spherical detonations (89, 109, 110), etc. A brief look at the literature indicates that none of the interesting phenomena associated with detonations, other than the thermodynamic procedure for calculating steady detonation velocities at the upper Chapman-Jouguet point, has proven amenable to unambiguous and unimpeachable analytical interpretation.

*Constant volume explosions.*—Starting with the concepts of thermal and branched-chain explosions, which were perhaps first clearly defined by Semenov (111), slow but significant progress has been made in the quantitative description and interpretation of many chemical processes. We refer to a series of recently published books for detailed discussions of these important problems (8, 89, 111).

*Unsteady flames.*—Many interesting flame phenomena are not adequately described by the steady-state fluid-dynamical equations together with appropriate reaction terms. In this connection, we have already noted briefly recent work on ignition and on the transition from deflagration to detonation. Other interesting phenomena are connected with vibratory motion, e.g., cellular flames which appear to depend on preferential diffusion of light and heavy constituents [Markstein (112) and others]. Non-steady flame phenomena have also been discussed by Rosen (113), Jost *et al.* (114), and others. A comprehensive review of this subject is currently in preparation (115).

*Thermochemical research.*—No discussion of flames is adequate without some consideration of related thermochemical studies which, in principle, define at least the final equilibrium state after completion of combustion. Interest in exotic propellants has led to renewed basic studies on compounds containing such elements as F, B, Be, Cl, Li, Si, etc. (116 to 120). Significant uncertainties remain at the present time even with regard to the proper standard heats of formation for many important oxides of light metals. Although the experimental and theoretical procedures used for studies of this type may be said to be classical, there is little doubt that continued work, particularly on high-temperature thermodynamics, will constitute an integral part of present and future combustion activities.

*Ionization in flames.*—No modern discussion of experimental and theoretical studies concerned with combustion problems is complete without mention of ions and electrons in flames (121 to 128). The weight of available experimental evidence suggests the prevalance of "excessive" degrees of ionization in flames when a comparison is made with the corresponding calculated equilibrium data. This phenomenon of "chemiionization" must be directly related to the elementary processes producing ions and electrons in flames and may therefore be appropriately classified as a special branch of (high-temperature) reaction kinetics.

## SELECTED COMBUSTION PROCESSES MOTIVATED BY CURRENT DEVELOPMENT STUDIES

One of the most difficult tasks facing the specialist in combustion involves the proof that the results of basic research have a more or less direct bearing on the development or production of any type of combustion device. In so far as the authors are able to judge, the results of combustion research can often be shown to clarify important concepts, to provide broad guide lines for development procedures, and to facilitate the qualitative prediction of new performance results or the semi-quantitative correlation of available data. However, combustion research has not proved to be directly useful in the solution of important practical problems that have arisen as a direct consequence of engine development studies. We proceed to demonstrate the validity of this last contention by examining four troublesome development problems that have provided direct motivation for a great deal of combustion research. Although interesting results have been derived from these studies, the practical problems have certainly not been solved or even ameliorated by the use of research results.

*Combustion and ablation in boundary layers.*—In connection with the design of nose cones for reentry studies on intercontinental and shorter range ballistic missiles, a great deal of basic work has been done on heat transfer through hypersonic boundary layers with and without combustion (129 to 154). Comprehensive reviews of this work have been published by Lees (130), Allen (131), Stalden (132), Griffith (133), and Rosner (134).

Because of large aerodynamic heating rates at hypersonic speeds and the low heat capacity of sharp-nosed boides, interest has centered on blunt-nosed bodies and the heating rate at the stagnation point. Of particular interest are studies on the heating rates with recombinations of atoms. Lees (143) and Fay & Riddell (152) have presented solutions to the problem employing the assumption of a binary mixture of atoms and molecules. For the case of chemical equilibrium, their results have been substantiated by shock tube experiments performed by Rose & Stark (151) and by Rabinowicz (139). The assumption of a fully catalytic wall, corresponding to zero atom fraction at the surface but with finite recombination rate, employed by both of the aforementioned authors was questioned and investigated further by Scala (146) and Goulard (140). They showed that the atom fraction at the wall could be small but never zero. The case of arbitrary catalytic activity at the wall has been studied by Rosner (136), Chambré & Acrivos (153), and others. The catalytic activity of specific metallic and ceramic surfaces for atom recombination has been investigated by Linnett & Marsden (154). Rutowski (149) has considered the stagnation point heat transfer for ionized gases.

The theory for ablation of surfaces subjected to aerodynamic heating has been developed by Bethe & Adams (155) and others (156 to 161). The analytical studies developed by Lees (156) and Roberts (157) started with an assumed velocity profile whereas Bethe & Adams assumed the form of the temperature profile. Carrier (159) has improved the analyses. A comparison of these theories has been given by Sutton (160). Apparently all of the theories yield heating and melting rates that are too high.

While theoretical and experimental shock-tube studies were in progress on hypersonic flow over bodies of various shapes, experimental flight tests were, of course, also performed. These flight tests have shown that a blunt, ablating nose cone that serves as a heat sink can be constructed in such a way that it is able to withstand the heat transfer and thermal stresses following almost any missile trajectory.

*Chemical changes during nozzle flow.*—The theoretical performance differences for rocket engines between nozzle flow without composition change (i.e., frozen or constant-composition flow) and nozzle flow with maintenance of complete chemical equilibrium (i.e., "shifting" or equilibrium flow) are known to amount to from 2 to perhaps 15 per cent depending on the propellant composition and on the adiabatic flame temperature. For conventional, low-energy propellants (i.e., propellants with a specific impulse $I_{sp}$ of less than about 250 lb. thrust-sec/lb. mass of propellant) the theoretical performance differences are relatively small; however, for high-energy propellants (i.e., $I_{sp}$ of 275 to 400 sec.) the larger performance differences are encountered. A change of a few seconds in specific impulse for a long-range missile of conventional design generally corresponds to range differences of hundreds of miles.

Because of the numerical complexities of an exact solution of the one-dimensional nozzle-flow problem with chemical reactions, various approximate procedures have been developed. Early Work by Penner (162 to 164) yielded criteria for near-equilibrium and near-frozen flows. More recently, Bray (165) employing Lighthill's (166) ideal dissociating gas and Freeman's (167) rate parameter has investigated the flow of initially dissociated nitrogen and oxygen through a hypersonic nozzle. He found that the flow could be described by three regions of flow: an initial equilibrium flow, a short transitional region in which there is marked deviation from equilibrium, and finally, an essentially frozen flow. This behavior may also be observed in the complete calculations of Krieger (168) and Heims (169). Based on his study, Bray has proposed an approximation in which the flow is initially in equilibrium and then suddenly freezes, the point of sudden freezing being determined by the rate equations. Wegener, who has observed experimentally the flow of dissociated $N_2O_4$ in a supersonic nozzle (170, 171), applied Bray's approximation to his data and found good agreement (172).

In spite of the availability of *procedures* for analyzing nozzle-flow problems, little or no useful predictions for real rocket engines are possible because (*a*) reliable experimental data are not available for high-temperature reaction rates of propellant reaction products and (*b*) the theoretical calculations start from the premise that thermodynamic equilibrium has been reached in the combustion chamber. This assumption is unjustified for most propellant systems and, in particular, must be viewed with doubt for high-energy solid propellants. For this reason, the study of refined nozzle calculations with chemical reactions has been of no direct aid in assessing the actual attainable engine performance which must still be evaluated empirically.

*Burning rates of solid propellants.*—Following war-time studies on the burning rates and decomposition mechanism of double-base propellants by Daniels *et al.* (173), Crawford & Parr (174), Rice & Ginell (175), and others, basic research in this field went through a long period of dormition. Recently, the corresponding problem has been attacked with vigor for composite solid propellants and simplified model studies have been performed for selected propellant ingredients and even for specially synthesized composite powders. References and a discussion of this work, including consideration of contributions by Geckler (176, 177), Summerfield *et al.* (178), Friedman *et al.* (179), Nachbar (180), Schultz & Dekker (181, 182), and others, may be found in a recently published survey paper (183). An exhaustive compilation of basic knowledge on solid propellants is in preparation (184).

The diverse theoretical studies on the burning mechanism of composite solid propellants lack a firm foundation because of the sparsity of definitive experimental data. The work of Schultz and colleagues (181 to 183) on pyrolysis rates of pure oxidizers and binders has led this investigator to the conclusion that the mean temperatures during steady burning are different for the oxidizers and fuels. Geckler (176, 177) has been concerned with the forumulation and solution of the gas-phase chemical reactions by using models and methods that are analogous to those employed in laminar flame theory. Summerfield and his colleagues (178) have performed experimental studies primarily on ammonium perchlorate propellants and have explored the implications of a "granular diffusion flame model" in which the combustion rate is controlled by both transport processes and chemical reaction rates. Fundamental experimental studies on pure ammonium perchlorate have recently led Friedman *et al.* (185) to the conclusion that radiative heat losses play an important part in determining flammability limits. Various attempts to construct "complete" theories of burning are in progress and will presumably be reviewed at the *Eighth International Combustion Symposium* in 1960.

We may justifiably start from the premise that the objective of basic research on the burning mechanism of solid propellants must be the development of useful, predictive procedures for designing propellants with arbitrary, specified burning rates. However, when viewed with this objective in mind, we must assert categorically that neither the published studies on double-base propellants nor the current work on composite propellants has had, or is likely to have, a profound influence on propellant development. Propellant design and development is done by specialists on the basis of intuitive insight or of artistic notions developed through long experience. The day when propellants can be manufactured to predetermined specifications by the use of scientific principles appears to lie in the distant future.

*Combustion of sprays.*—Propulsion devices utilizing liquid propellants ultimately involve the burning of sprays. The recognition of this fact has provided the immediate motivation for experimental and theoretical studies on the burning of single fuel droplets (32 to 37) and of droplet arrays (40, 44 to 47) in oxidizing media. These investigations have led to a satisfactory understanding of heterogeneous diffusion flames and to an acceptable first approximation for an analytical description of the phenomenon. Experiments by Kumagai & Isoda (36) on burning droplets in a freely falling apparatus constitute the culminating tests of the theory and have shown that a steady-state theory is, in fact, not strictly applicable.

The task of integrating the knowledge derived from single-droplet studies into a theory of spray burning has been pursued by Williams (44) who has pointed out the need for developing a statistical theory and who has invented a Boltzmann-type equation in which the individual liquid droplets play the same role as the molecules in the mathematical theory of nonuniform gases. The essential validity of this procedure, if it requires proof, has been demonstrated by quantitative calculation of the (laminar) burning velocity in a monodisperse, dilute spray for which a direct comparison with experimental data is possible.

Application of the theory of spray burning to engine combustion studies presents difficulties of staggering magnitude. To begin with, the effective drop-size distribution and flow velocity in sprays produced by any injector used in an engine are unknown. Such troublesome problems as droplet breakup on collision, droplet generation during burning, etc., are completely beyond our present comprehension of the behavior of heterogeneous systems. Simplified models for the combustion of liquid propellants in rocket engines have been treated by Priem (138), Spalding (186), and Mayer (187).

In view of the impossibility of using the available spray combustion theory for useful predictions, it is only reasonable to consider the possibility of employing the theory as a framework for the correlation of experimental results. A serious test of the theory has been worked out (40) for a diverging liquid-fuel rocket engine with the obvious conclusion that the precision of correlation of experimental data depends only on the number of adjustable parameters employed in the analysis.

## ENGINE COMBUSTION PROBLEMS

In addition to strongly motivated research, examples of which have been considered in the preceding section, it is appropriate to mention briefly the representative development problems that are of major importance in connection with current developments of actual (rocket) engines.

*Liquid-fuel rocket engines.*—Perhaps the single most troublesome and costly problem encountered in liquid-fuel rocket engine development is associated with the uncontrolled development of high-frequency combustion oscillations. Significant progress in unravelling the essential features of this phenomenon has been made by Crocco (188), who has replaced the entire complex combustion processes through a symbolic time-delay step. These results are, however, at the present time more useful for *post mortem* commentary than for *a priori* predictions and elimination of difficulties. For more recent considerations of this controversial problem, we refer to discussions by Zucrow & Osborn (189, 190) and Crocco *et al.* (191, 192).

Another approach for reducing the costly development difficulties was initiated by Penner (43) and Crocco (42) and involves utilization of the principles of similarity analysis for rational scaling of well designed engines to larger sizes. This approach is also of limited utility because maintaining exact similarity with respect to all of the important dimensionless groups is impossible; furthermore, the rate-controlling combustion processes cannot be defined properly, nor is it possible to predict even the changes in over-all conversion time as functions of injector configuration and motor size. Thus the design of liquid-fuel rocket engines, as well as the scaling to larger sizes, has remained an empirical art.

*Solid-Fuel rocket engines.*—Among the most troublesome practical problems in solid-fuel rocket engineering is the uncontrolled development of resonance burning, i.e., of large pressure maxima that may lead to rupture of the engine or disintegration of the propellant charge. Theoretical studies by Grad (193), Smith & Sprenger (194), Green (183, 195), Green & Nachbar (196), and McClure & Hart (197) have indicated possible causes for this phenomenon. Experiments performed by Brownlee (198) and Price & Sofferis (199) suggest that the phenomenon, though reproducible, is an exceedingly sensitive function of propellant composition, i.e., of combustion rates. Resonance burning is probably also dependent on the elastic properties of the solid and on the coupling between propellant and container walls. Needless to say, the theories that "predict" a discrete spectrum of unstable operating frequencies, as well as the more elaborate and more appealing analyses that suggest continuous regions of instability, have no current impact on the design of propellant charges and contain so many unknown parameters that useful predictions are not likely to be made in the near future.

*Air-breathing engines.*—The principles of similarity analysis have proved of some value in the design of turbojet combustors (200, 201). Furthermore, studies on the mechanism of flame holding behind bluff bodies (202 to 207) have yielded useful concepts for engine builders although the practical design involves flame spreading in ducts and interference between wakes.

## CONCLUDING REMARKS

The preceding examination of the relation between combustion in flames and practical propulsion development leads inevitably to the conclusion that a major stumbling block in understanding and utilizing combustion processes is directly connected with lack of information concerning high-temperature kinetics. Combustion research is more likely to be ultimately useful if it is really fundamental and thorough, and is less likely to be of value if confined to a specific process or procedure. All good research is justifiable on gas-phase, liquid-phase, and solid-phase kinetics, on transport properties, on mixing in low-velocity and high-velocity streams, on the theory of turbulence, on mass and energy transfer by diffusion, on flame spectroscopy, etc. Much greater circumspection is required, however, in the selection of so-called developmental research: it is so easy to invent a problem and to study the invention and so difficult to construct a meaningful approximation to the real thing!

In the preceding survey we have made no effort to furnish an exhaustive literature summary. For this reason, we present a separate list of specialized texts and symposium proceedings (208 to 231) which should serve as adequate starting material for more complete literature coverage, particularly on experimental problems and on the numerous theoretical topics that we have not treated specifically.

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II. <u>APPROXIMATE THEORETICAL PERFORMANCE EVALUATION FOR A DIVERGING ROCKET</u>; A PAPER, REPRODUCED HERE FROM PROOF, TO APPEAR IN <u>ASTRONAUTICA ACTA</u> (JULIUS SPRINGER, VIENNA).

# Approximate Theoretical Performance Evaluation for a Diverging Rocket

By

**T. A. Jacobs[1], S. S. Penner[1], G. Gill[2] and E. F. Eckel[2]**

### Abstract – Zusammenfassung – Résumé

***Approximate Theoretical Performance Evaluation for a Diverging Rocket.*** A simplified combustion model, which is motivated by available performance studies on the diverging rocket reactor, has been used as basis for an engine performance evaluation. Comparison with conventional rocket configurations shows that an upper performance limit for the diverging reactor is comparable with performance estimates for engines using an adiabatic work cycle. Development of the diverging reactor for engine applications may, however, offer some advantages for very hot, high-energy, propellant systems.

## I. Introduction

In previous publications we have discussed application of the diverging reactor for the determination of overall kinetic parameters under the conditions actually existing in rocket combustion chambers [1], [2]. In the present discussion we shall outline an approximate engine performance evaluation for a diverging rocket chamber[3]. As basis for this evaluation we choose a simplified combustion model that we have used previously for the computation of various dimensionless groups [1].

A schematic diagram of the engine and combustion front is shown in Fig. 1. For the sake of simplicity, we assume that all of the heat release occurs at the plane 1, 2 in Fig. 1, that the gases behave as ideal gases with a constant ratio $\gamma$ for the specific heat at constant pressure to the specific heat at constant volume, and that isentropic, one-dimensional, expansion occurs in the regions upstream and downstream from the reaction front. We are led to the model implicit in these approximations through the experimentally observed fact that the sonic plane occurs very close to the injector[1] and that the effective reaction rates are very fast (with low overall activation energy) near the injector end whereas they are relatively slow farther downstream (with large effective activation energy). Since the limited available experimental data suggest that most of the reactions are completed very close to the injector end, we may consider the present analysis with the characteristic length $L$ in Fig. 1 equal to zero, or at least very small, to provide a reasonable upper limit for the performance which can be achieved with a diverging reactor.

## II. Outline of Theoretical Considerations

### *1. Pressure Ratio Across the Reaction Front*

The performance of a diverging rocket engine is a sensitive function of the stagnation pressure ratio $p_{s2}/p_{s1}$ across the reaction plane. Fortunately it turns out that reasonable values of the heat release lead to values of $p_{s2}/p_{s1}$ which are practically constant at about 0.8. We shall now prove the validity of this last statement by utilizing appropriate, simplified, versions of the conservation equations.

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[1] Division of Engineering, California Institute of Technology

[2] Rocketdyne, North American Aviation Corporation

[3] With appropriate changes in wording, the present analysis applies also to a throatless motor.

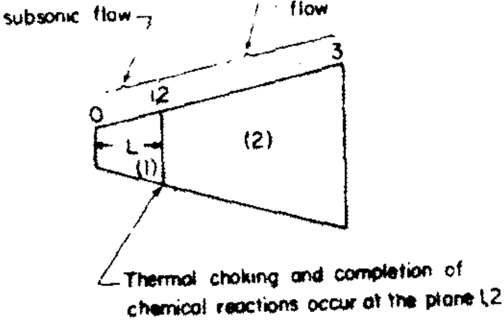

Fig. 1. Schematic diagram of a diverging rocket engine

The overall conservation of mass equation at the plane 1, 2 in Fig. 1 is

$$\varrho_1 v_1 = \varrho_2 v_2$$

where $\varrho$ and $v$ identify, respectively, the density and linear flow velocity. Multiplying and dividing by $\sqrt{\gamma R_g T}$ and replacing $\varrho$ by $p/R_g T$ we find that

$$\varrho v = \frac{p}{R_g T}\sqrt{\gamma R_g T}\,\frac{v}{\sqrt{\gamma R_g T}} = \left(\frac{\gamma W}{T}\right)^{1/2} p M$$

where $R_g = R/W$ is the specific gas constant, $R$ denotes the molar gas constant, $W$ is the molecular weight of the gas mixture, $T$ stands for the local (random translational) temperature, and $M$ identifies the local MACH number. Hence the continuity equation becomes

$$\left(\frac{\gamma_1 W_1}{T_1}\right)^{1/2} p_1 M_1 = \left(\frac{\gamma_2 W_2}{T_2}\right)^{1/2} p_2 M_2. \tag{1}$$

Similarly, the equation for conservation of momentum is

$$p_1 + \varrho_1 v_1^2 = p_2 + \varrho_2 v_2^2$$

where

$$p + \varrho v^2 = p\left(1 + \frac{\varrho}{p}\,\frac{v^2}{\gamma R_g T}\,\gamma R_g T\right) = p\,(1 + \gamma M^2)$$

whence

$$p_1\,(1 + \gamma_1 M_1^2) = p_2\,(1 + \gamma_2 M_2^2). \tag{2}$$

In terms of an integral over stagnation temperatures and the total heat release per unit mass $q$, the energy equation reduces to

$$q = \int_{T_{s1}}^{T_{s2}} c_p\,dT_s \tag{3}$$

where $c_p$ is the specific heat at constant pressure.

The stagnation temperature $T_s$ and the translational temperature $T$ are related through the expression

$$T_s = T + \frac{v^2}{2 c_p}$$

or

$$T_s = T\left(1 + \frac{v^2}{2 c_p T}\,\frac{\gamma R_g T}{\gamma R_g T}\right) = T\left(1 + \frac{\gamma R_g}{2 c_p} M^2\right) = T\left(1 + \frac{\gamma - 1}{2} M^2\right)$$

since $R_g = c_p - c_v$ and $\gamma = c_p/c_v$. Hence Eq. (1) becomes

$$\left(\frac{\gamma_1 W_1}{T_{s1}}\right)^{1/2} p_1 M_1 \left(1 + \frac{\gamma_1 - 1}{2} M_1^2\right)^{1/2} = \left(\frac{\gamma_2 W_2}{T_{s2}}\right)^{1/2} p_2 M_2 \left(1 + \frac{\gamma_2 - 1}{2} M_2^2\right)^{1/2}.$$

We may now eliminate the pressure between the continuity and momentum equations by dividing this last relation by Eq. (2). We then find that

$$U_2(\gamma_2, M_2 = 1) = U_1(\gamma_1, M_1)\left(\frac{T_{s2}}{T_{s1}}\frac{W_1}{W_2}\right)^{1/2} \tag{4}$$

where

$$U = \frac{\gamma^{1/2} M \left(1 + \frac{\gamma - 1}{2} M^2\right)^{1/2}}{1 + \gamma M^2} \tag{5}$$

The function $U$ has been tabulated in [3] for various values of $\gamma$ and $M$.

For specified values of the heat release and $c_p$, the change in stagnation temperature and, therefore, the stagnation temperature ratio, are defined by Eq. (3). Hence Eq. (4) may be used to determine $M_1$ for known values of $\gamma_1$, $\gamma_2$, $W_1$ and $W_2$. The stagnation pressure loss may then be evaluated by using the expression

$$\frac{p_{s2}}{p_{s1}} = \left(\frac{p_{s2}}{p_2}\right)\left(\frac{p_1}{p_{s1}}\right)\left(\frac{p_2}{p_1}\right) = \left(\frac{p_{s2}}{p_2}\right)\left(\frac{p_1}{p_{s1}}\right)\left(\frac{1 + \gamma_1 M_1^2}{1 + \gamma_2}\right) \tag{6}$$

since $M_2 = 1$. The pressure ratios $(p_{s2}/p_2)$ and $(p_1/p_{s1})$ are conveniently obtained by using existing tabulations for isentropic expansions [4]. For these calculations it is actually not necessary to utilize constant values of $W$ and $\gamma$.

The stagnation pressure ratio $p_{s2}/p_{s1}$ has been calculated as a function of the parameter $(T_{s2}/T_{s1})(W_1/W_2)$ from Eq. (6) for $\gamma_1 = \gamma_2 = 1.3$ by using Eq. (4) for the determination of $M_1$. The results are plotted in Fig. 2. Reference to Fig. 2 shows that $p_{s2}/p_{s1} \cong 0.8$ for $(T_{s2}/T_{s1})(W_1/W_2)$ greater than about 10; additional data may be obtained from [6].

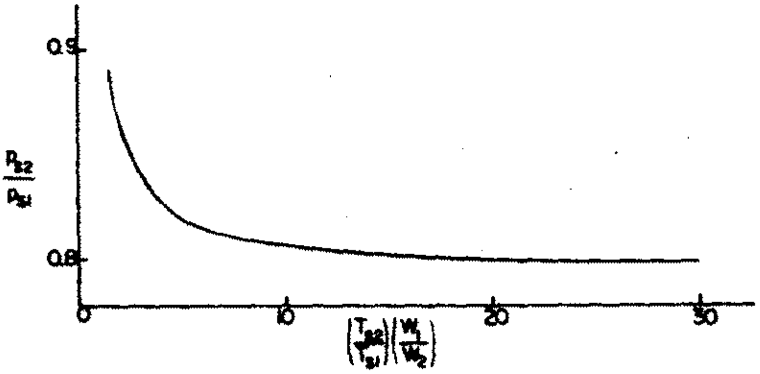

Fig. 2. The stagnation pressure ratio $p_{s2}/p_{s1}$ as a function of the parameter $(T_{s2}/T_{s1})(W_1/W_2)$ for a diverging rocket $(\gamma_1 = \gamma_2 = 1.30)$

## *2. Definitions of the Thrust Coefficient for Diverging and for Conventional Rocket Engines*

The thrust coefficient $C_{F,con}$ for a conventional rocket engine (see Fig. 3) is defined by the expression

$$C_{F,con} = \frac{F}{p_{s0} A_*} \tag{7}$$

where $F$ is the thrust on the engine, $p_{s0}$ identifies the chamber pressure, and $A_*$ is the cross-sectional area at the nozzle throat. For properly expanded nozzles with $p_3$ equal to the external pressure,

$$F = (\varrho_3 v_3 A_3) v_3 = A_3 p_3 \gamma_2 M_3^2 \tag{8}$$

if $\gamma_2$ denotes the (constant) heat capacity ratio for the expanding gases. We note that in a conventional rocket

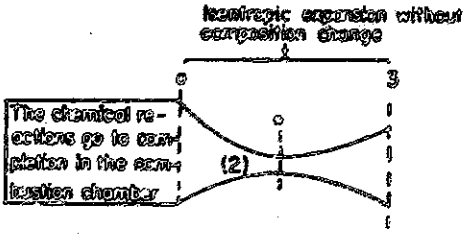

Fig. 3. Schematic diagram of a conventional rocket engine

$$p_{s0} = p_{s3}$$

if we neglect dissipative terms during expansion and chemical reactions during nozzle flow. Thus

$$C_{F,con} = \frac{\gamma_2 M_3^2 (A_3/A_0)}{(p_{s0}/p_3)} . \tag{9}$$

For the diverging reactor we define a thrust coefficient by the analogous expression

$$C_{F,div} = \frac{F}{p_{s2} A_{1,2}} = \frac{\gamma_2 M_3^2 (A_3/A_{1,2})}{(p_{s3}/p_3)} . \tag{10}$$

But

$$\frac{p_{s3}}{p_3} = \frac{p_{s2}}{p_3} = \left(\frac{p_{s2}}{p_{s1}}\right)\left(\frac{p_{s1}}{p_3}\right) = \left(\frac{p_{s2}}{p_{s1}}\right)\left(\frac{p_{s0}}{p_3}\right)$$

whence

$$C_{F,div} = \frac{\gamma_2 M_3^2 (A_3/A_{1,2})}{\left(\frac{p_{s2}}{p_{s1}}\right)\left(\frac{p_{s0}}{p_3}\right)} . \tag{11}$$

It is interesting to observe that Eqs. (9) and (11) differ formally only through the occurrence of the term $(p_{s2}/p_{s1})$ in the denominator of Eq. (11) since $A_0$ and $A_{1,2}$ are analogous quantities. This pressure ratio, in turn, has been related to the heat release through $(T_{s2}/T_{s1})(W_1/W_2)$ in the preceding Section II 1.

### *3. Performance Evaluations for the Diverging Reactor*

It is clearly possible to make a number of different performance evaluations for the diverging rocket. The performance estimate will then depend somewhat on the predetermined design restrictions. We shall now consider two instructive examples. We restrict our discussion to the representative case with $\gamma_2 = 1.30$ and $(T_{s2}/T_{s1})(W_1/W_2) > 10$ for which Fig. 2 shows that $p_{s2}/p_{s1} = 0.80$. The numerical work is facilitated by constructing a universal plot in which $p_{s3}/p_3$, $A_3/A_0$, $A_3/A_{1,2}$, and $M_3$ are related to the pressure ratio (cf. Fig. 4). For conventional rockets this calculation involves only the use of tabulated isentropic functions which first yield $M_3$ through the expression

$$\frac{p_{s0}}{p_3} = \left(1 + \frac{\gamma - 1}{2} M_3^2\right)^{\gamma/(\gamma-1)}$$

and then $A_3/A_0$ in terms of $M_3$ [4]. The curve $p_{s3}/p_3 = p_{s0}/p_3$ for the conventional engine is not plotted in Fig. 4. For the diverging rocket it is convenient to compute first the ratio $p_{s3}/p_3$ and then to evaluate $M_3$ and $A_3/A_{1,2}$ through use of the isentropic expansion relations.

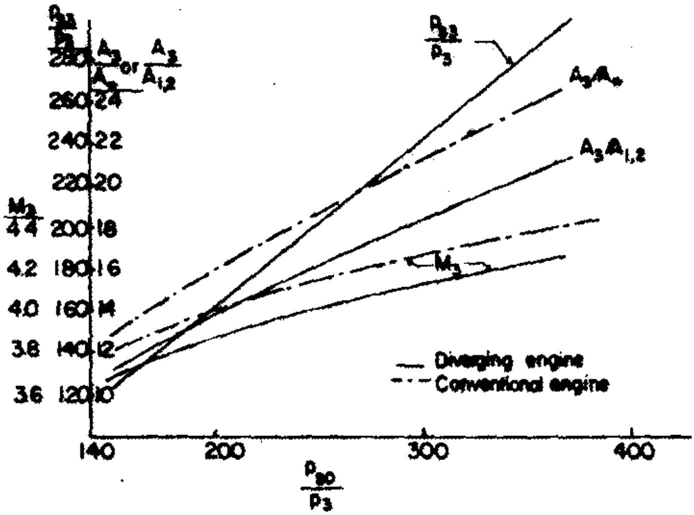

Fig. 4. The quantities $M_3$ and $A_3/A_*$ (for a conventional rocket) and $M_3$, $p_{s3}/p_3$ and $A_3/A_{1,2}$ (for a diverging rocket) as a function of the pressure ratio $p_{s0}/p_3$. $(T_{s2}/T_{s1})(W_1/W_2) = 10$ for the diverging rocket, $\gamma_4 = 1.30$.

## III. Comparison of Engines with Fixed Thrust and Pressure Ratio $p_{s0}/p_3$

Consider a conventional and a diverging engine both of which deliver the thrust $F = 25{,}000$ lbs and which are designed with pressure ratios $p_{s0}/p_3 = 200$. Also assume that $p_3 = 1$ psia and $(T_{s2}/T_{s1})(W_1/W_2) > 10$.

For the conventional engine we find from Fig. 4 that $M_3 = 4.0$ and $A_3/A_* = 15.9$. Hence, using Eq. (9), $C_{F,\mathrm{conv}} = 1.63$; it now follows from Eq. (7) that

$$A_* = \frac{2.5 \times 10^4}{1.64 \times 200} = 76.3 \text{ in}^2$$

and

$$A_3 = 15.9\,A_* = 1211 \text{ in}^2.$$

Similarly, for the diverging rocket, $M_3 = 3.87$, $A_3/A_{1,2} = 13.8$, $p_{s3}/p_3 = 162$, $C_{F\,\mathrm{div}} = 1.64$ [from Eq. (10)],

$$A_{1,2} = \frac{2.5 \times 10^4}{1.63 \times 162} = 94.8 \text{ in}^2,$$

and

$$A_3 = 13.8\,A_{1,2} = 1308 \text{ in}^2.$$

Using customary design estimates, the weight ratio of the diverging nozzle sections for the two engines [5] is given by the relation

$$\frac{m''_{\mathrm{div}}}{m''_{\mathrm{conv}}} = \frac{\left(\dfrac{A_3}{A_{1,2}}\,\dfrac{F}{p_{s3}}\right)_{\mathrm{div}}}{\left(\dfrac{A_3}{A_*}\,\dfrac{F}{p_{s3}}\right)_{\mathrm{conv}}} = 1.07.$$

Hence it follows that the diverging rocket will be relatively lighter provided the chamber and converging sections of the conventional engine have more than about 7% of the weight of the diverging section and the effective weight of the diverging reactor between the injector and reaction planes is negligibly small. We expect in practice that the combined weights of the motor and converging sections of a conventional engine will constitute about 10% of the total weight. Hence it follows that optimal design of the diverging reactor will be roughly comparable with the usually achieved design of a conventional rocket for equivalent engine thrust and pressure ratio $p_{s0}/p_3$.

## IV. Comparison of Engines with Identical Diverging Sections but Different Pressure Ratios $p_{i0}/p_3$

Consider two engines which develop equivalent thrust but with

$$\frac{A_3}{A_*} = \frac{A_3}{A_{1,2}} = 15.9.$$

Then, from Fig. 4, $p_{i0}$ = 244 psia for the diverging reactor whereas $p_{i0}$ = 200 psia for the conventional engine. The corresponding weight ratio for the pumping equipment (5) is

$$\frac{\mathfrak{M}^p_{\text{div. pump}}}{\mathfrak{M}^p_{\text{conv. pump}}} = \frac{(p_{i0})_{\text{div}}^{2/3}}{(p_{i0})_{\text{conv}}^{2/3}} = 1.14.$$

Therefore, if the chamber and converging section of the conventional engine weigh about 14% more than the pumping equipment, then the diverging rocket will be the lighter engine if we neglect the influence of the slightly higher injector end pressure on the weight of the diverging reactor and, furthermore, assume again that the chemical reactions are completed very close to the injector plane.

Comparison of the preceding two examples suggests that the use of relatively large pressure ratios $p_{i0}/p_3$ for the diverging rocket is impractical since the pumping equipment makes a major contribution to the mass of the engine.

## V. Conclusions

Examination of the performance data specified in the preceding paragraph shows that diverging and conventional rocket engines should yield comparable facilities after optimum development of the relatively untried diverging rocket. It is difficult to assess the practical utility of the new device since it possesses both an obvious advantage and an obvious disadvantage. The advantage lies in the possibility of utilizing very hot, high-energy, propellant systems under conditions in which excessive temperatures and heat losses are not encountered because the chemical energy may be transformed directly into translational energy and because the diverging rocket may be relatively easier to cool[1]. On the other hand, in order to approximate our assumed combustion model (compare Fig. 1), it is apparent that the diverging reactor must give very efficient combustion near the injector plane, i.e., severe heat transfer and erosion should occur when the practical performance of the device approximates optimum design.

In conclusion it is appropriate to speculate on the possible existence of high-frequency instabilities in diverging reactors for which neither experimental nor theoretical data are available. The nature of the design actually appears to be rather favorable for the suppression of high-frequency instabilities: transverse modes should be damped out because of the rapidly changing cross-sectional area of a device in which strong composition inhomogeneities must accompany chemical changes; furthermore, it is probably impossible to sustain longitudinal oscillations because of extreme damping which must accompany diverging, supersonic, flow with chemical reactions. On the basis of the preceding considerations, it appears highly desirable to initiate a large-scale engine program for a high-energy liquid propellant mixture (e.g., $ClF_3$-$N_2H_4$). It is unlikely that small-scale engine tests will provide significant information either concerning the practical difficulties inherent in proper injector design or concerning the nature of combustion instabilities.

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[1] A practical diverging rocket design might well involve the use of ablating material near the injector end. The performance of the engine should not suffer significantly because of enlargement of cross-sectional area near the injector associated with ablation.

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