

PRECISE MEASUREMENTS OF DIATOMIC DISSOCIATION RATES IN SHOCK WAVES*

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The dissociation of H_2 in mixtures of 5%, 10%, and 20% H_2 in Ar and Xe has been studied behind incident shock waves over the temperature range 3500°–8000°K. Dissociation rates were determined by measurement of postshock density gradients using a laser-beam deflection technique. The postshock density-gradient profiles exhibit the same highly characteristic “dip” observed previously with O_2 -rare gas mixtures [J. Chem. Phys. 55, 4017 (1971)], and the magnitude of the gradient at this point is again interpreted as a measure of the initial dissociation rate. The over-all rate coefficients so obtained are of high precision, and the values determined for k_d^M , the coefficient due to H_2 -M collisions are given by

$$k_d^{Ar} = 9.35 \times 10^{13} \exp(-88\,900/RT) \text{ cc/mole-sec,}$$

$$k_d^{Xe} \cong k_d^{Ar},$$

$$k_d^{H_2} = 3.30 \times 10^{15} \exp(-105\,300/RT) \text{ cc/mole-sec,}$$

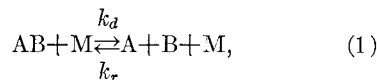
with R in cal/mole-deg. By numerical integration of the measured density-gradient profile from the point of the initial rate measurement, the density, and thus the composition, temperature, and over-all rate coefficient, were determined at subsequent points in the reaction course. From this data, values of the hydrogen-atom coefficient were obtained which are described by

$$k_d^H = 2.12 \times 10^{15} \exp(-87\,200/RT) \text{ cc/mole-sec.}$$

Values for all the rate coefficients determined are in general agreement with previously reported values. More significantly, in contrast with the results of previous work, the data are of sufficient precision to provide strong support for the traditional assumptions concerning diatomic dissociation; i.e., the interpretation of the various k_d^M as true chemical rate “constants.”

Introduction

The thermal dissociation of diatomic molecules,



has been the subject of considerable experimental and theoretical study over the past decade, particularly in the case of homonuclear molecules,

where $A=B$ ($A=H, O, N, F, Cl, Br, I$).¹ Experimental measurements of dissociation rates have been made exclusively in shock waves, and the results, taken as a whole, present a somewhat discouraging picture. While the over-all rates reported for a given system are in general agreement within an order of magnitude or better, considerable question remains about the relative contributions of various collision partners M to the over-all rate. Most measurements have been made in mixtures of the molecule with a rare-gas diluent (usually Ar) and, unless the molecule is present initially in very high dilution, a complete description of the dissociation process requires determination of the contributions due to the

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diluent gas, the molecule A_2 , and the atoms A produced by dissociation. In addition, in such an experiment, the temperature decrease accompanying dissociation is far from negligible, adding further complexity to the effects of changing composition. Atom effects have been subject to particular uncertainty.

Experimental data have been analyzed assuming diatomic dissociation to be describable as an elementary reaction by the rate law

$$-d(A_2)/dt = k_d(M)[(A_2) - (A)^2/K_{eq}], \quad (2)$$

where k_d is the over-all dissociation rate coefficient, M represents all species present, K_{eq} is the equilibrium constant for Reaction (1), and the relation,

$$k_d/k_r = K_{eq}, \quad (3)$$

is assumed. The over-all rate coefficient k_d has been assumed to be a linear function of composition; i.e.,

$$k_d = \sum_M X_M k_d^M, \quad (4)$$

where k_d^M is the rate coefficient due to A_2 - M collisions (for specific M) and X_M is the mole fraction of species M in the mixture. Equation (4) is the basis on which contributions of the various M to the over-all rate have been extracted.

Much discussion has arisen concerning the validity of Eqs. (2)–(4).^{1,2} In particular, the interpretation of the coefficients k_d^M as true chemical rate “constants,” i.e., functions of kinetic temperature only and thus independent of composition, departure from equilibrium, etc., and the consequent applicability of Eq. (3) have been seriously questioned. The experimental observation of induction periods for diatomic dissociation^{3,4} clearly indicates that the assumptions implicit in Eqs. (2)–(4) are not valid during the very early course of the reaction; nevertheless, they may be applicable during the “steady state” which follows the induction period. The degree of scatter usually present in dissociation rate data from shock-wave experiments has prevented satisfactory tests of the assumptions given above. In particular, the validity of Eq. (4) has not been subjected to experimental test.¹ It has been suggested that failure of these assumptions might account for discrepancies between results obtained in different laboratories.⁵

We have initiated a study of diatomic dissociation in shock waves using the laser-schlieren

technique developed by Kiefer and Lutz.⁶ This technique, in which the postshock density gradient is measured with high sensitivity and space/time resolution, has been used successfully to study vibrational relaxation in a variety of systems. In essence, it provides a time-resolved point measurement of the rate of an endothermic process behind the shock front. In a study of O_2 dissociation in mixtures with various rare-gas diluents,⁴ the postshock density gradient was observed to exhibit a highly characteristic local nonzero minimum immediately following the period of vibrational relaxation, at times which correlate well with the dissociation induction times observed by others.³ The density-gradient magnitude at the minimum of this “dip” was interpreted as a measure of the initial dissociation rate, i.e., the rate corresponding to conditions of vibrational equilibrium in the thermal sense but with negligible extent of dissociation. Rate coefficients thus determined exhibit a high degree of precision and provide a basis for testing one of the assumptions described above. In particular, analysis of data for mixtures of 2.5%, 5%, and 10% O_2 in Ar, Kr, Xe, and 1:1 He-Kr using Eq. (4) yields the same values for $k_d^{O_2}$ from each diluent to within a few percent over the temperature range 4500°–8000°K. This result strongly suggests that Eq. (4) is valid for initial dissociation rates in O_2 -rare gas mixtures of arbitrary composition.

In the present paper, we describe measurements in mixtures of H_2 with Ar and Xe diluents in the temperature range 3500°–8000°K. In addition to the determination of k_d^M for M =Ar, Xe, and H_2 from initial rate measurements, values of the hydrogen-atom coefficient, k_d^H , have been obtained by numerical integration of the measured density-gradient profiles through the reaction course. The data are again of high precision, and afford further tests of some of the features of diatomic dissociation which heretofore could only be assumed.

Experimental

The shock tube, associated equipment, and the procedure for measuring postshock density-gradient magnitudes have been described in detail previously.⁴ Briefly, the laser-schlieren technique involves measurement of the deflection of a 632.8-nm helium-neon laser beam as it passes through the shocked gas normal to the tube axis. Beam deflection, which is proportional to the axial density gradient in the shocked gas, is measured by a prism beam splitter-dual photomultiplier arrangement. During each experiment, photomultiplier-output voltage is re-

corded photographically from an oscilloscope trace. The characteristic features observed in the experiments with mixtures of H₂ in Ar and Xe are qualitatively similar to those described in the O₂-rare gas study,⁴ namely, an initial large "spike" in the signal corresponding to arrival of the shock front,⁶ a rapid decay to the minimum of the "dip," a slight rise, and the subsequent much slower decay during the bulk of the H₂ dissociation.

Shock waves were initiated by spontaneously bursting scribed brass diaphragms with hydrogen or helium. Shock velocities were measured using a series of five piezoelectric pressure gauges mounted in the shock-tube wall.⁴ These gauges and the associated electronic circuitry were designed to provide optimum reproducibility in the measurement of shock-wave arrival times, and the resulting precision in shock-velocity determination no doubt contributes to the high precision of the data presented below.

Commercial "extra dry" grade H₂, of 99.9% specified minimum purity, was passed through a copper coil immersed in liquid nitrogen prior to use. Argon, 99.99% specified minimum purity, supplied by National Cylinder Gas Co., was treated in a similar manner, with dry ice-acetone in place of liquid nitrogen. Research grade Xe, of 99.99% specified minimum purity from Air Products and Chemicals, Inc., was used without further treatment. Mixtures of 5.0%, 10.0%, and 20.0% H₂ in Ar, and 5.0%, 10.0%, and 20.2% H₂ in Xe were prepared in a stainless-steel tank using a Texas Instruments Model 145 precision pressure gauge, and were allowed to stand at least 16 h prior to use. Mixture compositions were checked mass spectrometrically. Prior to each experiment, the shock tube was pumped to a pressure below 5×10^{-5} torr, and had a combined leak and outgassing rate less than 5×10^{-4} torr/min. Initial tube-loading pressures were in the range 3–50 torr.

Analysis

The relation between the dissociation rate of a diatomic gas and the postshock density gradient associated with that rate, under conditions where the rate of recombination, i.e., the reverse of Reaction (1), is negligible, was derived in Ref. 4 [Eq. (9)]. Assuming a rate law of the form of Eq. (2) for conditions where recombination may not be negligible, an entirely analogous derivation yields the relation

$$k_d = M_0 \rho_0 U_s (d\rho/dx) (d\alpha/d\rho) / \rho^2 n_M \\ \times [(1-\alpha) - 4n_{A_2} \alpha^2 \rho / K_{eq} M_0]. \quad (5)$$

Here, M_0 is the average initial molecular weight of the gas, ρ_0 and ρ are pre- and postshock densities, respectively, U_s is the shock velocity, $d\rho/dx$ the density gradient, n_i the number of moles of species i per initial mole of total gas (superscript zero indicates initial value), and α , the degree of dissociation, is defined by

$$n_{A_2} = n_{A_2}^0 (1-\alpha).$$

If dissociation is assumed to proceed from a vibrational population distribution which is thermally equilibrated, $d\alpha/d\rho$, ρ , n_M , and the temperature T can be evaluated by appropriate solution of the Rankine-Hugoniot equations for any value of α . Thus, measurement of $d\rho/dx$ and knowledge of any one of the quantities α , ρ , or T permit the determination of k_d at any point in the course of dissociation.

In the present experiments, only the postshock density gradient is measured; i.e., no information concerning the postshock composition and/or thermodynamic state of the gas is obtained directly. We refer to the arguments presented in detail in Ref. 4 to support our interpretation of the postshock density-gradient magnitude at the minimum of the "dip" as a measure of the initial dissociation rate; i.e., the rate corresponding to conditions of vibrational equilibrium in the thermal sense with $\alpha=0$. With this interpretation, the density, and thus, through the Rankine-Hugoniot relations, the composition and temperature, can be obtained at subsequent points in the reaction course by numerical integration of the measured density-gradient profile from the minimum of the "dip." Then, by Eq. (5), the over-all rate coefficient k_d can be evaluated throughout the reaction course.

Results

Values of the initial over-all dissociation-rate coefficient determined by means of Eq. (5) from density gradient magnitudes measured at the minimum of the "dip" are shown in Figs. 1 and 2 for mixtures of 5%, 10%, and 20% H₂ in Ar and Xe, respectively. Postshock conditions for each experiment at $\alpha=0.0$ were obtained by programmed solution of the Rankine-Hugoniot equations on a Hewlett-Packard Model 9100B calculator. In these computations, harmonic oscillator functions were used to represent the vibrational enthalpy of H₂. Comparison with selected computer calculations using H₂ enthalpy data given in the JANAF Thermochemical Tables⁷ revealed differences of 1% or less in postshock temperature over the experimental

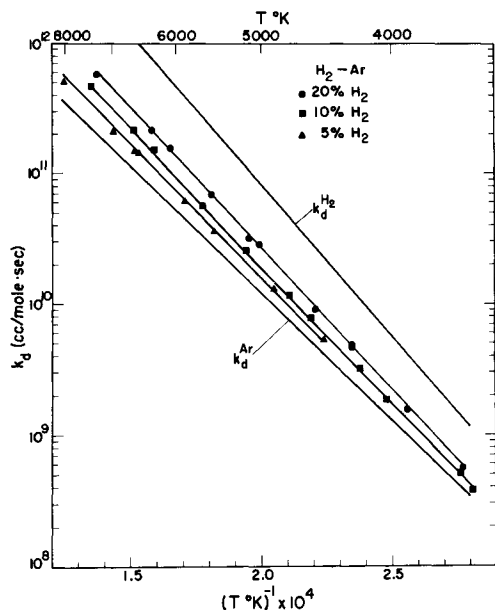


FIG. 1. Values of the initial over-all dissociation-rate coefficient k_d , obtained for mixtures of H_2 in Ar. The solid lines result from a least-squares fit of Eq. (4) to the data. The lines indicated for k_d^{Ar} and $k_d^{H_2}$ are given by Eqs. (7) and (8), respectively.

temperature range. The quantity $d\alpha/d\rho$ in Eq. (5) was approximated by the ratio $\Delta\alpha/\Delta\rho$, where $\Delta\rho$ is the density increment between solutions obtained at $\alpha=0.0$ and $\alpha=1\times 10^{-3}$.

The high precision of the data obtained in this manner is readily apparent in Figs. 1 and 2. The solid lines in these figures result from least-squares fits of Eq. (4) to the combined data for each diluent. In the fitting procedure, the rate coefficient for each collision partner M was represented by the Arrhenius expression

$$k_d^M = A_M \exp(-E_M/RT), \quad (6)$$

with A_M and E_M serving as adjustable parameters. The resulting values for k_d^M , $M=Ar$, Xe , and H_2 , are also shown, and are given by the expressions, with R in cal/mole-deg,

$$k_d^{Ar} = 9.35 \times 10^{13} \exp(-88\,900/RT) \quad \text{cc/mole-sec,} \quad (7)$$

$$k_d^{H_2} = 3.30 \times 10^{15} \exp(-105\,300/RT) \quad \text{cc/mole-sec,} \quad (8)$$

for the lines in Fig. 1, and

$$k_d^{Xe} = 8.96 \times 10^{13} \exp(-89\,600/RT) \quad \text{cc/mole-sec,} \quad (9)$$

$$k_d^{H_2} = 2.46 \times 10^{15} \exp(-103\,700/RT) \quad \text{cc/mole-sec,} \quad (10)$$

for the lines in Fig. 2. As seen in the figures, these values, combined according to Eq. (4), satisfactorily describe the data over the range of composition and temperature covered. The values given by Eqs. (8) and (10) differ by 15% or less throughout the experimental temperature range. Thus, as was found with O_2 -rare gas mixtures,⁴ the rate coefficient for the molecule as collision partner appears to be independent of the diluent gas, a finding which is consistent with and lends support to the validity of Eq. (4).

Records from some experiments were analyzed in further detail. The measured density-gradient profile was integrated numerically, using the trapezoidal rule from the point of the initial rate measurement to obtain the density at subsequent

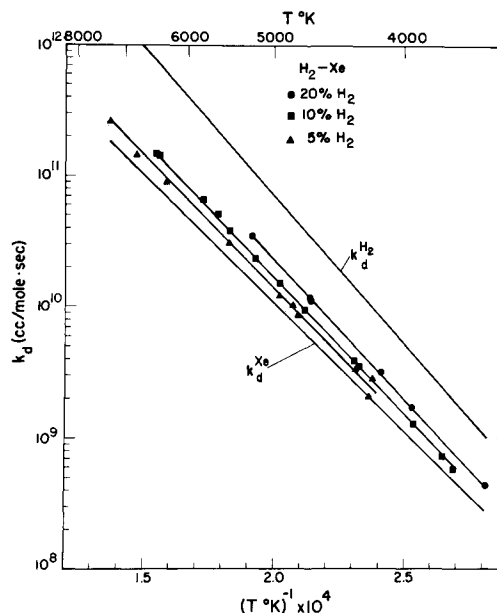


FIG. 2. Values of the initial over-all dissociation-rate coefficient k_d , obtained for mixtures of H_2 in Xe. The solid lines result from a least-squares fit of Eq. (4) to the data. The lines indicated for k_d^{Xe} and $k_d^{H_2}$ are given by Eqs. (9) and (10), respectively.

points in the reaction course. Through the Rankine-Hugoniot relations, the corresponding values of α , $d\alpha/d\rho$, and T were then determined, and k_d was evaluated from Eq. (5). The apparent hydrogen-atom coefficient, k_d^H , was then evaluated at each point, using Eq. (4) with Eqs. (7)–(10) as appropriate. Thus, for each experimental record so analyzed, values of k_d^H , covering a range of temperature and composition, were obtained. This analysis is basically the same type employed by Sutton⁸ and Hurle *et al.*⁹ To check for possible errors in the analysis, the quantity $4n_{H_2}^0\alpha^2\rho/(1-\alpha)M_0K_{eq}$, which increases from zero for no dissociation to unity at equilibrium, was evaluated for the final point analyzed in each experiment. The largest value so obtained was 0.97. For each experiment the early values of k_d^H (usually only 2 to 3 out of a total of approx. 20 to 50) corresponding to points at which the contribution of hydrogen atoms to the total rate is $<10\%$ were arbitrarily discarded. Likewise, late values (usually fewer than 5) corresponding to density gradients $<5\times10^{-6}$ g/cm⁴ for the Ar mixtures and $<8\times10^{-6}$ g/cm⁴ for the Xe mixtures were also discarded.

The data so obtained are far too numerous for graphical presentation. However, the values of k_d^H obtained within each experiment exhibit Arrhenius temperature dependence to a high degree. Therefore, the Arrhenius function,

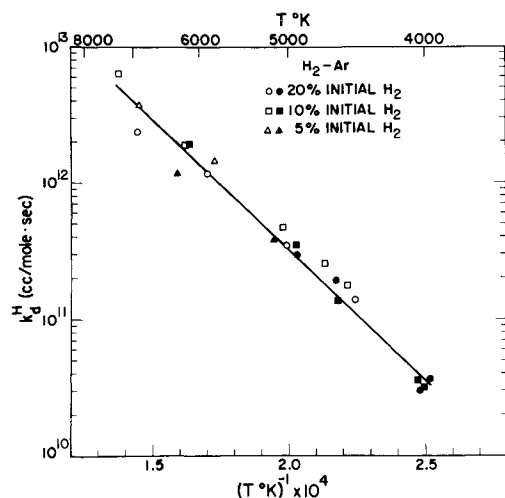


FIG. 3. Values of the hydrogen-atom coefficient for H_2 dissociation k_d^H , obtained from H_2 -Ar mixtures. The initial (open symbols) and final (filled symbols) points obtained in each experiment are shown (see text). The solid line is a least-squares fit to the points shown, and is given by Eq. (11).

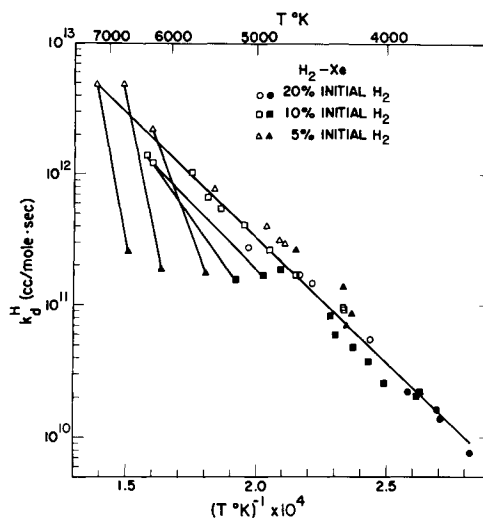


FIG. 4. Values of the hydrogen-atom coefficient for H_2 dissociation k_d^H , obtained from H_2 -Xe mixtures. The initial (open symbols) and final (filled symbols) points obtained in each experiment are shown (see text). The short-line segments connect initial and final points for the highest temperature data. The solid line extending through the entire experimental temperature range was obtained from the H_2 -Ar mixture data (see Fig. 3 and text), and is given by Eq. (11).

Eq. (6) with $M=H$, was fitted to the data for each experiment by the method of least squares. The initial (open symbols) and final (filled symbols) points of the resulting line segments for each experiment are shown in Figs. 3 and 4 for the mixtures of H_2 with Ar and Xe, respectively. It is apparent from these figures that, with few exceptions, initial and final points are indistinguishable, and the magnitudes are independent of composition. Data from the five experiments shown in Fig. 4 for which the initial temperature exceeds $6000^\circ K$, and for which the initial and final points are joined by line segments, appear to deviate from these trends. While these effects may indeed be real, a possible explanation is the following. Considerably lower shock-wave velocities are required to achieve a given post-shock temperature in the mixtures of H_2 with Xe than in those with Ar, resulting in a proportionately broader signal "spike" corresponding to shock-front arrival at the laser-schlieren observation point.⁶ Consequently, at high temperature, the "dip" is less well resolved in the Xe-mixture experiments. While such reduced resolution may affect the initial rate measurements

only slightly, any error in assignment of the time of this measurement point will accumulate in the numerical integration of the measured density gradient, with resulting errors in the density and composition assigned to subsequent measurement points. Such errors could account for the behavior of the data from the five highest temperature experiments with the Xe mixtures.

The solid line shown in Fig. 3 results from a least-squares fit of the Arrhenius expression to the data displayed there, and is given by

$$k_d^H = 2.12 \times 10^{15} \exp(-87\,200/RT) \quad \text{cc/mole-sec, (11)}$$

with R in cal/mole-deg. The solid line in Fig. 4 extending through the entire experimental temperature range is also given by Eq. (11), and, with the few exceptions noted above, satisfactorily describes the values of k_d^H obtained from the H_2 -Xe mixtures also. Thus, for mixtures of H_2 with Ar and Xe, the dissociation-rate coefficient for hydrogen atom as collision partner, as well as that for the parent molecule, is found to be independent of the diluent gas.

Discussion

The values determined in this study for the dissociation-rate coefficient of H_2 with various collision partners, k_d^M , $M = \text{Ar}$, Xe , H_2 , and H , are summarized in Fig. 5. The line shown for $k_d^{H_2}$ is that determined from the H_2 -Ar mixture data, as given by Eq. (7). The dissociation of H_2 in mixtures with Ar has previously been studied by several investigators.⁸⁻¹³ Rink¹¹ also studied the effect of Kr and Xe diluents, while Gardiner and Kistiakowsky¹⁴ studied H_2 -Xe mixtures only. The values shown in Fig. 5 are in general agreement with the results of these studies. For example, the present values of both k_d^{Ar} and $k_d^{H_2}$ are within a factor of ~ 2 of those reported in Refs. 8, 10, 11, 12, and 13, in the respective ranges of common temperature. The values of k_d^{Xe} reported by Rink¹¹ and by Gardiner and Kistiakowsky¹⁴ are both 2 to 3 times larger than those shown in Fig. 5. The present determination of k_d^H is in similar agreement with those of Refs. 8, 10, 12, and 14. Agreement with the values of Hurle *et al.*⁹ is good below 4000°K, but the unusual temperature dependence reported by these authors is not supported by this work. At 7000°K, their value lies nearly an order of magnitude below the present result. Although the results of Hurle *et al.*⁹ for k_d^M , $M = \text{Ar}$, H_2 , and H , were obtained using a rather sophisticated scheme of data reduction, they

form a disparate set in comparison with the bulk of reported data.

An interesting feature of the present results is the ~ 15 kcal/mole difference in apparent activation energies between $k_d^{H_2}$ and k_d^M , $M = \text{Ar}$, Xe , and H . This difference is well outside the statistical uncertainties in the determination of these quantities (the largest least-squares standard deviation in any E_M is 4.9 kcal/mole). Systematic errors in the experimental measurements could of course account for this difference, but, lacking any indication of such errors, we suggest that the effect is real. Previous measurements of H_2 -dissociation rates have lacked sufficient precision to detect a difference of this magnitude. The difference may be associated with the additional degrees of freedom; i.e., rotation and vibration, available in the H_2 molecule as a collision partner. The effects of internal energy transfer in molecule-molecule collisions on diatomic dissociation rates have been investigated by different approaches in recent theoretical treatments.^{15,16}

Shui and Appleton¹⁷ have recently employed the modified phase-space theory of Keck¹⁸ to calculate dissociation and recombination rates for H_2 with various collision partners. Their calculated values for k_d^{Ar} and k_d^{Xe} are in remarkable agreement with the present results,

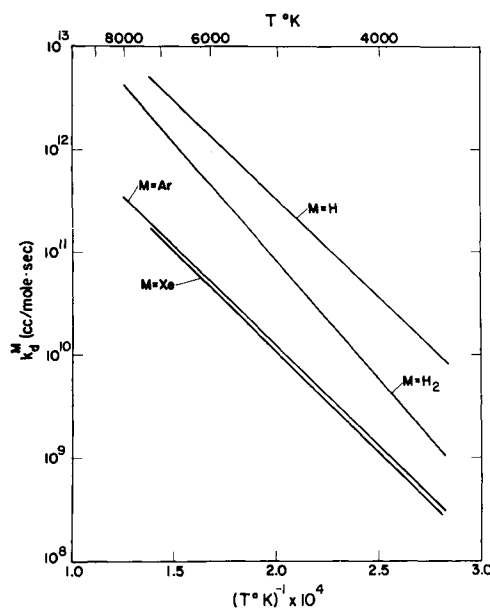


FIG. 5. Values of the dissociation-rate coefficient for H_2 with various collision partners k_d^M , determined in this study. The values shown for k_d^{Ar} are given by Eq. (7), those for $k_d^{H_2}$ by Eq. (8), those for k_d^{Xe} by Eq. (9), and those for k_d^H by Eq. (11).

differing from the values shown in Fig. 5 by less than 25% over the temperature range 4000°–7000°K. The agreement for $k_d^{\text{H}_2}$ is less satisfactory, with the theoretical values lying below those of Fig. 5 by factors of 3 to 5, depending on the temperature.

The results of the present work, and those of the earlier O₂-rare gas study, constitute the strongest evidence yet reported supporting the validity of the traditional assumptions concerning diatomic dissociation. This evidence can be stated as follows (the points below are not necessarily independent, and are separated only for ease of enumeration):

1. For the systems studied, the linear or additive mixture formula, Eq. (4), is found to hold for the initial dissociation rate over a range of diatomic molecule-rare gas compositions containing up to 20% of the molecule. Further, the apparent molecule coefficient is independent of the diluent gas.

2. For the mixtures of H₂ with Ar and Xe, Eq. (4) is also found to hold in the presence of hydrogen atoms; i.e., the same hydrogen-atom coefficient is obtained from mixtures of different initial composition and diluent gas.

3. With few possible exceptions, the hydrogen-atom coefficients obtained are independent of both the degree of dissociation and the extent of departure from equilibrium.

To summarize the above points, diatomic dissociation-rate data of high precision have been analyzed within the framework of Eqs. (2)–(4) to yield results which are wholly consistent, both among themselves and with the interpretation of the various k_d^{M} , as true chemical rate “constants.”

Acknowledgments

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COMMENTS

H. Teitelbaum, *Dept. of Chemistry, University of Toronto, Toronto, Ontario, Canada*. I think it should be borne in mind that there is an alternative interpretation of the observed signal shape. In view of the fact that the signal is proportional to k_d , you may be measuring directly the time dependence of k_d . At the “dip,” vibrational relaxation is essentially complete. But, as far as dissociation is concerned, k_d may not be con-

stant. Instead, it may be increasing to its constant value near the maximum—i.e., the induction zone may not be complete at the dip. The choice of the dip for measuring k_d may be somewhat uncertain if, indeed, the process being measured is a nonequilibrium one. Unfortunately, at present, there is no way of distinguishing between this interpretation and the one given in your paper.

Authors' Reply. We refer to the arguments summarized in the paper, and presented in detail in Ref. 4 of the paper, to support our interpretation of the dip. We note that, since the relative change in signal between the dip and the subsequent maximum is small (see Ref. 4 for examples), the alternative interpretation offered above would alter the magnitude of the initial rate measurements only slightly. However, in most cases, the integrated density change from the dip to the maximum corresponds to more than 5% dissociation, so that the initial rate assumption would not be valid at this point. Further, and most significantly, the self-consistency of the results obtained for k_d^H , using our interpretation, shows that the behavior of k_d beyond the dip can be attributed solely to the effects of changing temperature and composition, in terms of true chemical rate constants, k_d^M .

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John P. Appleton, Mechanical Engineering Dept., Massachusetts Institute of Technology, Cambridge, Mass. I would like to report some recent extensions of our modified-phase space-theory calculations, as applied to the case of the dissociation of H_2 , with atomic hydrogen as the collision partner. The theoretical approach is essentially the same as that which has been described in our previous publications (see, for example, Shui, Appleton, and Keck¹ and Shui²), except that the semi-empirical Porter-Karplus potential-energy surface³ has been used to de-

scribe the interaction of the three hydrogen atoms. The classical transition rates used in the theory are therefore based on the results of Monte-Carlo trajectory calculations carried out using this surface.

Our theoretical results for k_d^H at 10^4 , 5×10^3 , and 3×10^3 °K are 2×10^{-11} , 5×10^{-13} , and 8×10^{-16} cm³/molecule-sec, respectively. These theoretical values of k_d^H are in excellent agreement with the majority of the experimental measurements made over the past decade (including the present work of the authors, and the recent work of Hurle *et al.*⁴). I feel that this substantiates the general observation that hydrogen atoms are considerably more efficient as collision partners in promoting dissociation than are the noble-gas atoms or hydrogen molecules. The theoretical calculations do not support the extremely low values for the apparent activation energy obtained by Hurle, Jones, and Rosenfeld,⁴ at temperatures greater than about 4×10^3 °K.

More-complete details of the theory and comparison with experimental results will be published elsewhere in the near future.

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