THE DISSOCIATION RATE OF HYDROGEN FLUORIDE
BEHIND INCIDENT SHOCK WAVES

DR. JAY A. BLAER

TECHNICAL REPORT AFRPL-TR-67-66

MARCH 1967

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FOREWORD

This report contains the results obtained during one phase of the Air Force Rocket Propulsion Laboratory Project 314801101, Shock Tube Kinetic Studies. The period covered is from January 1965 to December 1966.

This study was conducted by the author at the Air Force Rocket Propulsion Laboratory. The author wishes to acknowledge his appreciation to Dr. T. E. Jacobs and Dr. N. Cohen of Aerospace Corporation, El Segundo, California, for lending assistance in the planning and data-reduction phases of the research described herein. All calculations necessary to this study were conducted by Aerospace Corporation.

This report has been reviewed and approved.

ELWOOD M. DOUTHETT
Colonel, USAF
Commander
ABSTRACT

The rate of dissociation of hydrogen fluoride behind incident shock waves has been studied in the temperature range of 3700 to 6100° K. Gaseous mixtures containing 0 to 4% hydrogen fluoride, 0 to 6% molecular fluorine, and 0 to 0.5% molecular hydrogen in an argon carrier were used in this study. The course of the dissociation was followed by monitoring the emission intensity of the 1-0 band of hydrogen fluoride at 2.5 μ.

Resort was made to a determination of initial reaction rates to obtain values for the rate constant of the reaction \( HF + M = H + F + M \). The expression \( k_1 = 0.47 \times 10^{19} e^{-13410/RT} \) was found to give the best fit to all of the data. The effect of excess fluorine upon the initial reaction rate demonstrated that the reaction \( F + HF = F_2 + H \) is inconsequential to the present study. Similarly, it was found that atomic fluorine has roughly the same third-body efficiency as argon for the recombination of \( H \) and \( F \).

Computer calculations based upon the whole reaction profile and including all the data indicate a value for the rate of the hydrogen exchange reaction, namely, \( HF + H = H_2 + F \), of \( k_2 = 2 \times 10^{12} e^{-35000/RT} \)

The data were too scattered to allow an accurate determination of the temperature dependencies of the pre-exponential factors.
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INTRODUCTION

With the increasing use of energetic but unfamiliar or less understood chemicals in propellant formulations, kinetic considerations become of increasing importance. When working knowledge of these substances is lacking, kinetic data must supplement other data to allow optimum design and utilization of new propellant systems.

A shock tube is one tool which can be used to generate the conditions of temperature and pressure of interest without a previous time-temperature history of the reacting gas. A rapid response measuring technique, such as the infrared emission method described herein, can then be used to follow the course of the reaction as a function of time.

When this program was initiated, no published data were available concerning the dissociation of hydrogen fluoride, although two other studies\(^1\,^2\) of the subject were under way at other laboratories.

DISCUSSION

A. BACKGROUND

1. Calculation of Shock-Wave Parameters

The Rankine-Hugoniot equations were used in the calculation of the state of the gas immediately behind the shock wave. When fluorine was added to the mix, it was found necessary to assume it to be completely dissociated within the shock wave at all temperatures considered. This was necessary because of the extreme instability of molecular fluorine\(^3\) under the experimental conditions.
The shock velocities necessary to define the conditions of the reacting gas were obtained by means of spark-gap shock detectors accurately spaced at known distances along the tube. The spark plug signals were displayed on an oscilloscope equipped with a raster sweep. Superimposed upon this trace was a signal from a crystal-driven timing generator. Hence, the timing trace enabled an accurate determination of shock-wave velocity. The data were fitted to a quadratic equation of the form

$$t = AX + BX^2 \quad (1)$$

Where A and B are constants, t is the elapsed time, and X is the distance traveled by the shock wave. The parameter B is then a measure of the attenuation suffered by the shock wave as it traveled down the tube (about 1%).

The shock velocity at the test station was evaluated from the test data by means of the equation

$$V = \frac{1}{A + 2BX} \quad (2)$$

with a standard deviation of

$$S_v = (S_A + 2X_S_B)\sqrt{V^2} \quad (3)$$

Where $S_v$, $S_A$, and $S_B$ are the standard deviations of V, A, and B respectively. The value of $S_v$ was usually about 1 to 1.5% of the value of V.

2. Reduction of Rate Data

In this study, the course of the reaction was followed by monitoring the emission intensity of the 2.5-micron band of hydrogen fluoride as a function of time. Consequently, it becomes necessary to relate the measured intensity to the density of unreacted HF in the test gas.
The emission intensity was converted to voltage by means of an infrared
detector. The voltage was displayed as a function of time on an oscillo-
scope.

The emission intensity will be given at any time by the
following relationship:

\[ R = \int_{\omega_0}^{\omega} R_0(T) c_\omega(T) g(\omega - \omega_0) d\omega \]  

where \( R_0(T) \) and \( c_\omega(T) \) are the Planck blackbody function and the spectral
emissivity of HF respectively at temperature \( T \). The quantity of \( g(\omega - \omega_0) \)
is the slit function for the spectrometer and is a measure of
detection efficiency of the apparatus for radiation of frequency \( \omega \) when
it is set to detect radiation of frequency \( \omega_0 \). The slit function for
our spectrometer is triangular with a half-width of 560 cm\(^{-1}\) when it is
centered at 4000 cm\(^{-1}\).

The Doppler half-width for rotational lines is given by
the expression

\[ b_D = \left( \frac{2kTm^2}{mc^2} \right)^{1/2} \omega_0 \]  

where \( c \) is the velocity of light, \( m \) is the mass of the rotating body, and
\( \omega_0 \) is the frequency, in wave numbers of the radiation. At 5000°K equa-
tion (5) gives a Doppler half-width of 0.023 cm\(^{-1}\) for the rotational lines
of HF centered in the 2.5-micron band. A collision half-width for broaden-
ing of the rotational lines of HF by Ar at 293°K may be estimated at 0.03
cm\(^{-1}\) based on the data of Oksengorn. The theoretical temperature depen-
dence of \( T^{-1/2} \) for collision broadening then gives a value of 0.007 cm\(^{-1}\)
for the collision half-width at 5000°K. A comparison of these half-widths
indicates that one can select the experimental conditions based upon
calculations which employ the Doppler shape for the rotational lines without incurring significant error.

Detailed theoretical calculations of the spectral emissivities of HF were reported by Malkmus (6) who based his results upon Kniper's (7) experimentally determined value of 314 cm² atm⁻¹ at 117°C for the integrated intensity of the fundamental. These calculations were made for four different optical densities ranging from 10⁻² to 10 atm·cm at each of four temperatures ranging from 1800°C to 7000°C.

Based on the spectral emissivities given by Malkmus, it is possible to evaluate the integral appearing in equation (4) as a function of both optical density and temperature. The required values for the slit function of our apparatus are given by

\[ g (|\omega - \omega_0|) = 1 - \frac{1}{560} \omega - \omega_0 \quad \text{for} \quad |\omega - \omega_0| \leq 560 \]

\[ = 0 \quad \text{for} \quad |\omega - \omega_0| > 560 \quad (7) \]

Values for the Planck blackbody function were calculated from the following relation:

\[ R^0(T) = \frac{2\pi \hbar c^2 \omega^3}{e^{\hbar c \omega / kT} - 1} \quad (8) \]

Figures 1 and 2 illustrate this spectral radiance integral, equation (4), as functions of optical density and temperature respectively. A close inspection of these two figures reveals that if the optical density does not exceed 10⁻⁰.⁵ atm·cm, the radiance, \( R \), will not only be a nearly linear function of optical density, but will also be independent of temperature provided the temperature does not fall below 3500°C. Accordingly, these limits define the optimum experimental conditions and are met by our equipment behind incident shocks for 2.5% HF in Ar at an initial total
pressure of 40 mm Hg. If the experimental conditions are held within these limits, one can write

$$\frac{B}{B_0} = \frac{\rho_T}{\rho_{T_0}}$$

(9)

with an error of not more than 10%. Here $\rho_T$ refers to the density of HF behind the shock and the subscript zero refers to the initial conditions.

The proposed kinetic scheme is given by the following series of equations:

$$\text{HF} + \text{M} = \text{H} + \text{F} + \text{M}$$

(10)

$$\text{HF} + \text{H} = \text{H}_2 + \text{F}$$

(11)

$$\text{H}_2 + \text{M} = 2\text{H} + \text{M}$$

(12)

The fluorine exchange reaction and the subsequent fluorine dissociation reaction

$$\text{HF} + \text{F} = \text{H} + \text{F}_2$$

(13)

$$\text{F}_2 + \text{M} = 2\text{F} + \text{M}$$

(14)

are not favored due to the high endothermicity of reaction (13) in reference to reaction (11).

If $f$ is the fraction of HF dissociated at time $t$ and $C$ is the original weight fraction of HF in the gaseous mixture, the density of HF in the gaseous mixture behind the shock wave at time $t$ will be

$$\rho_T = (1-f)\rho_{g}$$

(15)

where $\rho_g$ is the total gas density behind the shock wave. Differentiation of equation (15) with respect to time yields (for the region immediately behind the shock wave, i.e., for the initial conditions
of dissociation of HF)

\[ \dot{\rho}_T = C \rho \frac{d}{dt} - \rho_c \]

Equations (9), (15), and (16) can now be combined to give for the initial conditions of reaction

\[ \dot{f} = \frac{3\ln \rho}{3t} - \frac{3\ln \rho}{3t} \]

It can readily be shown on the basis of the equations of conservation that

\[ \frac{3\ln \rho}{3t} = \frac{C}{M} \left\{ \frac{A T D + D_H F}{A(u - D R T) - (D R) T} \right\} \]

Where the symbols not already defined have the following definitions:

- \( R \) = the gas constant.
- \( M_{HF} \) = the molecular weight of HF.
- \( A = \left\{ \frac{C_{AR}}{M_{AR}} + \frac{C_F}{M_F} \cdot \frac{3}{2} R \cdot \frac{C_{H_2}}{N_{H_2}} \cdot \frac{C_{HF}}{M_{HF}} \cdot \frac{C}{C_{HF}} \right\} \)
- \( C_{AR} \) = the weight fraction of argon in the initial shocked mix.
- \( M_{AR} \) = the molecular weight of argon.
- \( C_F \) = the weight fraction of atomic fluorine in the initial shocked mix.
- \( M_F \) = the atomic weight of atomic fluorine.
- \( C_{H_2} \) = the weight fraction of hydrogen in the initial shocked gas.
- \( M_{H_2} \) = the molecular weight of hydrogen.
- \( \overline{C_{VHF}} \) = the specific heat of hydrogen fluoride at constant volume, averaged over the temperature step across the shock wave.
volume averaged over the temperature step across the shock wave.

\[ D_{HF} = \text{the dissociation energy of gaseous hydrogen fluoride.} \]

\[ D_{H_2} = \text{the dissociation energy of hydrogen.} \]

\[ \dot{H}_2 = \text{the rate of dissociation of hydrogen.} \]

\[ u = \text{the gas velocity relative to the shock wave.} \]

\[ D = \frac{C_A}{M_A} + \frac{C_F}{M_F} + \frac{C_{H_2}(1 + \dot{H}_2)}{M_{H_2}} + \frac{C_{HF}(1 + \dot{f})}{M_{HF}} \]

Equations (17) and (18) may now be solved for \( \dot{r} \), the result being

\[ \dot{r} = \left[ \frac{CR_{HF}}{M_{HF}} \right] \left( \frac{A\dot{T} - D\cdot D_{HF}}{A(u^2 - DRT) - (DR)^2 T} \right) - 1 \left\{ \frac{\dot{H}_2 \cdot C_{H_2} \cdot R}{M_{H_2}} \right\} \]

\[ \left[ \frac{1}{A(u^2 - DRT) - (DR)^2 T} \right] + \frac{\delta \ln R}{\delta t} \cdot \frac{1}{\rho_{21}} \]  

Equation (19) offers a ready means of obtaining an estimate of \( k_1 \), the forward rate of reaction (10), since by definition

\[ \dot{r} = k_1(M)_0 \cdot (HF)_0 - k_{-1}(M)_0 \cdot (H)_0 \cdot (F)_0 + k_2(H)_0 \cdot (HF)_0 - k_2 \]

\[ (F)_0 \cdot (H_2)_0 \]  

(20)

Where \( k_2 \) and \( k_{-2} \) refer to reaction (11). For the initial condition of dissociation

\[ (H)_0 = 0 \]

\[ (F)_0 = 0 \]
and for mixes containing initial atomic fluorine

\[(H_2)_o = 0\]

\[(H)_o = 0\]

It follows that if the density of HF can be monitored during the very early stages of the reaction, the value of \(k_1\) can be obtained from the initial slope of the reaction profile as recorded on the oscilloscope.

The overall reduction of the rate data proceeds by matching observed and calculated reaction profiles. This necessitated having a set of initial estimates of the rates of equations (10) through (12). The initial estimate of \(k_1\) was obtained by taking the initial slopes of the observed reaction profiles as described above. The initial estimate of \(k_2\) was taken from reference 1, the value being

\[k_2 = 1 \times 10^{13} e^{-35000/RT}\]  \hspace{1cm} (21)

The value of \(k_3\), the reverse rate of reaction (12), was also taken from reference 1, the value being

\[k_3 = 10^{18.3} T^{-1}\]  \hspace{1cm} (22)

Since the density of excess hydrogen was not widely varied, no attempt to improve \(k_3\) was made. The reverse rates of all three reactions were computed from the forward rates and thermodynamic data. The reaction profile was then computed from the estimates of all the rates coupled with the shock parameters. The profiles were calculated by an integration technique with time and temperature as interdependent variables. Computer analysis was necessary since the reaction temperature changes by as much
as 1000°C during the course of the reaction (see Table II). Several oscilloscope traces representing typical reaction profiles are illustrated in Figure 7.

In comparing observed and calculated reaction profiles, it becomes necessary to know the initial height of the observed profile. This necessitated a usable extrapolation procedure. A simple logarithmic expression of the form

$$\log E = \log E_0^c - \frac{t}{T}$$

was found to fit the data for the early stages of reaction in nearly every instance. In this expression, $T$ and $E_0^c$ are constants, the value of $E_0^c$ being the initial height of the voltage trace (see Figure 8). Accordingly, initial intensities were obtained by simple logarithmic extrapolation.

In the computer analysis, $M$ in equations (10) and (11) was considered to be any third body. After comparing observed and computed profiles, new estimates of the rates were made and the process repeated. Only the pre-exponential factors of the rates were changed in this process, it being assumed that the activation energies for reactions (10) and (11) are approximated by their respective endothermicities.

B. EXPERIMENTAL

1. Shock Tube

The shock tube is of stainless steel and has an inside diameter of 1.5 inches. The overall length of the test section is 25 feet, and the entire inside surface is finished to a grade 8 smoothness.
The driver has an overall length of 66 inches. The driver section was static-tested to 20,000 psi and the downwind section to 4000 psi. The driver pressurizing manifold was connected to 10,000 psi helium and 6000 psi nitrogen supply lines. The downwind section emptied into a 55-gallon dump tank. The driver and downwind sections were separated by means of a scribed steel diaphragm designed to burst at a pre-selected pressure. The downwind section and the dump tank were separated by means of a thin sheet of mylar.

2. Shock Velocity Recording System

Automobile spark plugs of type 45XL whose points were filed smooth were fitted flush with the inside wall of the downwind section of the shock tube at intervals of 30 inches (+ 0.015 inches). The spatial resolution of these plugs was approximately 1 mm. Spark plugs were also placed 5 1/4 inches from each side of the observation port. A circuit diagram of the associated electronics is shown in Figure 3. The electronic system was designed by Avco Research Company of Wilmington, Massachusetts. One spark signal box was provided for each spark plug. The outputs, from J1, of all boxes were fed to a Tektronix 535 oscilloscope equipped with a raster sweep. Timing markers were placed at 50 usec. intervals along the sweep by means of a Radionic Model TWM-2A crystal-driven timing generator. The oscilloscope trace was recorded on a 3000-speed polaroid film by means of a Fairchild Model 296 camera. Data were taken directly from the film with the aid of a ruler graduated in units of 1/50th of an inch. The data could be read in this manner
with a reproducibility of 0.5%.

3. Observation Port

Synthetic sapphire was selected as the best compromise window material. Sapphire transmission lies between 80-90% from the visible to 5.5μ. The good mechanical strength of sapphire permits tube pressures of 5000 psi.

The two transmission windows are held in compression by close-tolerance brass collets. The collets are retained in the section by hollow nuts. Window-to-shock-tube sealing is effected with indium wire gaskets.

4. Infrared Spectrometer

The analytical system* (Figure 4) consists of two sub-systems: (a) a source system from which blackbody light can be collected and imaged in the shock tube for absorption measurements, and (b) the radiometric system in which light from or through the shock tube is spectrally resolved by a Perkin-Elmer prism monochrometer.

The system is designed to employ a dual-element detector, which, in conjunction with an adjustable light mask, permits simultaneous two-path measurements. Detector output is amplified and displayed on an oscilloscope.

Absorption measurements may be taken with or without optical chopping. A removable chopper, consisting of an air turbine directly driving a 90-slot wheel, may be positioned at a focal plane on either

*Designed and constructed by Rocketdyne, Inc., Canoga Park, California, Contract AF 04(611)-8592.
The detector used in this study is of the indium antimonide variety used in a photoconductive mode. The two detector elements are separately biased by a 16.2-volt mercury battery shunted with a 100-kilohm potentiometer, as shown in Figure 5. Bias current is measured while the detector is operative and adjusted for optimum signal-to-noise ratio. The entire optical signal is focused on one detector element. The outputs of both elements are then fed to a Tektronix 555 dual-trace oscilloscope where the difference in the two signals is displayed and photographed.

The signal amplifier consists of two stages of capacitance-coupled cascode amplification with cathode followers for interstage coupling and as output stages (see Figure 6). A feedback loop from the cathode of the output stage to the cathode of the input stage is used to obtain an overall amplifier gain of about one thousand. Two of these amplifiers are used, each with its own filament supply and power supply decoupling filter.

Wire screens of known blocking efficiency for radiant energy were placed between the detector and blackbody source to test the linearity of the response of the detector to radiant intensity. The linearity was found to be good to within 5% over the whole range of detector response. The signal-to-noise ratio obtainable with the system varied from 30 to 1 to as high as 150 to 1, depending upon the amplification required for the particular shot.

A lower limit for the time resolution of the detector can
be estimated from the shapes of reaction profiles taken at temperatures below the point of observable reaction (see Figure 7a). The equation

$$\frac{dE}{dt} = \frac{1}{\tau} (E_0 - E)$$

(24)
describes these data with good precision and gives a value of 3.5μ sec. for τ at 3231°K corresponding to Figure 7a. At higher temperatures, the time resolution will improve due to the shorter time required for the shock wave to pass through the width (approximately 1 mm) of the gas envelope in which the HF content is monitored. The upper limit of time resolution is approximated by the rated time constant of the detector itself which is given by the manufacturer\(^*\) as 2μ sec.

A Beckman DU was used as the source of 4000 cm\(^{-1}\) light to measure the slit function of the instrument. The resulting slit function was found to be triangular with a half-width of 560 cm\(^{-1}\) when the slit of the Perkin-Elmer monochrometer was open to 2 mm.

5. Data Read-Out from Spectrometer

The emission intensities were recorded as a function of time on 3000-speed Polaroid film by photographing the single sweep of the Tektronix 555 dual-beam scope to which the detector outputs were fed. Prior to each shot, accurate voltage marks were placed on the film by means of an SRC\(^*\) Model 3512B DC power supply, calibrated to

\(^*\)Santa Barbara Research Center, Goleta, California.

\(^{**}\)Systems Research Corporation
1.0 mv accuracy at three-month intervals. Timing marks were placed on the film by means of a Radionix Model TW7 crystal-driven timing generator.

Transparencies were made of the photographic records and these were enlarged and superimposed on 10 x 10 to the centimeter standard graph paper by means of a projection lantern.

6. Gauges

Heise gauges were used for all sample preparations. These gauges were equipped with stainless-steel Bourdon tubes. These proved very reliable in the presence of fluorine gas. The lack of change in the 90-day calibration was very good, the largest error in their use being in reading the dial. This reading error was about 0.1% of the maximum gauge pressure.

A Wallace & Tiernan Model FA-15 gauge was used to measure gaseous pressure in the shock tube itself prior to each shot.

Thermocouple gauges purchased from Veeco* were used to detect the evacuation point (approximately 1u) of the shock tube prior to charging it with test gas for each shot.

7. Gaseous Purities

a. Hydrogen Fluoride

Hydrogen fluoride having a minimum stated purity of 99.9% was purchased from Matheson and used without further purification. A mass spectrum of the gas as received with argon as an internal standard was made.

*Vacuum Electronics & Equipment Corporation,
standard indicated the presence of approximately 0.1% O₂, 0.03% N₂, and trace amounts of SiF₄ as the only detectable impurities.

b. Argon and Hydrogen

Argon and hydrogen having minimum purities of 99.998% were purchased from Matheson and used without further purification. A mass spectrometric analysis indicated only trace amounts of H₂O and N₂ in each gas, i.e., less than 0.01% impurities.

c. Fluorine

Gaseous fluorine with a minimum stated purity of 98.2% was purchased from Allied Chemical Company. A mass spectrometric analysis revealed the presence of about 0.7% O₂ and 0.2% HF. Before use, the gas was passed over NaF pellets for removal of all HF. The resulting gas was used without further purification.

8. Cleaning and Passivation Procedures

Prior to any gas mixing operations the entire system, including the shock tube itself, was flushed with liquid freon, after which everything was purged with nitrogen until dry. After evacuating the system overnight, gaseous fluorine at 50 psi was admitted and allowed to stand for two hours, after which the apparatus was again flushed with nitrogen, the gases being passed into a propane burner which was vented to the outside of the building.

After the system had been passivated, it was kept evacuated at all times except when in use.

9. Sample Preparation and Analysis

Mixtures of Ar and F₂ containing from 0.1 to 10.0% F₂ were prepared and stored in stainless steel mix tanks. The partial pressure of
F₂ in each mix was determined during the mixing operation by noting the pressure increase in the vessel as each gas was added. The optical density of each sample was then determined at 285 µm by means of a Beckman DK-2 recording spectrophotometer. The absorption cell was of stainless steel, had a pathlength of 7.5 cm, and was equipped with 1/8" thick sapphire windows. An inlet and an outlet were placed at opposite ends of the cell to allow flushing it with sample prior to each reading. All optical densities were read at a total pressure of 50 psi. Repeated readings of optical densities over a period of four weeks revealed no change. The extinction coefficients for F₂ determined from these measurements were used in all subsequent gas analyses. Beer's law was found to describe the data over the entire range.

In a manner similar to that described above, samples of HF and Ar were prepared and stored. After sitting overnight, the optical absorption cell was flushed with sample until no changes in the optical densities of the sample at 2.5µ and 2.4µ were observed with additional flushing. After recording the final value of the optical density, the gaseous mixture was passed into distilled water and the argon was collected by displacement. The resulting acidic solution was titrated with standard NaOH with phenolphthalein as indicator. In this manner, the actual partial pressure of HF in each mix was determined simultaneously with its optical density. The extinction coefficients for HF determined in this manner were reproducible to within 5%. All optical densities were again determined at a total pressure of 50 psi. In agreement with the results
of Spinnler(2), the results were well-defined by Beer's law up to a total HF pressure of 2.0 psi. This limit was observed in all subsequent measurements.

Individual mixes of argon with each reagent gas were prepared in the ratio of 10:1 and stored in stainless steel mix tanks. The partial pressure of each reagent gas in its respective mix with argon was determined during the mixing operation with the aid of a Heise gauge having a usable range of 0 to 500 psi. The mixes were each prepared at a total pressure of 200 psi.

Gaseous samples for dissociation studies were prepared by mixing pre-selected amounts of each the diluted reagent gases with argon and storing in stainless steel mix tanks.

The partial pressure of \( \text{H}_2 \) in mixes containing added hydrogen was determined by pressure difference during the mixing operation. The accuracy of this determination was approximately 2% over all. These samples were used within 48 hours of preparation to avoid any concentration changes which might occur on standing.

The partial pressures of HF and \( \text{F}_2 \) in the gaseous mixtures were determined immediately before use from optical density measurements in the appropriate spectral ranges, always at a total pressure of 50 psi.

10. Data Run Procedure

a. Before each shot, the shock tube, optical absorption cell, and all interconnecting lines were evacuated to \( 1 \times 10^{-3} \) torr. The leak rate was found to be of the order of \( 2 \times 10^{-3} \) torr/min.

b. The time and calibrated voltage markers were placed on the
film in preparation for the planned shot. Trigger circuits and spark plug voltages were adjusted to the proper levels.

c. The indium antimonide detector was cooled with liquid nitrogen and all of its associated electronics were activated. Alignment of the detector was accomplished with the aid of the optical chopper and blackbody source. After alignment was accomplished, the blackbody source was extinguished.

d. The test gas was now introduced into the shock tube and allowed to remain there for 10 to 15 minutes at a total pressure greater than that of the initial pressure of the planned shot. The optical absorption cell was flushed with sample gas during this period until no further change in optical density at 2.5μ was observed with continued flushing. The shock tube was again evacuated to 1 x 10^{-3} torr, after which it was refilled to the desired pressure with test gas. This preliminary conditioning of the shock tube was necessary to allow saturation of the walls with adsorbed HF. Only after these precautions were taken could reproducible results be obtained. The gaseous pressure in the shock tube was determined with the aid of a Wallace and Tiernan gauge having a usable range of 0 to 200 mm. The pressure could be read accurately to the nearest 0.2 mm.

e. The driver section was immediately pressurized with helium until the diaphragm burst, initiating the shock wave. The elapsed time between the tube-filling operation and the initiation of the shock wave never exceeded 2 minutes.

f. The contents of the dump tank and shock tube were passed
into the propane burner. The entire system was then purged for 15 minutes with low pressure $N_2$ (ca. 200 psi), after which the metal and mylar diaphragms were replaced and the shock tube reevacuated.

11. Background Emission Intensity

Several shocks were initiated in mixtures of the reagent gases which contained no HF. The resultant oscillograms showed no detectable radiation at 2.5μ to 7000°K. Accordingly, no background intensity was assumed in the analysis of the data.

111. RESULTS AND INTERPRETATION

A. Internal Consistency of Initial Emission Intensities

Several shocks were initiated in test gases under identical conditions of detector bias current and amplifier plate voltage. The results should lend themselves well to a test of the validity of the assumptions made in the derivation of equation (9).

In Table I the observed initial emission intensities for several shocks are listed as functions of both the initial concentration of HF in the mix and the temperature of the gas. The ratios of initial emission intensity to the initial concentration of HF are shown in column 5 of the table. It is seen that concentration varies by a factor of 5 and the temperature by 3000°C. Although there is 30% scatter in the data, it is immediately apparent that within experimental error equation (9) is valid.

B. Rate Constants from Initial Rates

Equations (19) and (20) were used to compute initial estimates for the forward rate of reaction (10). The initial slopes of the observed reaction profiles were estimated with the aid of equation (23). The
resultant estimates of $k_1$ are shown in Figure 9 as a function of the reciprocal absolute temperature. The results are also tabulated in Table II.

An analysis of the results illustrated in Figure 9 shows that large amounts of initial, monatomic fluorine in the reacting mix have no significant effect upon the initial reaction rate. If reaction (13) made a significant contribution to the rate of disappearance of HF, the initial rate of reaction would be given by

$$ \dot{r} = k_1(M) + k_4(F) $$

(25)

where $k_4$ is the forward rate of reaction (13). Under these circumstances an increase in the initial rate would be observed due to the contribution of the second term on the right. The absence of this effect (see Figure 9) can only mean that the contribution of reaction (13) to the rate of disappearance of HF is insignificant compared with the contribution of reaction (10).

Also shown in Figure 9 are Arrhenius-type models fitted to the data with $T^{-1}$ and $T^{-2}$ temperature dependencies for the pre-exponential factor. As can be clearly seen from the figure, the data are not of sufficient accuracy to distinguish between the two forms. The resulting expression for $k_1$

$$ k_1 = \frac{0.47 \times 10^{19}}{T} e^{-134100/RT} $$

(26)

compares favorably with the value obtained by Jacobs et al. (1), i.e.,

$$ k_1 = \frac{10^{19.053}}{T} e^{-134100/RT} $$

(27)

A further consequence of the results listed in Figure 9 is that the third-body efficiency of atomic F for the recombination of H and F atoms is not grossly different from the efficiency of Ar atoms. For
shots 49 through 53, the atomic F content of the reacting gas immediately
behind the shock wave is 11%, yet no significant effect is noted in the
values of $k_1$, except possibly at low temperature (ca. 4100°K).

C. Rate Constants from Computer Analysis

A random selection of data taken for mixes containing no added
fluorine was used to evaluate the rate of the hydrogen exchange reaction,
equation (11). The value of $k_1$ was taken from the initial slopes of these
data and set equal to

$$k_1 = \frac{0.25}{T^2} \times 10^{23} e^{-34100/RT}$$

(28)

The $T^{-2}$ dependence of the pre-exponential factor was found to give a
slightly better fit for these data, Figure 9. The reaction profiles were
computed for these data for each of several values of $k_2$ and the results
were then compared with the observed profiles (see Figures 10a, 10b, and
10c). Figure 11 illustrates the effect of $k_2$ on the shape of the reaction
profile for a single run corresponding to a mix containing added hydrogen.

The resulting best value for $k_2$ is given by the expression

$$k_2 = 0.2 \times 10^{13} e^{-35000/RT}$$

(29)

This value is low by a factor of five in comparison to the value obtained
by Jacobs et al (11), i.e.,

$$k_2 = 0.1 \times 10^{14} e^{-35000/RT}$$

(30)

An examination of the computed profile $R_1$ of Figure 11 with the experi-
mental data, $R_4$, reveals that this difference in the two values of $k_2$
cannot be ascribed to scatter in the experimental data.

The rates described by equations (28) and (29) were then
applied to a random selection of data for mixes containing various amounts
of added fluorine. The results indicated that the value of \( k_1 \) as given by equation (28) was slightly high at low temperatures (ca. 4000°K). Accordingly, the values of \( k_1 \) given by (26) were tried. The results are illustrated in Figure 12. The good fit attests to the applicability of the selected values of \( k_1 \) and \( k_2 \).

The fact that equation (28) gives values of \( k_1 \) which are slightly high at low temperature (ca. 15%) indicates that the value chosen for \( k_2 \) is probably low by a small amount, as \( k_2 \) has its greatest relative influence at low temperatures. Even though this seems probable, it does not warrant an attempt to improve the value of \( k_2 \), as this would only mean an increase in its value of 20% at most.

D. Recombination Rate Constants

In an effort to quantitatively reproduce the temperature dependence of the rates of atom-atom recombinations, Benson and Fueno\(^{(9)}\) describe a cascade mechanism for vibrational deactivation of newly formed and highly excited diatomic molecules. They assume that deactivation or activation proceeds by collision with neighboring molecules and occurs by one vibrational quantum at a time.

Figure 13 illustrates the agreement between our experimentally determined recombination rates and the values given by this cascade model. The agreement must be considered as excellent in view of the fact that the model gives both the negative temperature dependence of the recombination rates as well as the correct magnitude (within a factor of 2).
Of course, the theory of Benson and Fueno\(^{(9)}\) can be used conversely to reproduce the correct temperature dependence and magnitude of the corresponding dissociation rates of diatomic molecules. This is illustrated in Figure 9 for the cases IA and IIA of the model (see reference 9).

In all of these calculations the effective collision diameter of the collision complex was taken as just half the value given by reference 9 for homogeneous complexes. This approximation becomes necessary due to the relative inefficiency of energy transfers for collision of inert species with the heavy F end of the complex in comparison to collisions with the light H end.

E. Conclusions

In conclusion, the best fit of the experimental data is obtained for \(k_1\) given by equation (26) and \(k_2\) given by equation (29).

The presence of added fluorine in the reacting mix appears to have no influence on the reaction rate except for the simple mass-action suppression of reactions (10) and (11). Since the presence of added fluorine suppresses the hydrogen exchange reaction, the values of \(k_1\) taken from the initial rates for these data should more nearly reflect reality than those values of \(k_1\) taken from the initial rates of reaction for mixes containing no added fluorine.

The rate of reaction (13), the fluorine exchange reaction, cannot be obtained from the present study due to its apparent insignificance compared with the rates of reactions (10) and (11).

The third-body efficiency of atomic fluorine for the recombination of atomic hydrogen and fluorine does not grossly exceed the third-
body efficiency of argon for the same recombination.

If atomic hydrogen has an efficiency for third-body recombination of atomic hydrogen and fluorine grossly in excess of that for argon, it would be difficult to separate the effect from the effect of the hydrogen exchange reaction.

The cascade model of Benson and Fuoco appears to be qualitatively and quantitatively correct when compared with the experimentally determined recombination rates of atomic H and F.
REFERENCES


5. B. Oksengorn, Spectrochimica Acta 19, 541 (1943).


**TABLE I**  
INTERNAL CONSISTENCY OF INITIAL EMISSION INTENSITIES

<table>
<thead>
<tr>
<th>Run No.</th>
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<th>(E°/C°HF x 10°6)</th>
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* Refers to individual settings for bias current and amplifier plate voltage.
### Table II

**Compositions and Shock Parameters for Individual Shots**

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<th>Shot No.</th>
<th>% HF</th>
<th>% H₂</th>
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<th>U°° (mm/μsec)</th>
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* Shock Velocity  
** Standard Deviation of Shock Velocity  
† Temperature of Gas Immediately Behind Shock Wave  
‡ Temperature of Gas at Equilibrium
Fig. 1, SPECTRAL RADIANCY AS A FUNCTION OF OPTICAL DENSITY

Fig. 2, SPECTRAL RADIANCY AS A FUNCTION OF TEMPERATURE
Fig. 3, SCHEMATIC DIAGRAM OF SPARK SIGNAL BOX
(ONE FOR EACH SPARK PLUG)
AS PER AVCO RESEARCH CO.
Fig. 4, SCHEMATIC OF THE INFRARED SPECTROPHOTOMETER OPTICS
Fig. 5, SCHEMATIC OF DETECTOR BIAS SUPPLY
Fig. 6, SCHEMATIC OF DETECTOR AMPLIFIER
Fig. 7a, REACTION PROFILE FOR
SHOT NO. 71 2.06%HF, 0.375%F₂,
323°C, 10 µ SEC TIME MARKERS,
0.2 VOLT ORDI NATE DIVISIONS

Fig. 7b, REACTION PROFILE FOR
SHOT NO. 99 2.23%HF, 1.48%F₂,
586°C, 5 µ SEC TIME MARKS
0.1 VOLT ORDI NATE DIVISIONS
Fig. 7c, REACTION PROFILE FOR
SHOT NO. 58 2.35% HF, 1.80% F₂,
10 µSEC. TIME MARKS 0.2 VOLT,
ORDINATE DIVISIONS, 4871°K

Fig. 7d, REACTION PROFILE FOR
SHOT NO. 60 2.47% HF, 1.80% F₂,
5862°K, 10 µSEC TIME MARKS
0.1 VOLT ORDINATE DIVISIONS
Fig. 8, LOGARITHMIC EXTRAPOLATION ILLUSTRATED FOR SHOT NO. 52, 5.84%F₂, 3.02% HF, 5283°K
Fig. 9, TEMPERATURE DEPENDENCE OF INITIAL RATES
Fig. 10a, COMPARISON OF COMPUTED & OBSERVED REACTION PROFILES FOR MIXES CONTAINING NO ADDED FLUORINE; $k_2$ TOO LARGE
\[ k_1 = \frac{0.25}{T^2} \times 10^{23} \exp \left( \frac{-134100}{RT} \right) \]

\[ k_2 = 0.20 \times 10^{13} \exp \left( \frac{-35000}{RT} \right) \]

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Fig. 10c, COMPARISON OF COMPUTED & OBSERVED REACTION PROFILES FOR MIXES CONTAINING NO ADDED FLUORINE; BEST VALUE FOR \( k_2 \)
Fig. 11, ILLUSTRATION OF THE DEPENDENCE OF THE REACTION PROFILE ON THE VALUE OF $k_2$ 1.97% HF, 0.32% $H_2$, 4274°K INITIALLY, SHOT NO. 98
\[ k_1 = \frac{0.47 \times 10^{19}}{T} \exp\left(\frac{-134100}{RT}\right) \]
\[ k_2 = 0.20 \times 10^{13} \exp\left(\frac{-35000}{RT}\right) \]

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**Fig. 12, COMPARISON OF COMPUTED & OBSERVED REACTION PROFILES FOR MIXES CONTAINING ADDED FLUORINE**
Fig. 13, RECOMBINATION RATE CONSTANTS COMPARED TO THE CASCADE MODEL OF BENSON & FUENO (Ref. 9)
The dissociation rate of hydrogen fluoride behind incident shock waves has been studied in the temperature range of 3700 to 6100 K. Gaseous mixtures containing 0 to 4% hydrogen fluoride, 0 to 6% molecular fluorine, and 0 to 0.5% molecular hydrogen in an argon carrier were used in this study. The course of the dissociation was followed by monitoring the emission intensity of the 1-0 band of hydrogen fluoride at 2.5 μm. Resort was made to a determination of initial reaction rates to obtain values for the rate constant of the reaction HF + M = H + F + M. The expression

\[ k_1 = 0.47 \times 10^{19} \text{ e}^{-134100/RT} \]

was found to give the best fit to all of the data. The effect of excess fluorine upon the initial reaction rate demonstrated that the reaction F + HF = F₂ + H is inconsequential to the present study. Similarly, it was found that atomic fluorine has roughly the same third-body efficiency as argon for the recombination of H and F.

Computer calculations based upon the whole reaction profile and including all the data indicate a value for the rate of the hydrogen exchange reaction, namely, HF + H = H₂ + F, of \( k_2 = 2 \times 10^{12} \text{ e}^{-35000/RT} \).

The data were too scattered to allow an accurate determination of the temperature dependencies of the pre-exponential factors.
Hydrogen Fluoride Dissociation
Infrared emission measurements
2500°K temperature range

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