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Shock-Tube Measurement of Dissociation Rates of Hydrogen

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The rate of dissociation of hydrogen was measured in a shock tube by following the absorption of ultraviolet light by the H_2 $^1\Pi_u - ^1\Sigma_g^+$ Werner transition. Dissociation was observed in mixtures of from 1.00 to 30.1% hydrogen over the temperature range from 2950° to 5330°K. A digital computer program was used to calculate reaction profiles behind a normal shock wave for arbitrary reaction rate coefficients assuming that the reaction proceeded by the mechanism

$$H_2 + M \underset{k_r}{\overset{k_d}{\rightleftharpoons}} 2H + M,$$
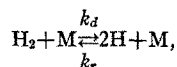
where the third body, M, may be Ar, H_2, or H. By varying the reaction rate coefficients, it was possible to match the computed reaction profiles with the observed profiles for all experiments; however, the temperature range covered was not sufficiently wide to permit an accurate determination of the temperature dependence of k_r. Consequently, a T^{-1} dependence was arbitrarily chosen. The recombination rate coefficients in cm^6 $mole^{-2}$ sec^{-1} were 7.5×10^{17} T^{-1} for argon as the third body, 7.5×10^{18} T^{-1} for H_2, and 5×10^{19} T^{-1} for H, where T is in °K.

INTRODUCTION

THE rate of recombination of dissociated hydrogen is important in the chemical kinetics of flames and can have a large effect on the performance of rocket propulsion systems employing hydrogen as the working fluid. When this study was initiated, only Bulewicz and Sugden[1] had measured the recombination rate coefficient of hydrogen at high temperatures. Their measurements were made in flames where the principal third body was H_2O. Since then Gardiner and Kistiakowsky[2] and also Rink[3] have determined the dissociation rates of H_2 in a shock tube by using x-ray densitometers. Sutton[4] measured the dissociation rates of H_2 by using an interferometer in conjunction with a shock tube. In general, the results of these various studies are not in quantitative agreement.

The objective of this study was to obtain dissociation rate coefficients for a wide range of temperatures for various third bodies. In order to accomplish this objective, an ultraviolet absorption technique for measuring H_2 concentration with microsecond resolution was developed and this technique was employed to measure the dissociation rate of hydrogen behind a normal shock wave. Recombination rate coefficients were determined from these measurements by assuming the principle of detailed balancing.

THEORETICAL CONSIDERATIONS

For quantitative absorption spectroscopy it is desirable to utilize a line, band, or continuum at a wavelength where only one chemical species will absorb. The absorption coefficient of the species should result in from 20 to 90% light transmission for the experiment being planned, and, if a line or band is used, one mechanism of broadening should predominate. For shock-tube work, the wavelength must be selected so that a material can be found to serve as a window. The (0, 3) band of the $H_2 ^1\Pi_u - ^1\Sigma_g^+$ Werner transition (see Fig. 1) was found to fulfill all these requirements. It appears with good intensity in hydrogen glow-discharge lamps and, as a result, the lamp produces predominately light which H_2 will absorb. Previous quantitative absorption spectroscopy of molecules had been accomplished almost entirely on (0, 0) bands to minimize possible errors due to vibrational nonequilibrium. However, Bauer[5] obtained consistent results using (0, 0) and (0, 1) bands of CN during the dissociation of C_2N_2. Moreover, theoretical studies[6] have shown that at least the lowest four vibrational levels of H_2 should be in equilibrium during dissociation. Due to H_2 population changes, H_2 concentration determination based on absorption of the (0, 3) band is somewhat sensitive to temperature. However, this is not a problem because conditions can be calculated just behind the shock before dissociation takes place, and the dissociating gas has only one degree of freedom. This single degree of freedom results from the constraints imposed by the energy, momentum, continuity, and state equations. Consequently, the fraction of light transmitted uniquely determines the percent of dissociation. The temperature dependence is actually an advantage, because it increases the change in light transmission due to dissociation. The (0, 3)

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[1] E. M. Bulewicz and T. M. Sugden, Trans. Faraday Soc. **54**, 1855 (1958).

[2] W. C. Gardiner, Jr. and G. B. Kistiakowsky, J. Chem. Phys. **35**, 1765 (1961).

[3] John P. Rink, J. Chem. Phys. (to be published).

[4] Emmett A. Sutton, *Measurement of the Dissociation Rates of Hydrogen and Deuterium* (Cornell University Press, Ithaca, New York (1961).

[5] S. H. Bauer, "The energetics and kinetics of dissociation reactions as studied in a shock tube," Paper presented at American Chemical Society Sectional Meeting, Princeton University (March 16, 1961).

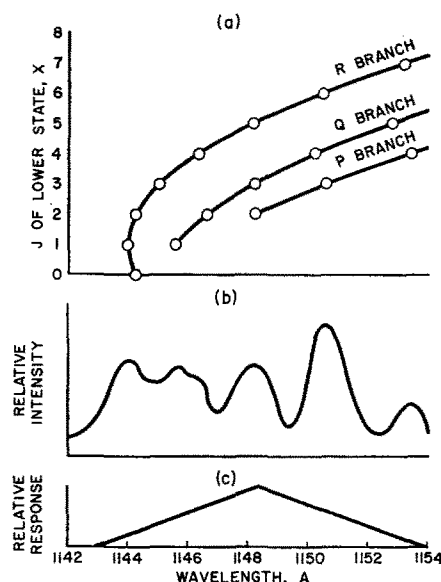[6] Kurt E. Shuler, J. Chem. Phys. **31**, 1375 (1959).

FIG. 1. (a) A Fortrat diagram of the (0, 3) band of the $H_2 \, {}^1\Pi_u - {}^1\Sigma_g^+$ Werner transition. (b) The intensity of a 150-ma-dc glow discharge in H_2 at 0.9 mm Hg measured with 25 μ wide entrance and exit slits on a 0.5 m Seya-Namioka monochromator. (c) The calculated response of the same monochromator with the 380 μ wide slits used for the shock tube experiments.

band has such a high absorption coefficient that mixtures of 1% H_2 in 99% argon can be used, enabling a more accurate determination of the dissociation rate coefficient k_d with argon as the third body than is possible with other techniques.

The mechanism of the dissociation and recombination of hydrogen is

$$H_2 + M \underset{k_r}{\overset{k_d}{\rightleftarrows}} 2H + M, \tag{1}$$
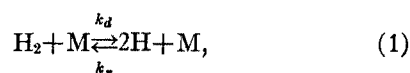
where M may be any third body. For this study, M was Ar, H_2, or H. Consequently, the rate equation at constant density ρ is

$$\partial[H_2]/\partial t \,|_\rho = -k_{d,Ar}[Ar][H_2] - k_{d,H_2}[H_2]^2$$
$$-k_{d,H}[H][H_2] + k_{r,Ar}[Ar][H]^2 + k_{r,H_2}[H_2][H]^2$$
$$+ k_{r,H}[H]^3, \tag{2}$$

where brackets denote the molar concentration of the species indicated.

If kinetic energy and the internal degrees of freedom are in equilibrium, then the principle of detailed balancing gives

$$k_d/k_r = K_C, \tag{3}$$

where K_C is the equilibrium constant defined by

$$K_C = [H]^2/[H_2] \quad \text{(equilibrium)}. \tag{4}$$

Therefore Eq. (2) may be expressed as

$$\partial[H_2]/\partial t \,|_\rho = (k_{r,Ar}[Ar] + k_{r,H_2}[H_2] + k_{r,H}[H])$$
$$\cdot ([H]^2 - K_C[H_2]). \tag{5}$$

In this study $k_{r,M}$ was represented by the common assumption[3]

$$k_{r,M} = A_M T^{B_M} \tag{6}$$

where A_M and B_M are arbitrary constants which can be adjusted to fit the data.

If the initial conditions in the shock tube before the shock wave together with the shock velocity are known, then conditions just behind the incident shock wave before the composition has changed can be calculated from the momentum, energy, continuity, and state equations. This was done on an IBM 704 digital computer using thermodynamic data from reference 7. The procedure was repeated to find conditions far behind the incident shock wave at chemical equilibrium. With the conditions just behind the incident shock wave determined, the energy, momentum, continuity, and state equations together with Eq. (5) may be numerically integrated to determine conditions at intermediate distances behind the shock wave. This was accomplished by generalizing Matthew's equation[8] to include in inert diluent and integrating by the Runge-Kutta method on an IBM 7090 digital computer. Because Matthew's equation is based on coordinates moving with the shock wave whereas spectroscopic measurements are made at a fixed point along the shock tube, a transformation of coordinates was necessary. A spectroscopic calibration curve was also included in the program, so that the output was a light-transmission profile (light transmission vs time) for assumed values of A_M and B_M. The values of A_M and B_M were adjusted so the computed light-transmission profile matched the experimental light-transmission profile.

EXPERIMENTAL PROCEDURE

The experimental apparatus is shown in Fig. 2. The gaseous discharge lamp produced ultraviolet light which passed through slits on either side of the shock tube and into a monochromator, where light of the desired wavelength was measured. The absorption of some of this light by H_2 in the shock tube made it possible to follow the dissociation process.

The Z1400-025 Hanovia gaseous discharge lamp was made of quartz with aluminum electrodes. The capillary was 5-mm i.d. and 27.5 cm long. A flow rate of about 3×10^{-6} moles per sec of Matheson prepurified H_2 was maintained through the lamp at a pressure of 0.9 mm Hg to 1.1 mm Hg measured downstream of the capillary. A trickle current of 150 ma was maintained continuously in the lamp, and a trapezoidal pulse of 150 μsec duration was superimposed during each experiment to increase the light intensity. Initially the pulse was 2.9 amp, but it rose linearly to 3.2 amp. The circuit to

[7] Vearl N. Huff, Sanford Gordon, and Virginia E. Morrell, NACA Report 1037 (1951).
[8] D. L. Matthews, Phys. Fluids 2, 170 (1959).

accomplish this included a Penta PL-172 beam pentode in series with the lamp.[9]

The lithium fluoride windows had cleaved surfaces and were supplied by the Harshaw Chemical Company. They were cemented to Lucite with epoxy resin. The two slits were both flush with the inside diameter of the shock tube. The slit on the lamp side was 3×10 mm, whereas the slit on the monochromator side was $380 \mu \times 10$ mm.

The 0.5 m Seya-Namioka monochromator was designed specifically for this study in order to maximize the signal and minimize the stray light. The 1200 line/mm concave diffraction grating was coated with aluminum and lithium fluoride to increase its reflectance in the region around 1148 A. The baffles and interior of the monochromator were coated with Aquadag to
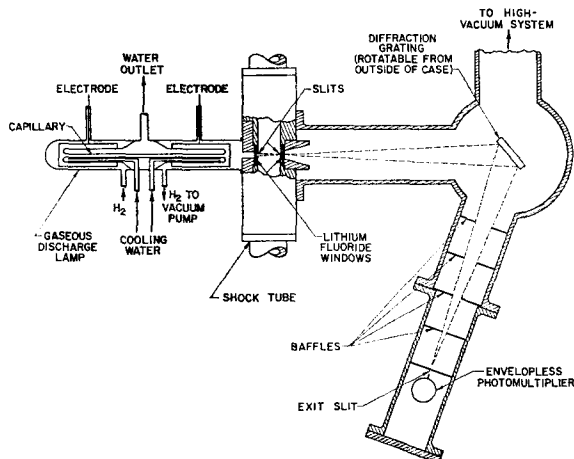
FIG. 2. The experimental apparatus for measuring H_2 concentration in a shock tube by quantitative absorption spectroscopy. The Seya-Namioka monochromator is on the right.

decrease their reflectance. The exit slit was $380 \mu \times 10$ mm, and behind it was an envelopless photomultipler, described in reference 10, which had appreciable sensitivity only to wavelengths below about 1400 A. The monochromator was evacuated to 10^{-5} mm Hg to obtain proper operation of the photomultiplier. The photomultiplier circuit had linear response and had a rise time of 2 μsec, which was necessary to filter out some of the statistical fluctuations in the signal.

The shock tube was constructed of stainless steel and had a 3.8-cm i.d. throughout. The slits were 5 m from the diaphragm. Velocity was measured with five thin-film heat-transfer gages at different locations along the length of the tube, using a crystal-controlled time mark generator as a reference. The combined leakage and outgassing rate was about 5 μ Hg/min. To minimize contamination, the H_2-Ar mixture was injected into the shock tube just downstream of the

[9] Albert W. Penney (private communication).
[10] Richard W. Patch, Rev. Sci. Instr. **32**, 983 (1961).

FIG. 3. A typical oscillogram (experiment No. 8) showing the variation of light transmission behind a shock wave as a function of time.
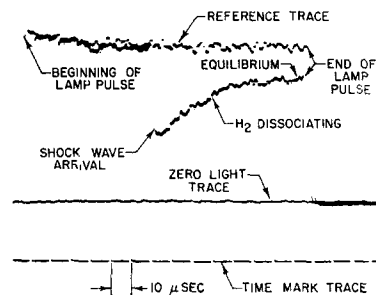
diaphragm and flowed continuously through the driven end of the shock tube, through check and throttling valves, and into a vacuum pump. Thus contaminants were continuously washed away. Reducing valves and a calibrated orifice between the H_2-Ar bottle and the shock tube provided a flow velocity of about 70 cm/sec in the driven end of the shock tube; consequently, the pressure drop along the length of the shock tube never exceeded 1%. The 70 cm/sec flow velocity, which was less than 0.04% of the shock velocity, was neglected in data reduction.

The four H_2-Ar mixtures were prepared by mixing Matheson prepurified (99.9% pure) H_2 with Linde Ar (99.995% pure). This was carried out in steel bottles 20-cm diameter by 120 cm high, which were placed on their sides for eleven days to obtain adequate mixing.

Before each experiment, the driven end of the shock tube and connecting tubing were evacuated to 15 μ Hg. The H_2-Ar mixture was then metered into the shock tube through the calibrated orifice. The pressure in the driven end was adjusted with the throttling valve at the shock-tube vacuum pump. A zero-light trace and a reference trace produced by pulsing the lamp were then recorded on the oscilloscope camera (see Fig. 3). The driver end of the shock tube was next filled with hydrogen, helium, or some mixture of hydrogen, helium, and nitrogen to obtain the desired shock velocity upon pressure-induced rupture of the scored diaphragm. The times of shock passage were detected
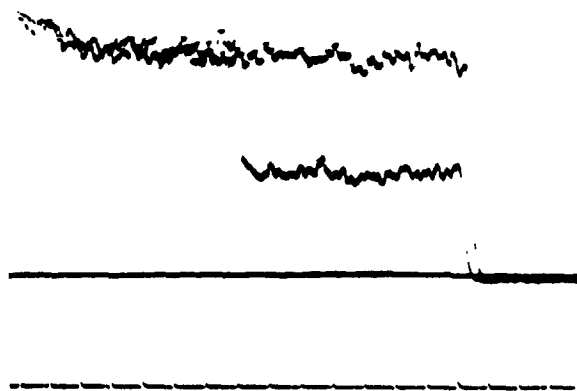
FIG. 4. A typical oscillogram of a calibration experiment where the temperature was too low (2770°K) to cause appreciable dissociation in the 70 μsec after shock-wave arrival.
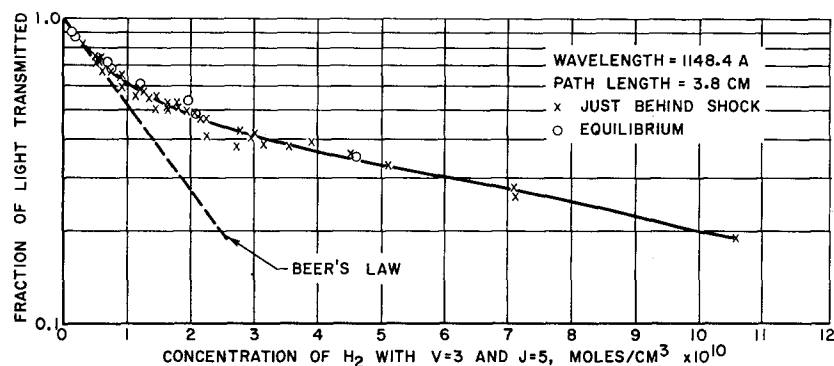
FIG. 5. The calibration curve for the (0, 3) band of the H_2 $^1\Pi_u - ^1\Sigma_g^+$ Werner transition. The temperatures of the calibration points were between 2740° and 5330°K.

by the five thin-film heat-transfer gages of the velocity system and by a sixth gage which triggered the lamp pulser and the two-beam oscilloscope. This caused two additional traces to be recorded: a crystal-controlled time-mark trace (lower part of Fig. 3) and the photo-multiplier output, which recorded the absorption of light by the H_2 behind the shock wave. The irregularities in the reference trace and dissociation trace in Fig. 3 are due to statistical noise caused by marginal light intensity.

After the experiment, the tube was filled with dry nitrogen to prevent atmospheric moisture from causing loss of transparency of the windows, which apparently were activated by the high temperature behind the shock wave. Since the windows were also activated by the glow discharge in the lamp, a vacuum was always maintained in the lamp after a window had been placed in service.

RESULTS

Typical oscillograms are shown in Figs. 3 and 4. In Fig. 3 the temperature just behind the shock wave was 4150°K, causing the H_2 to dissociate rapidly. However, in Fig. 4 the temperature just behind the shock wave was 2770°K, so dissociation took place too slowly to be detected. Figure 4 demonstrates the absence of pressure and expansion waves behind the shock wave and indicates that the boundary layer was negligible.

An empirical spectroscopic calibration was necessary due to experimental and theoretical uncertainties. Since room temperature H_2 does not absorb the (0, 3) band appreciably, the fraction of light transmitted was
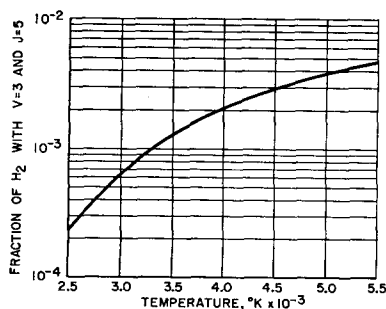
measured for three types of calibration points behind the shock wave: (1) just behind the shock wave with negligible dissociation occurring (see Fig. 4), (2) just behind the shock wave with appreciable dissociation occurring thus requiring extrapolation back to the time of shock wave arrival, and (3) far enough behind the shock wave for equilibrium to exist (see Fig. 3). As shown in Fig. 1, the monochromator slits were set to pass sixteen lines of the (0, 3) band; consequently a correlation of light transmission with any single population is just an approximation. After several trials it was found that a useful correlation was obtained by plotting light transmission versus the molar concentration of H_2 with a vibrational quantum number V of 3 and a rotational quantum number J of 5 (see Fig. 5). The fraction of H_2 with $V=3$ and $J=5$ is given in Fig. 6, based on a vibrating-rotator model with allowance for nuclear spin degeneracy. This correlation probably incidentally included the effect of Doppler broadening because both the linewidth and the fraction of H_2 with given quantum numbers depend solely on temperature. No collision broadening was detected. It is significant that all three types of calibration points agree, for this shows that the four lowest vibrational states of H_2 were essentially in equilibrium even when dissociation was proceeding rapidly.

The light transmission (Fig. 5) did not obey Beer's law for several possible reasons: (1) there were actually sixteen lines with different populations and absorption coefficients, (2) about 4% stray light was present,

FIG. 6. The fraction of H_2 molecules with the vibrational quantum number V equal to 3 and the rotational quantum number J equal to 5.
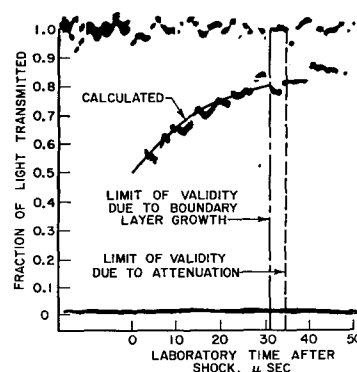

FIG. 7. A typical light transmission profile (experiment No. 13) and the calculated profile for the final set of rate coefficients.

TABLE I. Resume of dissociation experiments.

No.	Initial mole fraction		Pre-shock pressure mm Hg	Shock velocity mm/μsec	No-reaction temperature °K	% Dis. of H_2
	H_2	Ar				
1	0.0100	0.9900	43.1	1.985	3760	85.3
2	0.0100	0.9900	19.7	2.212	4600	99.4
3	0.0100	0.9900	20.0	2.016	3870	94.1
4	0.0100	0.9900	85.5	1.920	3530	64.4
5	0.0306	0.9694	3.4	2.170	4310	97.1
6	0.0306	0.9694	3.5	2.139	4200	95.7
7	0.0306	0.9694	3.4	2.185	4370	97.6
8	0.0306	0.9694	20.3	2.124	4150	83.0
9	0.0306	0.9694	29.5	2.019	3780	62.3
10	0.1008	0.8992	5.8	2.217	4070	47.6
11	0.1008	0.8992	5.9	2.423	4790	69.8
12	0.1008	0.8992	6.0	2.341	4490	60.8
13	0.1008	0.8992	2.2	2.456	4910	79.6
14	0.1008	0.8992	2.1	2.438	4840	78.1
15	0.1008	0.8992	2.1	2.371	4600	70.8
16	0.1008	0.8992	2.1	2.569	5330	90.1
17	0.3010	0.6990	10.1	2.449	3600	13.3
18	0.3010	0.6990	3.8	2.554	3880	19.1
19	0.3010	0.6990	2.0	2.476	3670	17.6
20	0.3010	0.6990	1.9	2.402	3480	15.0
21	0.3010	0.6990	2.1	2.354	3360	13.2
22	0.3010	0.6990	2.1	2.348	3340	13.0
23	0.3010	0.6990	2.0	2.448	3600	16.6

(3) the lamp may have produced some continuum between 1143 and 1154 A, and (4) the lines from the lamp may not have been narrow compared to the absorption lines in the H_2 in the shock tube. The use of empirical calibration curves such as Fig. 5 is not uncommon for cases where Beer's law is not applicable.[11-13]

The H_2-Ar mixture passed through two reducing valves and a needle valve between the mixing bottle and the shock tube, presenting the possibility that the H_2 might diffuse through the small openings in the valves more readily than a heavier gas such as argon. This phenomenon was observed by Breton.[14] To prove that this was not occurring to any extent, a second system was constructed in which the H_2 and Ar were passed through separate calibrated orifices, mixed in a long tube, and injected into the shock tube. The calibration curve obtained was not significantly different from Fig. 5. The separate-orifice system was not used for any of the dissociation experiments.

The 23 dissociation experiments are summarized in Table I. Shock wave attenuation was measured for each experiment; to minimize error, no oscillogram was used beyond the point where the mixture had been subjected to a shock wave of more than 1% greater velocity than the shock wave possessed when it passed the slits (see Fig. 7).

Another possible source of error was boundary-layer growth. Because the boundary layer had a lower temperature than the free stream, it was essentially transparent to the (0, 3) band. Consequently, the principal effect of the boundary layer should be to reduce the path length for light absorption, thereby increasing the fraction of light transmitted. Such an increase in transmission was not detected in any experiment, including calibration experiments such as that shown in Fig. 4. Nevertheless, the boundary-

[11] S. H. Bauer, G. L. Schott, and R. E. Duff, J. Chem. Phys. 28, 1089 (1958).

[12] Walter G. Berl, Physical Methods in Chemical Analysis (Academic Press Inc., New York, 1950).

[13] C. R. N. Strouts, J. H. Gilfillan, and H. N. Wilson, Analytical Chemistry (Oxford at the Clarendon Press, Glasgow, 1955) Vol. 2.

[14] M. J. Breton, Ann. office natl. combustibles liquides 11, 487 (1936).

layer growth was calculated for each experiment by the method of Mirels,[15] neglecting dissociation. No oscillogram was used beyond the point where the boundary-layer thickness exceeded 0.3 cm.

The 23 experimental light transmission profiles such as Fig. 3 and Fig. 7 were matched with calculated light-transmission profiles by an iterative procedure. The initial values of $k_{r,M}$ for the iteration were those of Sutton,[4] and the iteration was greatly facilitated by the predominance of each of the k_r's in at least one portion of several light-transmission profiles. Satisfactory matches were obtained with the assumed values $B_{Ar}=-1$ and $B_{H_2}=-1$. Because $k_{r,Ar}$ and k_{r,H_2} could be accurately determined only in narrow temperature ranges, it was futile to attempt to obtain more accurate values for B_{Ar} and B_{H_2}. However, the recombination rate coefficient, $k_{r,H}$, predominated over a wide temperature range, so it was expected that B_H could be determined from the data. The best match was obtained with $B_H=-1$, but its superiority over $B_H=-4$ depended solely on experiment No. 17. The final values obtained were

$$k_{r,Ar}=7.5\times10^{17}T^{-1},$$

$$k_{r,H_2}=7.5\times10^{18}T^{-1},$$

$$k_{r,H}=5\times10^{19}T^{-1}\text{ cm}^6\text{ mole}^{-2}\text{ sec}^{-1}.$$

Experimental and calculated light-transmission profiles are shown in Fig. 7.

ACCURACY OF THE EXPERIMENTS

The two principal sources of error in the experiments appeared to be inaccuracies in shock-wave-velocity measurement and shock-wave attenuation. The shock-wave velocity was measured to within 1%, which could cause errors up to 35% in the recombination rate coefficients. The light-transmission profiles were not used beyond the point where, due to attenuation, the mixture had been subjected to a shock wave of 1% greater velocity than the shock wave had when it passed the slits. This could also result in up to 35% errors in the recombination rate coefficients.

The vibrational relaxation of the third excited vibrational level of H_2 was too fast to detect. Consequently, based on Montroll[16] and Bazley's[17] analyses of vibrational relaxation of harmonic and anharmonic oscillators, it was concluded that any error due to lack of vibrational relaxation in any vibrational level should be negligible.

The value of $k_{r,Ar}$ given above should be within a factor of 2 of the true value for temperatures between 3430° and 4600°K. The values of k_{r,H_2} and $k_{r,H}$ should be within a factor of 3 of the true value for temperatures between 2950° and 5330°K.

COMPARISON WITH OTHER RESULTS

Based on the experiments in this study with 1% H_2 and 99% Ar, $k_{r,Ar}$ at 3500°K is 2.1×10^{14} cm^6 mole^{-2} sec^{-1}. The most reliable previous value at this temperature was 1.7×10^{14} obtained by Sutton[4] with mixtures with as little as 3% H_2. Rink[3] obtained a value of 4.3×10^{14} with 9.85% H_2.

In this study, $k_{r,H_2}=2.1\times10^{15}$ cm^6 mole^{-2} sec^{-1} at 3500°K. Sutton[4] obtained 7.2×10^{14}, whereas Rink[3] obtained 8.6×10^{14} at this temperature. A value of 1.3×10^{14} is obtained for Gardiner and Kistiakowsky's experiments[2] when one is aware[18] that they defined k_r by

$$\left.\frac{\partial[H]}{\partial t}\right|_\rho = -\sum_M k_{d,M}[M][H_2]+\sum_M k_{r,M}[M][H]^2 \quad (7)$$

instead of

$$\left.\frac{\partial[H_2]}{\partial t}\right|_\rho = -\sum_M k_{d,M}[M][H_2]+\sum_M k_{r,M}[M][H]^2. \quad (8)$$

The value $k_{r,H}=1.4\times10^{16}$ at 3500°K was obtained in this study, whereas Sutton[4] obtained 8.7×10^{15}, Rink[3] got 2.9×10^{15}, and Gardiner and Kistiakowsky[2] concluded that 3×10^{15} was too low.

When the values of $k_{r,H}$ obtained by Smallwood[19] and Amdur[20] from the recombination of H atoms at room temperature are compared with shock tube values of $k_{r,H}$, there is a consistency which contradicts Nikitin and Sokolov's[21] contention that k_d measured behind a normal shock wave is much less than k_d at equilibrium due to the preferential depopulation of vibrationally excited H_2 by dissociation. However, there is insufficient evidence for a definite conclusion.

CONCLUSIONS

(1) The concentration of H_2 at temperatures between 2740° and 5330°K can be measured by quantitative absorption spectroscopy with a time resolution of about 1 μsec.

(2) Vibrational relaxation of H_2 is fast relative to dissociative relaxation of H_2 for temperatures between 2950° and 5330°K.

(3) The dissociation of H_2 can be correlated by the accepted kinetic mechanism.

[15] Harold Mirels, N.A.C.A. Tech. Note 3401 (1955).
[16] Elliot W. Montroll and Kurt E. Shuler, J. Chem. Phys. 26, 454 (1957).
[17] Norman W. Bazley, Elliot W. Montroll, Robert J. Rubin, and Kurt E. Shuler, J. Chem. Phys. 28, 700 (1958).

[18] W. C. Gardiner, Jr. (private communication).
[19] Hugh H. Smallwood, J. Am. Chem. Soc. 56, 1542 (1934).
[20] I. Amdur, J. Am. Chem. Soc. 60, 2347 (1938).
[21] E. E. Nikitin and N. D. Sokolov, J. Chem. Phys. 31, 1371 (1959).