

**ATOM FORMATION RATES BEHIND SHOCK WAVES IN
HYDROGEN AND THE EFFECT OF ADDED OXYGEN**

**Prepared For:
FLUID PHYSICS BRANCH, RESEARCH DIVISION
OFFICE OF ADVANCED RESEARCH
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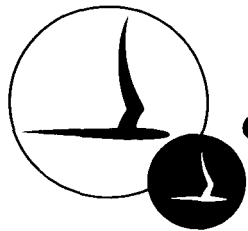
**By: A.L. Myerson, W.S. Watt,
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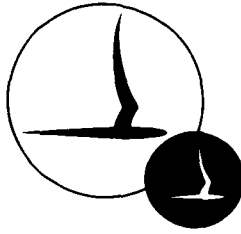
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PREPARED BY: A. L. Myerson
A.L. Myerson

APPROVED BY: J. Gordon Hall
J. Gordon Hall, Head
Aerodynamic Research Department

W. S. Watt
W.S. Watt

P. J. Joseph
P.J. Joseph

FOREWORD

The research reported herein was conducted by the Cornell Aeronautical Laboratory, Inc. for the National Aeronautics and Space Administration, on Contract No. NASr-109. This report covers work conducted from July 1965 to July 1966 under the technical cognizance of Mr. A. Gessow, Chief, Physics of Fluids Branch, Office of Advanced Research and Technology, NASA.

The authors wish to acknowledge the experimental assistance of Mr. R. Bedient and the computational help of Miss M. Williams.

ABSTRACT

A direct, isothermal measurement has been made of the rate of formation of atomic hydrogen behind shock waves in hydrogen-argon mixtures. This has been accomplished by using atomic resonance absorption spectrophotometry in the vacuum ultraviolet. The observations were made in an ultrahigh-purity shock tube. The sensitivity afforded by the technique and the simplicity of the interpretation bespeak a high degree of accuracy for the measurement. The value $k_d = 1.18 \times 10^{12} T^{1/2} \exp(-94,500/RT) \text{ cm}^3 \text{ mole}^{-1} \text{ sec}^{-1}$ was obtained over the temperature range 2150°K to 3640°K. Because of the sensitivity, it was also possible to determine quantitatively the catalytic effect of the addition of small amounts of oxygen. These observations have led to an unequivocal measurement of the rate of the limiting step $\text{H} + \text{O}_2 \longrightarrow \text{OH} + \text{O}$ in the mechanism of the $\text{H}_2\text{-O}_2$ reaction under the conditions of the experiment.

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INTRODUCTION

This paper describes a measurement of the rate of dissociation of molecular hydrogen in argon made by following directly the concentration of atomic hydrogen as it is formed behind a shock wave. Because of the painstaking control exercised on the gaseous composition, it has also been possible to study the effect of small amounts of oxygen on the rate of formation of hydrogen atoms and hence to determine the rate of the reaction

$$\text{H} + \text{O}_2 \longrightarrow \text{OH} + \text{O}.$$

The rate of dissociation of hydrogen behind shock waves has been studied previously¹⁻⁵ by a number of techniques. The rate constants obtained however, are in disagreement by as much as one-half to one order of magnitude for a given collision partner. The present research applies the method of atomic resonance absorption spectrophotometry (hereafter a. r. a. s.), a technique new to shock tube chemistry. The study, for which the feasibility was established in a preliminary account,^{6,7} was initiated with the intent of resolving the existing discrepancies by incorporating four basic features in the method of attack. The first of these was the directness of the approach in that the parameter measured was the concentration of the product itself. This is in contrast to previous studies in all but two^{4,5} of which the density of the gas behind the shock was followed. The second basic feature was the creation of an ultrahigh-purity shock tube whose leak rate, outgassing rate, and ultimate vacuum were such that the impurities in the driven gas, at the time of shock arrival, could be controlled to within

a few parts per million. This represents a significant departure from the preliminary observations^{6,7} where it was shown that with the sensitivity of this type of experiment, it is necessary to eliminate all sources of foreign gases (especially oxygen) such as leakage and outgassing. The third feature lay in the high sensitivity of the absorption coefficient of the Lyman α line to hydrogen atom concentration and this coefficient's relatively minor sensitivity (e.g., compared to the sensitivity of molecular spectra) to temperature and pressure. The fourth feature was the maintenance of isothermal conditions behind the shock since only small amounts of hydrogen atoms were formed during the observation. This small amount of dissociation eliminates the presence of any reverse reactions. The high sensitivity of the technique also allows the use of extremely dilute mixtures of hydrogen in argon and permits a precise determination of the efficiency of the rare gas collision partner without a contribution from other species.

These last features are in contrast to the conditions under which all previous data were obtained. There large temperature decreases occurred during the measurement and both forward and reverse reactions were taking place with all species present contributing to the net dissociation process.

The use of a. r. a. s. as a means of determining absolute atom concentrations was not exploited to any significant degree or used quantitatively until Vidale⁸ showed that accurate measurements could be made of minute partial pressures of atomic Na, Si et al existing over refractories in high temperature furnaces. The important point established there⁸ was that the measurements must be made with a thin-line source, i. e., one at low pressure and temperature, and with broad-line absorbing atoms, i. e., at

high temperature and pressure. It was then shown⁸ that errors introduced in calculating the absolute absorption coefficient were small. This combination of a thin-line source and a broad-line absorber, and other relevant principles established by Vidale,⁸ have now been applied to the present study. Thus, these observations were made with a low pressure, low temperature, radio-frequency-excited source and the absorption line profile of the hydrogen atoms was broadened by the high temperature and pressure behind the shock front. The details of the experiment and calculations will be described in the following sections.

It should be pointed out that our use of a. r. a. s. differs basically from its use in analytical flame determinations in which empirical calibrations of the concentration are applied, in contrast to the absolute calculation used herein. The earliest use of a. r. a. s. to determine hydrogen atom concentrations was apparently that of Preston⁹ who observed qualitatively and at room temperature, hydrogen atoms which had been produced in a discharge but recombined on a surface rather than in the gas phase. More recently, a. r. a. s. has been used^{10, 11} to observe static partial pressures of hydrogen atoms which were at essentially the same low pressure and temperature as the source.

The developments which were essential, then, to the present study were the intense but cool source of a thin Lyman α line and a shock tube capable of maintaining gaseous systems in the realm of ultrahigh purity. With these techniques, the rates of dissociation of the hydrogen molecule in argon have been determined to a high degree of accuracy.

EXPERIMENTAL

A schematic diagram of the apparatus is shown in Fig. 1. The experiments were performed by observing the attenuation of Lyman α radiation by hydrogen atoms formed behind a shock wave. The undispersed light passed through the shock tube after which the Lyman α wave length was selected by a vacuum-ultraviolet monochromator before detection.

The most important changes in the apparatus from that described in the preliminary note⁶ were the use of a newly developed high-purity shock tube which could be considered chemically clean and an improvement in the intensity of the Lyman α signal. The tube itself was constructed from one 24' length of seamless, 316 stainless steel. The internal dimensions are 1-1/2 x 2-1/2 inches with rounded corners of 1/2" radius. The few gaskets in close contact with the test gases are of high-purity aluminum so that no organic materials are directly exposed. The few other and less directly involved gaskets used are of vacuum-baked Viton or Teflon. The three gauges which measured the shock arrival consist of flush-mounted thin-film resistance thermometers (platinum on pyrex) and are completely free of organic matter.

The vacuum port is centrally located with respect to the tube which is separated from the pumping system by a special 2" all-metal, high-pressure, high-vacuum valve and a commercial 2" bakeable UHV valve. The pumping source was a 4" diffusion pump followed by a water-cooled baffle and a Cryosorb liquid-nitrogen trap which together reduced backstreaming to a

negligible amount. This system made it consistently possible to attain vacua in the 10^{-7} - 10^{-8} mm Hg range with effective leakage limited essentially to outgassing rates, e. g., $1-5 \mu/1000$ min. The tube was provided with facilities for baking but these have proved unnecessary thus far because of the apparent effectiveness of the repeated shocks in outgassing the stainless steel. By restricting the gases that entered the tube under any circumstances to H_2 , Ar and He, subsequent pump down and outgassing became routinely rapid and thorough.

The driver was constructed of the same seamless, stainless-steel tubing. Scored stainless-steel diaphragms were punctured in it by an electromagnetically driven plunger.

The Lyman α light source was developed specifically for this research and is shown schematically in Fig. 1. It was designed to emit continuously a thin line of sufficient intensity to follow the rapid transients involved. To achieve the thinness, the source was kept cool (near room temperature) and at low pressures by using 200 watts of 30 MC radio-frequency excitation and a very fast flow system with external air cooling. The pressure and temperature of the hydrogen atoms emitting the Lyman α radiation were thus approximately two orders and one order of magnitude lower, respectively, than the pressure and temperature of the hydrogen atoms behind the shock front. Hence there were two significant broadening effects, Doppler and Lorentz.

The high constant intensity was achieved without the use of the line-broadening environments of arcs or spark discharges, by using a "windowless" source as shown in Fig. 1. The RF discharge was maintained by

three external band electrodes around a quartz tube through which a 10% mixture of hydrogen in helium was flowing. The tube ended in an open slit 1 mm wide and 12 mm high. The gas was drawn through the slit into the expansion chamber which was continuously evacuated by a large mechanical pump. The ground state atoms formed by de-excitation near the exit slit were thereby removed rapidly thus minimizing self-absorption or reversal. The major contribution of this technique to the increase in intensity is illustrated by the fact that the intensity of the Lyman α signal from the "windowless" source finally adopted, was greater by a factor of 1800 than that from our first conventional closed source with LiF windows. It should be noted that whatever small amount of reversal remained under these conditions would not affect absorption calculations, as would broadening, but would act only as a limitation on source intensity. This follows from the fact that the width of the absorption line of the hydrogen atoms behind the shock, as broadened by the Lorentz and Doppler effects mentioned above, was more than two orders of magnitude greater than the corresponding width of the line emitted by the hydrogen atoms in the source. The conditions under which the lamp operated were selected⁷ to maximize Lyman α and minimize the adjacent bands which are mostly due to molecular hydrogen.

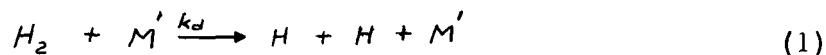
In our initial experiments^{6,7} complete attenuation of the Lyman α signal was observed. However, as the research progressed and purer shock tube conditions were attained, it was noticed that complete attenuation could no longer be achieved. A series of experiments revealed that a small percentage (approximately 15%) of the signal picked up by the photomultiplier was due to radiation other than Lyman α . The source of this stray radiation

was not positively identified but was found to be efficiently absorbed by small amounts of water vapor. It was found that the amount of stray radiation was constant (see Figures 2b and 2c) so all data were reduced with allowance for this. The 1215.7 \AA Lyman α signal passed through LiF windows masked by $1 \times 12 \text{ mm}$ slits mounted in the shock tube and then immediately entered the monochromator. A mirror chamber previously used⁷ was eliminated, resulting in a considerable gain in source intensity. The signal, after leaving the monochromator, was focused on a sodium salicylate-coated aluminum mirror which then emitted most of its fluorescence in the direction of an uncoated EMI 9558C photomultiplier which was cooled to dry ice temperatures. The output was observed on an oscilloscope which was triggered, with varying delays, by the upstream time of arrival gauge and which produced traces such as those shown in Fig. 2. The incomplete attenuation previously mentioned can be noted in these data. While the signal output was high for a continuously operating, ultranarrow band source, it was found preferable to increase the signal-to-noise level by insertion of a load resistance into the RC circuit of the scope-cable network and then to correct for the filtering process. The method used is described in Appendix A of Reference 7.

All gases used were obtained commercially and of "ultrahigh purity." They were analyzed for impurities to within a few parts per million (ppm, hereafter).

RESULTS AND DISCUSSION

The rates measured herein are for the dissociation of hydrogen in argon



through direct observation of the increasing partial pressure of atomic hydrogen behind a shock wave. Thus, for $[M] = [M'] + [H_2]$

$$-\frac{d[H_2]}{dt} = k_d [H_2] [M] = \frac{1}{2} \frac{d[H]}{dt} \quad (2)$$

Assuming Beer's Law, the concentration of hydrogen atoms in the shock tube width ℓ , was calculated from

$$\frac{I}{I_0} = \exp(-k_{\alpha\nu} [H] \ell) \quad (3)$$

and $k_{\alpha\nu}$, the absorption coefficient of the Lyman α transition at its line-center (frequency ν_0) was used for the reasons explained in the previous sections. As indicated previously the two major sources of broadening of the absorption line of the hydrogen atoms behind the shock are Doppler, due to temperature and Lorentz, due to pressure. Other types of broadening such as Holtzmark, Stark and natural, may be neglected under the present conditions for reasons of low hydrogen atom concentrations, low ion levels and relatively large Doppler effects. The error introduced if the source line is not thin compared to the absorbing line, as assumed, has been discussed

quantitatively for conditions comparable to the present.⁸ This error amounts to approximately 10% so that it too has been neglected in the calculations. The only other possible source of error in the spectroscopic calculations is that due to a shift in frequency and asymmetry of Lyman α with pressure. The effect has been shown⁸ to be small, of the order of 5 to 10% under conditions similar to the present and thus can be omitted.

On the basis of the foregoing, the coefficient $k_{0\nu}$ for the absorption of the 1215.7 Å line from the source, by the ground-state hydrogen atoms behind the shock-wave can be accurately calculated:¹²

$$k_{0\nu} = k_0 \frac{a'}{\pi} \int_{-\infty}^{\infty} \frac{e^{-y^2} dy}{a'^2 + (\omega - y)^2} \quad (4)$$

where

$$\omega = \frac{z(\nu - \nu_0)(\ln z)^{1/2}}{\Delta\nu_D} \Big|_{\nu=\nu_0} = 0 \quad (5)$$

$$a' = \frac{\Delta\nu_N + \Delta\nu_L}{\Delta\nu_D} (\ln z)^{1/2} \quad (6)$$

$$y = \frac{z\delta}{\Delta\nu_0} (\ln z)^{1/2} \quad (7)$$

and where k_0 is the absorption coefficient at the line center (frequency ν_0) for the case of Doppler broadening only and is given by

$$k_0 = 8.51 \times 10^{15} \frac{f M^{1/2}}{\nu_0 T^{3/2}} \quad (8)$$

for a partial pressure of hydrogen atoms of 1 atmosphere. Here $\Delta\nu_n$, $\Delta\nu_D$ and $\Delta\nu_L$ are the half-widths of the natural, Doppler and Lorentz broadened lines, respectively, and f is the oscillator strength for the hydrogen atom for absorption due to the Lyman α transition. Calculation of $\Delta\nu_L$ required the assumption of a value for σ_L^2 , the effective cross-section for Lorentz broadening. The value used, $\sigma_L^2 = 70 \times 10^{-16} \text{ cm}^2$, was obtained by extrapolation of data given in Reference 12. A small error in σ_L^2 cannot greatly affect the final result since a change of 10% in σ_L^2 produces less than a 3% change in $k_{0\nu}$.

All temperatures were calculated from the measured shock speeds and available shock wave data, correcting for attenuation as observed. Calculation revealed that laminar boundary-layer effects were unimportant for the test times used here and shock-tube wall temperatures were monitored to ensure that turbulent boundary layers were not encountered. All experiments were isothermal and completely free from reverse reaction since the fraction of hydrogen dissociated was about 3×10^{-5} for 1% hydrogen in argon. The calculations of k_d were thus direct and simple, not requiring relationships involving the equilibrium constant and reverse reaction rates, or the assumption of a rate-temperature formulation. Then integrating Equation (2) with constant hydrogen concentration, Equation (3) becomes

$$I/I_0 = \exp(-2 k_{ov} k_d [M][H_2] t_p l) \quad (9)$$

where k_{ov} , $[M]$ and $[H_2]$ are expressed in concentration units and t_p is the shocked particle time, which is related to the oscilloscope time t_s by

$$t_p = \frac{\rho_2}{\rho_1} \cdot t_s \quad (10)$$

where ρ is the gas density with the appropriate subscripts. The rates were calculated from the time required to reach 50% absorption which occurs at a concentration of hydrogen atoms of approximately 3×10^{-12} moles cm^{-3} . This time was usually 25-150 μ seconds of oscilloscope time.

Experiments were carried out for a number of hydrogen-argon mixtures at reaction pressures of approximately 1 atmosphere and at temperatures in the range 2150°K to 3640°K. The results obtained are shown in Fig. 3, and the dissociation rate constant can be described by the equation

$$k_d = 1.18 \times 10^{12} \cdot T^{1/2} \exp(-94,500/RT) \text{ cm}^3 \text{ mole}^{-1} \text{ sec}^{-1} \quad (11)$$

with an rms deviation of $\pm 18\%$. The indicated activation energy is approximately 10 k cal mole^{-1} less than the spectroscopic dissociation energy of hydrogen, and the calculated pre-exponential factor is approximately 8% of the hard sphere collision frequency at 2500°K assuming an argon-hydrogen collision diameter of 3 Å.

Classical simple collision theory gives

$$k_d = P Z \left(\frac{D}{RT} \right)^s \cdot \frac{1}{s!} \cdot \exp \left(- \frac{D}{RT} \right) \quad (13)$$

where P is the collision efficiency, Z the collision frequency, D the spectroscopic dissociation energy and s half the number of classical degrees of freedom of internal energy, other than those of translational energy along the line of centers, which contribute to dissociation. Expressing our results in this form we find

$$k_d = 4.75 \times 10^{-3} \cdot Z \left(\frac{D}{RT} \right)^{1.5 \pm 0.1} \cdot \exp \left(- \frac{D}{RT} \right) \quad (14)$$

This implies the participation of three squared terms which is less than the maximum number available and the apparent collision efficiency is then 6.3×10^{-3} . A value of s of 1.5 was found previously by Camac and Vaughan in their detailed study of oxygen dissociation in argon.

Our over-all pre-exponential temperature dependence of T^{-1} (when allowing for $T^{1/2}$ included in Z) agrees well with the results of Sutton² Rink³ and Patch⁴ but our measured rate constant is lower than any of their values as seen in Figure 4.

This difference will now be considered in light of the four basic features of this research as outlined in the introduction. The directness of the method, with its isothermal and constant density conditions is in complete contrast to previous measurements of hydrogen dissociation where the methods of interferometry,² x-ray densitometry^{1,3} and sodium line reversal⁵ were used.

Although Patch⁴ employed a more direct approach i. e., absorption by the Werner Bands ($\pi_u - \sigma_g^+$) of the hydrogen molecule, his method, along with those above lacked the sensitivity of atomic resonance absorption. For the reaction to be monitored by these techniques, large amounts of dissociation must occur which cause the translational temperature of the gas to fall, since the endothermicity of the reaction absorbs a considerable fraction of the available energy. This temperature decrease (sometimes as large as 2000°K) with the attendant increase in gas density, the large temperature dependence of the reaction rates involved and the necessary consideration of reverse reactions make difficult the extraction of accurate kinetic information.

A pertinent example of the above is illustrated by the results obtained, for hydrogen dissociation, by the line-reversal technique.⁵ There rate constants are derived from the slope of a relation between two parameters. The data illustrated, clearly supports a linear relationship although the temperature falls some 600°K during that particular experiment. The final rate constants however, indicate that the term evaluated from the slope is not constant but changes by an order of magnitude in these 600°K.

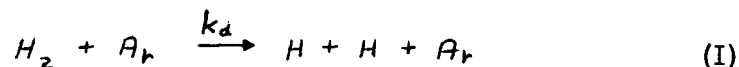
The high sensitivity of atomic resonance spectroscopy permits not only isothermal conditions for the experiment but allows the dissociation to be studied far from equilibrium where reverse reactions are unimportant. Although far from equilibrium our rate constant cannot be low as a result of an induction time in populating the upper vibrational levels since our reaction times are considerably greater than the measured vibrational relaxation time for hydrogen-argon mixtures.¹⁴

In the next section we show that the addition of small amounts of oxygen can have a large effect on the apparent rate of dissociation. Although the impurity levels in the previously published data¹⁻⁵ are considerably higher than in the present work it would not be warranted to ascribe the differences in the measured rate to this effect since we have not yet studied the effect of added oxygen under the conditions of these previous measurements.

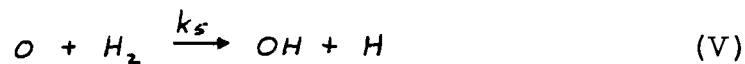
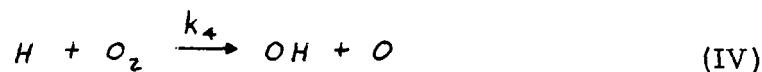
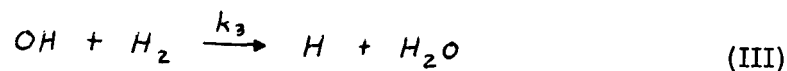
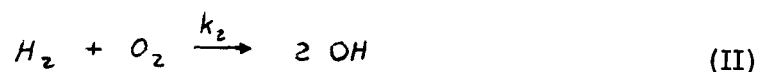
Effect of Added Oxygen

One of the important reasons for developing the high-purity shock tube used in this research was to study the effect of molecular oxygen on hydrogen dissociation as encountered in the preliminary work.⁶ A series of observations was made with mixtures of 1% hydrogen in argon containing either 100 ppm or 1000 ppm of oxygen and negligible amounts (< 2 ppm) of other impurities. The values for k_d obtained for these mixtures and pure hydrogen-argon mixtures, assuming only the mechanism of Equation (I) to be operative, are shown in Fig. 5. The effects of even 100 ppm oxygen are quite significant at temperatures below 2250°K and increase with decreasing temperature. It will also be noted that the effect of 1000 ppm oxygen begins at higher temperature than does that of 100 ppm oxygen. These effects, while peculiar to the unique nature of the experiment (particularly with respect to the small fraction of dissociation), nonetheless serve to illustrate the importance of controlling the intrusion of foreign gases.

By means of these data, we have been able to show that the catalytic effect of oxygen in the experiments of Fig. 5 can be explained in terms of the competition for hydrogen atom production, between the reaction



and the reactions



Calculations of the rate of hydrogen atom production under normal shock conditions were made by means of a computer program developed at this Laboratory.¹⁵ Not only were the rates of reactions I-V entered into the computation but rates of production as yielded by the individual reactions were monitored for hydrogen atoms and the other species. In this manner, it was possible to conclude that, when oxygen is present, the departure of k_d from the curve for pure hydrogen in argon provides a single unequivocal value for reaction IV which fits both the case of 100 ppm O_2 and 1000 ppm O_2 .

Reaction II was readily eliminated as a serious contributor to the mechanism for hydrogen atom production because of both too slow a rate and an incompatible temperature dependence. Reactions III and V are not rate determining for the conditions prevailing here and thus reaction IV is the rate-limiting step for the chain-branching mechanism. For this reason the values of k_3 and k_4 were not varied in the computer calculations.

A number of values of k_4 were available from the literature and a representative value was used for the initial calculations along with literature values for k_2 , k_3 , and k_5 and the value for k_d given by Equation 11. These initial calculations showed that the literature values for k_4 were too fast to explain our results. To decrease the value of k_4 we chose to increase the activation energy in the rate expression to 23,000 cal mole⁻¹ which is compatible with that predicted by the Hirschfelder rule.¹⁶ This yields the expression

$$k_4 = 1.3 \times 10^{13} T^{1/2} \exp(-23,000/RT) \text{ cm}^3 \text{ mole}^{-1} \text{ sec}^{-1} \quad (15)$$

where the pre-exponential factor was chosen so that the computer program matched the experimental result at 1820°K for 100 ppm oxygen.

The values for k_2 , k_3 , and k_5 taken from the literature¹⁷ were as follows:

$$k_2 = 5.6 \times 10^{12} T^{1/2} \exp(-67,000/RT) \text{ cm}^3 \text{ mole}^{-1} \text{ sec}^{-1}$$

$$k_3 = 3.3 \times 10^{12} T^{1/2} \exp(-6,450/RT) \text{ cm}^3 \text{ mole}^{-1} \text{ sec}^{-1}$$

$$k_5 = 2.66 \times 10^{11} T^{1/2} \exp(-9,200/RT) \text{ cm}^3 \text{ mole}^{-1} \text{ sec}^{-1}$$

with, of course, the value k_d taken from Equation 11.

Computation for all other temperatures was then carried out for both 100 and 1000 ppm oxygen. The computed and experimental results are shown on Fig. 5. Since the agreement is nearly perfect for both concentrations of O_2 , and since only reaction IV is rate-controlling at the lower temperatures, this may be considered to be a direct isothermal measurement of k_4 . However, while the rate is unequivocally obtained in this manner, it is not possible to uniquely determine a combination of an activation energy and pre-exponential factor. Thus, for the widely accepted activation energy of $17.75 \text{ k cal mole}^{-1}$ ¹⁷ the resulting rate expression to match the experimental result at 1820°K for 100 ppm oxygen is

$$k_4 = 3.07 \times 10^{12} T^{1/2} \exp(-17,750/RT) \text{ cm}^3 \text{ mole}^{-1} \text{ sec}^{-1} \quad (16)$$

Using this value for k_4 along with the above mentioned values for k_2 , k_3 , k_5 , and k_d we find at temperatures above 1820°K , only a 10% difference in the rate of hydrogen atom production, from that predicted by using expression (15), which is within experimental error.

Although we are unable to distinguish between expressions (15) and (16) (or any expression incorporating an intermediate activation energy which has the same overall rate) to describe reaction IV in this temperature range, our computed results are sensitive to small changes (25%) in the absolute magnitude of k_4 . The rate as expressed by either Equation (15) or (16) is only 30% lower than the rate suggested by Baldwin.¹⁶

Induction Periods for Hydrogen Atom Formation

In the experiments with 1000 ppm oxygen, at temperatures below 2000°K, induction periods up to 70 μ seconds were observed before hydrogen atom production was detected. An example of this is illustrated in Fig. 2c. This delay is a measure of the hydrogen atom concentration required for the chain-branching process to overtake the dissociation process as the predominant mechanism for producing hydrogen atoms. It would also indicate that, for the temperature range and reactant concentrations of these experiments, the dissociation of hydrogen is the initiating step in the H₂-O₂ reaction mechanism. The lengths of these induction times are predicted by the computed results within 15% of the experimentally measured values.

CONCLUSIONS

The technique of atomic resonance absorption spectrophotometry has been successfully applied to the measurement of the rate of hydrogen atom formation in a shock tube. The sensitivity afforded by the method has required the development of an ultrahigh-purity shock tube which in turn has made it possible to observe quantitatively the considerable effect of added oxygen on the reaction rate. Thus rates have been obtained for both H₂ + Ar = 2H + Ar and H + O₂ = OH + O, in a direct manner, at constant temperature and free from reverse or other complicating reactions. It is believed that these rates are correct to within $\pm 30\%$.

This method of atomic resonance absorption spectrophotometry is currently being used to study the dissociation of oxygen and nitrogen.

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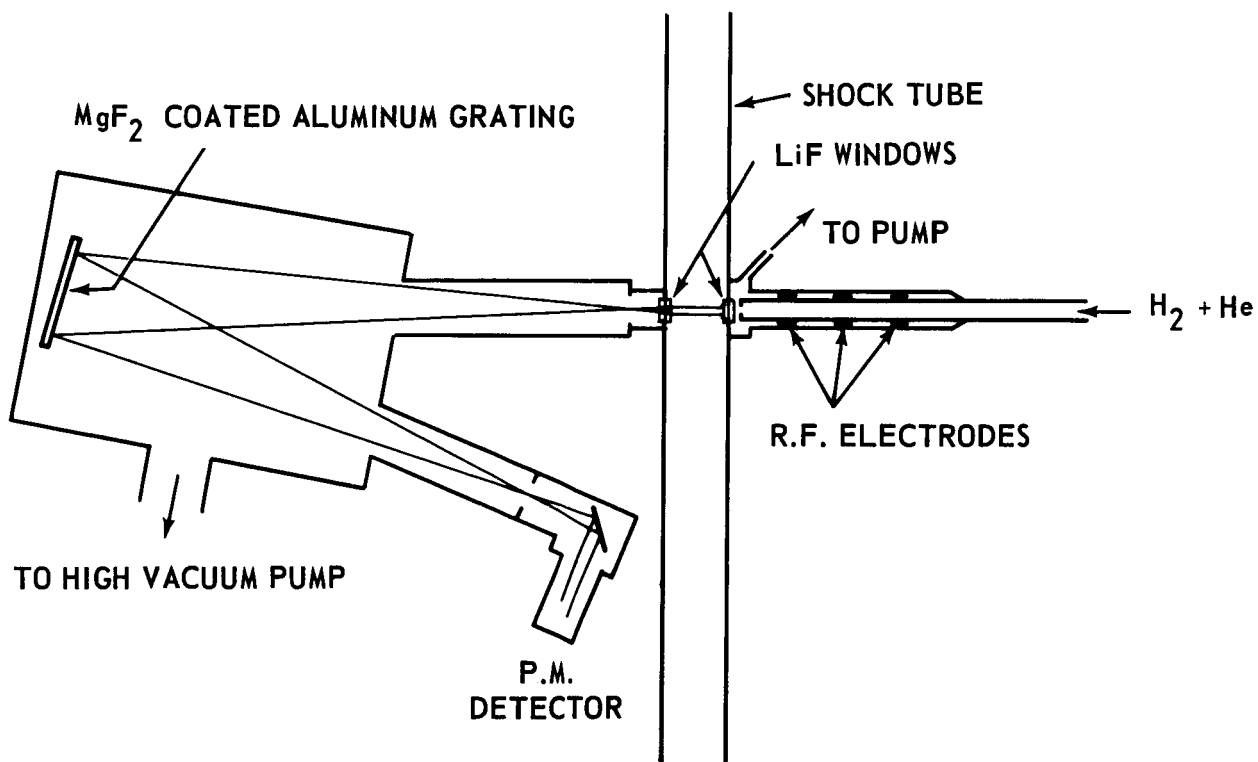
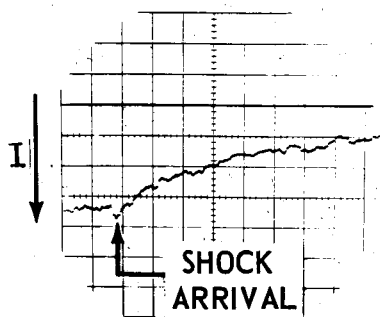


Figure 1 APPARATUS FOR DETECTING HYDROGEN ATOM FORMATION
 BEHIND SHOCK WAVES



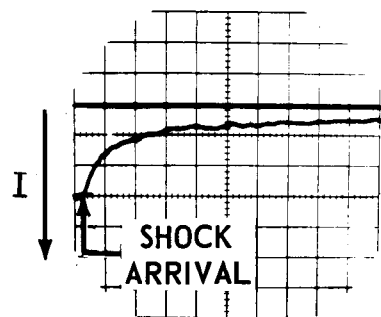
50 μ sec/div

1% H₂ IN ARGON

P₁ = 30 mm Hg

T₂ = 2160°K

(a)



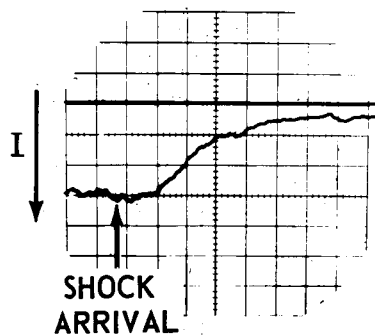
50 μ sec/div

0.1% H₂ IN ARGON

P₁ = 16.5 mm Hg

T₂ = 2725°K

(b)



50 μ sec/div

1% H₂ IN ARGON WITH 1000 ppm O₂,

p₁ = 13 mm Hg, T₂ = 1975°K

(c)

Figure 2 OSCILLOSCOPE RECORDS SHOWING THE TIME HISTORY OF ABSORPTION BEHIND SHOCK WAVES

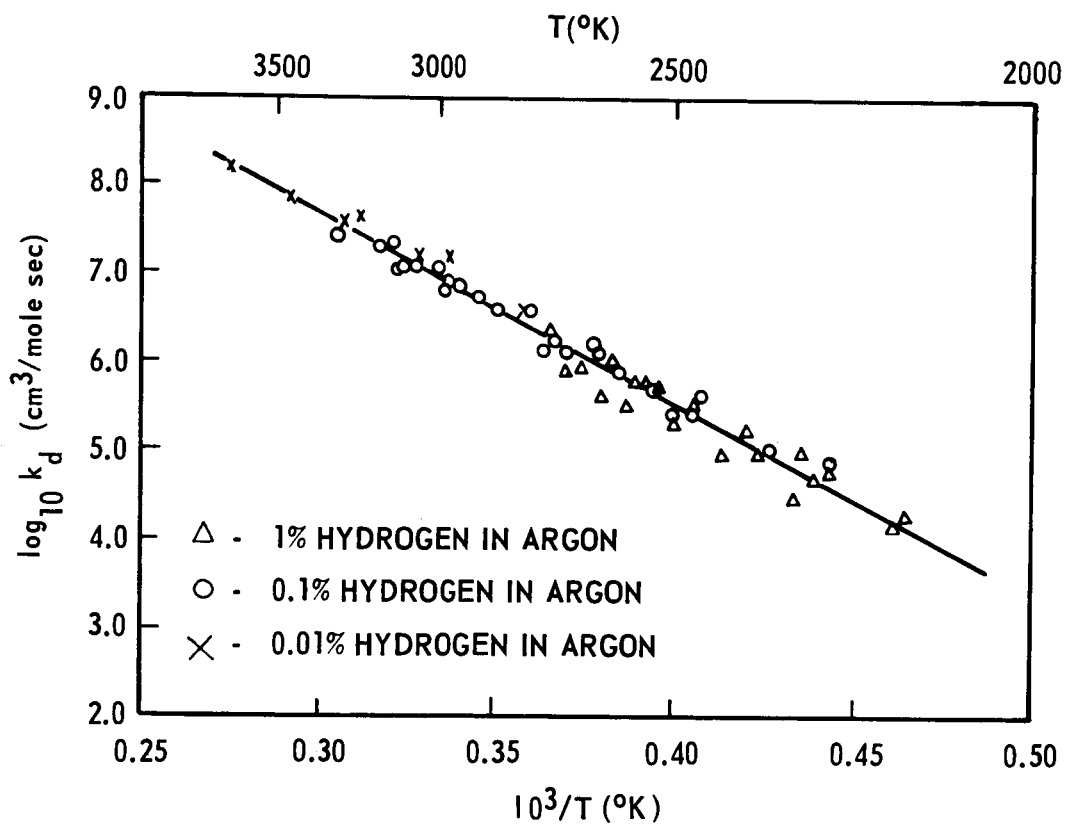


Figure 3 ARRHENIUS PLOT OF THE EXPERIMENTAL DATA FOR THE DISSOCIATION RATE CONSTANT (k_d)

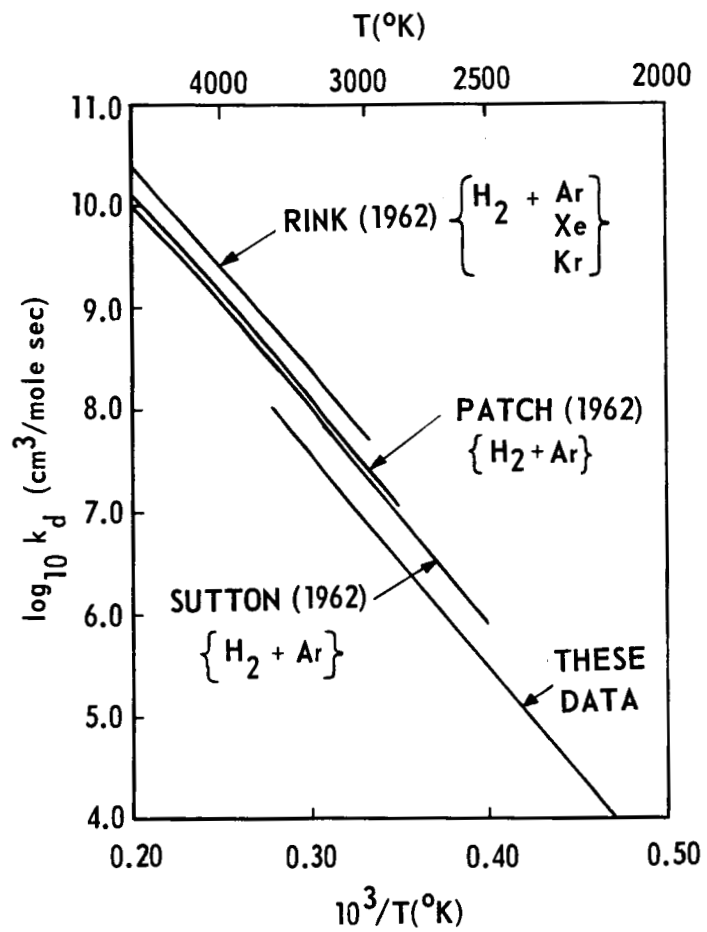


Figure 4 COMPARISON OF THESE DATA WITH PREVIOUS LITERATURE RATE CONSTANTS FOR HYDROGEN DISSOCIATION IN ARGON

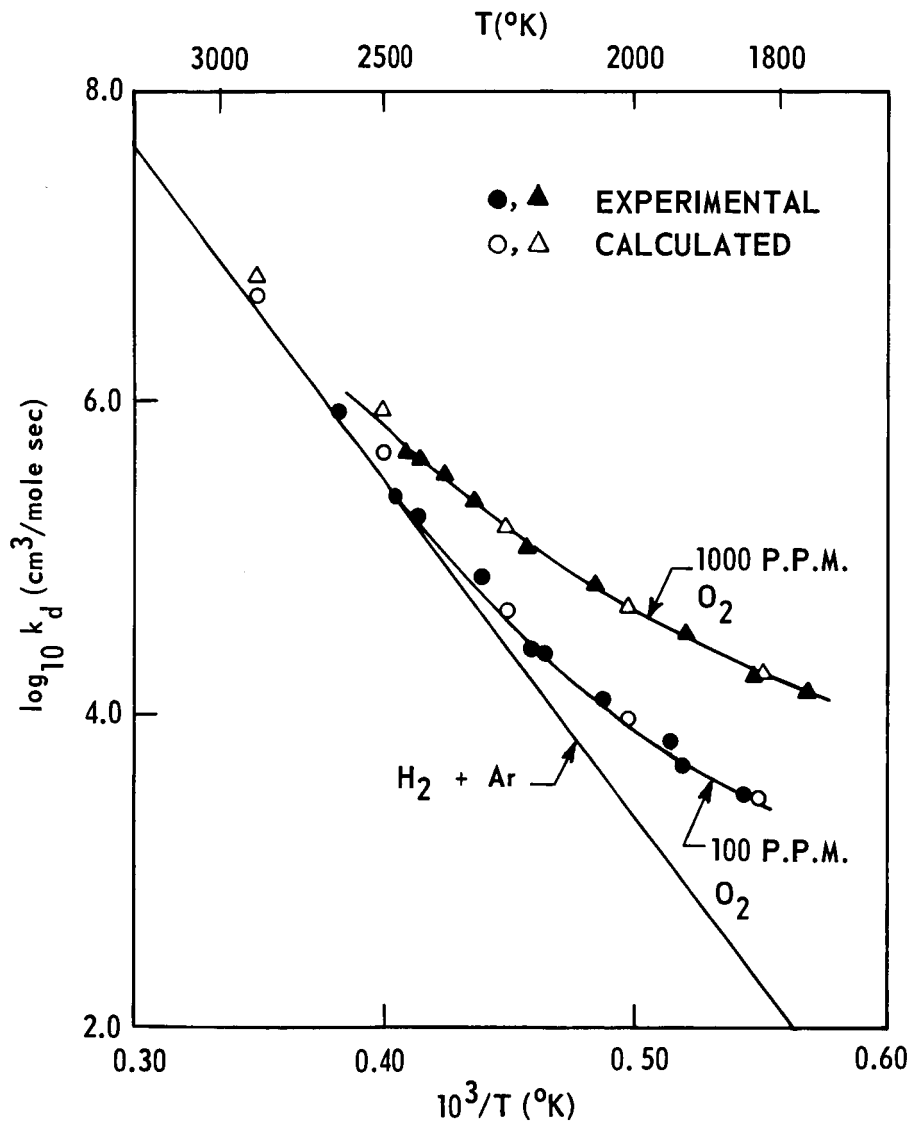


Figure 5 EFFECT OF ADDED OXYGEN ON THE DISSOCIATION RATE

The data points are for the indicated amounts of O₂ added to 1% hydrogen in argon.