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LOS ALAMOS SCIENTIFIC LABORATORY
OF THE UNIVERSITY OF CALIFORNIA ○ LOS ALAMOS NEW MEXICO

CALCULATIONS OF THE COEFFICIENTS OF VISCOSITY, DIFFUSION, AND THERMAL CONDUCTIVITY FOR DISSOCIATING HYDROGEN FOR A RANGE OF TEMPERATURES AND PRESSURES

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CALCULATIONS OF THE COEFFICIENTS OF VISCOSITY, DIFFUSION, AND THERMAL CONDUCTIVITY FOR DISSOCIATING HYDROGEN FOR A RANGE OF TEMPERATURES AND PRESSURES

by

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ABSTRACT

The coefficient of viscosity and the coefficient of thermal conductivity for dissociating hydrogen gas has been computed for the temperature range from 1500°K to 5000°K and for the pressures of 0.1, 0.5, 1, 2, 10, 50, and 100 atmospheres. The coefficient of diffusion in a binary mixture of the $H\text{-}H_2$ system and the coefficient of self-diffusion for H atoms and H_2 molecules have been computed for the same set of conditions.

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Appreciation is also expressed to Mrs. Beth Kennedy for the typing of the original manuscript.

INTRODUCTION

Coefficient of Viscosity

Dissociated hydrogen gas consists of a mixture of H atoms and H_2 molecules, so it can be considered as a binary mixture in which one gas has the properties of the diatomic gas and the second gas has the properties of the monatomic gas. In this work the coefficient of viscosity for the corresponding composition of the mixture at any given temperature and pressure has been calculated using the formula for a binary mixture of gases given in Molecular Theory of Gases and Liquids (MTGL).[1]

It is necessary to have the coefficients of viscosity corresponding to the H_2-H_2 interaction, to the H-H interaction, and to the H-H_2 interaction in order to calculate the coefficient of viscosity of the mixture.

The H_2-H_2 interaction was assumed to obey the modified Buckingham (exp-6) potential. The method of Hirschfelder and Eliason[2] has been applied to the two potential energy curves $\left({}^3\Sigma_u \text{ and } {}^1\Sigma_g\right)$ for the H-H interactions, and the weighted average of the effective rigid-sphere collision diameters so obtained was then used to calculate a coefficient of viscosity corresponding to the H-H interaction. The interaction energy of the H-H_2 system was taken to be those values as computed by Margenau[3] for two orientations of the H atom approaching the H_2 molecule, parallel ($\parallel$) and perpendicular ($\perp$) to the H-H molecular axis. The weighted averages of the parameters used to fit these two potential curves to Lennard-Jones (12-6) potential curves were then used as the parameters $\left(\sigma_{12}, \epsilon_{12}\right)$ for an "average" Lennard-Jones (12-6) potential function. These "average" Lennard-Jones (12-6) potential parameters were then used in the evaluation of the necessary collision integrals in the computation of the coefficient of viscosity.

Coefficients of Diffusion

In MTGL, the coefficient of diffusion in a binary mixture and the coefficients of self-diffusion have been shown to be functions of the collision integrals and cross sections. Therefore, if one decides to utilize certain interaction potentials for the viscosity calculations as outlined above, one can obtain diffusion coefficients consistent with the chosen molecular interactions.

The coefficient of diffusion in a binary mixture was computed using the formula given in MTGL and the potential parameters $\left(\sigma_{12}, \epsilon_{12}\right)$ for an "average" Lennard-Jones (12-6) potential which was obtained as outlined above.

The coefficient of self-diffusion for the H_2-H_2 system was computed using the formula given by Mason and Rice[4] for a system that obeys the modified Buckingham (exp-6) potential.

The coefficient of self-diffusion for the H-H system was computed from the formula given in MTGL for a system obeying the rigid-sphere type of potential. The effective rigid-sphere collision diameter for the H-H system was obtained by the method of Hirschfelder and Eliason[2] as applied to the two potential energy curves $\left({}^3\Sigma_u \text{ and } {}^1\Sigma_g\right)$ for the H-H interactions.

Coefficient of Thermal Conductivity

For the calculation of the coefficient of thermal conductivity of dissociating hydrogen it was treated as a reacting gas mixture. The analysis used for this system was a combination of the methods given by Hirschfelder[5] and Butler and Brokaw.[6]

Following the procedure of Butler and Brokaw for a reacting gas mixture, it is first necessary to compute the coefficient of thermal conductivity for the "frozen" mixture. This "frozen" mixture is a binary mixture of H atoms and H_2 molecules and can be considered a mixture of polyatomic gases.

Hirschfelder[7] has given a method of computing the thermal conductivity of a polyatomic gas mixture and his procedure was used here. In this method it is necessary to have the thermal conductivity of the gas mixture which the mixture would possess if the gases had no internal degrees of freedom. This latter hypothetical thermal conductivity will be called the thermal conductivity of the monatomic mixture. It is obtained from the mixing formula for binary monatomic mixtures as given in MTGL, and involves the three coefficients of thermal conductivity corresponding to the thermal conductivities of monatomic gases which have molecular interactions corresponding to the interactions evidenced by H_2-H_2, H-H, and H-H_2. These three coefficients of thermal conductivity are obtained from the previously computed viscosities and the relationship between viscosity and thermal conductivity for monatomic gases as given in MTGL.

After obtaining this thermal conductivity of the monatomic mixture as prescribed above, the thermal conductivity of the polyatomic gas mixture is obtained by applying the Eucken-type correction as given by Hirschfelder.[7]

Utilizing this coefficient of thermal conductivity for the polyatomic gas mixture as the thermal conductivity of the "frozen" mixture, we next apply the correction as given by Butler and Brokaw[6] and get the coefficient of thermal conductivity of the reacting mixture.

METHOD AND RESULTS

Coefficient of Viscosity

The coefficient of viscosity of a binary mixture of monatomic gases as expressed in MTGL and utilized in this work is:

$$\frac{1}{\eta_{mix}} = \frac{X_\eta + Y_\eta}{1 + Z_\eta}, \tag{1}$$

$$X_\eta = \frac{x_1^2}{\eta_1} + \frac{2x_1x_2}{\eta_{12}} + \frac{x_2^2}{\eta_2}, \tag{2}$$

$$Y_\eta = \frac{3}{5}A^*_{12}\left\{\frac{x_1^2}{\eta_1}\left(\frac{M_1}{M_2}\right) + \frac{2x_1x_2}{\eta_{12}}\left(\frac{(M_1 + M_2)^2}{4M_1M_2}\right)\left(\frac{\eta_{12}^2}{\eta_1\eta_2}\right) + \frac{x_2^2}{\eta_2}\left(\frac{M_2}{M_1}\right)\right\}, \tag{3}$$

$$Z_\eta = \frac{3}{5}A^*_{12}\left\{x_1^2\left(\frac{M_1}{M_2}\right) + 2x_1x_2\left[\left(\frac{(M_1 + M_2)^2}{4M_1M_2}\right)\left(\frac{\eta_{12}}{\eta_1} + \frac{\eta_{12}}{\eta_2}\right) - 1\right] + x_2^2\left(\frac{M_2}{M_1}\right)\right\}, \tag{4}$$

where x_1, x_2 = mole fractions of H and H_2, respectively,

M_1, M_2 = molecular weights of H and H_2, respectively,

A^*_{12} = a function of kT/ϵ_{12}, defined in Equation (8.2-15) of MTGL,

η_1, η_2 = coefficients of viscosity of H and H_2, respectively,

η_{12} = coefficient of viscosity of a hypothetical gas with molecular interactions characterized by Lennard-Jones (12-6) potential parameters σ_{12} and ϵ_{12}. See MTGL.

η_{mix} = coefficient of viscosity of the mixture.

Equation (1) was used to evaluate the coefficient of viscosity, η_{mix}, of the mixture resulting from hydrogen dissociating at any given temperature and pressure.

The mole fractions of the species present in the dissociated hydrogen at any given temperature and pressure were obtained by solution of the hydrogen dissociation equilibrium, $H_2(g) \rightleftharpoons 2H(g)$. The thermodynamic data used to solve this equilibrium were taken from the National Bureau of Standards Series III Circular.[8] Details of the method of solution are given in Appendix A. The results of these solutions are given in Table A-2 in Appendix A.

The coefficient of viscosity of pure H_2 gas was computed using the modified Buckingham (exp-6) potential[9] to describe the intermolecular potential. This potential is expressed as

$$\varphi(r) = \frac{\epsilon}{1 - 6/\alpha}\left[\frac{6}{\alpha}\, e^{\alpha\left(1 - r/r_m\right)} - \left(\frac{r_m}{r}\right)^6\right], \tag{5}$$

where $\varphi(r)$ = the potential energy of the two molecules at a separation distance r,

ϵ = the depth of the potential minimum,

r_m = the position of the minimum,

α = a parameter which is a measure of the steepness of the repulsion energy.

Evaluation of the necessary constants in Equation (5) from available experimental data for hydrogen has been made by Mason and Rice.[4] These authors have established that the use of this interaction potential function gives better agreement between calculated and experimental viscosities of hydrogen in the temperature range of about 320°K to about 1100°K than the Lennard-Jones (12-6) potential function.

The constants for Equation (5) appropriate to hydrogen as given by Mason and Rice are:

$$\alpha = 14.0, \tag{6}$$

$$r_m = 3.337\ \text{Å}, \tag{7}$$

$$\epsilon/k = 37.3\text{°K}. \tag{8}$$

In the third approximation, the viscosity of hydrogen (undissociated) is then expressed as

$$(9) \qquad \left[\eta_2\right]_3 \times 10^7 = \frac{266.93(MT)^{1/2}\, f_\eta^{(3)}(\alpha, T^*)}{r_m^2\, \Omega^{(2,2)*}(\alpha, T^*)} ,$$

where

$\left[\eta_2\right]_3$ = the coefficient of viscosity in gm/cm-sec,

M = the molecular weight,

r_m = position of minimum in angstroms,

$\Omega^{(2,2)*}(\alpha, T^*)$ and $f_\eta^{(3)}(\alpha, T^*)$ = dimensionless functions which are given in the references.[4,9]

Equation (9) was used to obtain the coefficient of viscosity of hydrogen $\left(H_2\right)$ over the temperature interval of interest.

The coefficient of viscosity of a gas with intermolecular interactions corresponding to the H-H interactions was calculated using the estimation method of Hirschfelder and Eliason[2] as applied directly to the potential energy curves for H-H interaction.

As two hydrogen atoms approach one another they may interact in accordance with either of two potential energy curves representing two different states, the $^1\Sigma_g$ and $^3\Sigma_u$ states. These potential energy curves have been established over a wide range of separations by a combination of theoretical treatments and spectroscopic experimental data for normal $H_2\left(^1\Sigma_g\right)$. These potential curves are shown in Figure 1 and have been generated here by the data given in References 10-13. These data and the respective sources are also tabulated in Appendix B.

The method of Hirschfelder and Eliason of obtaining an effective rigid-sphere collision diameter for two particles interacting has been amply

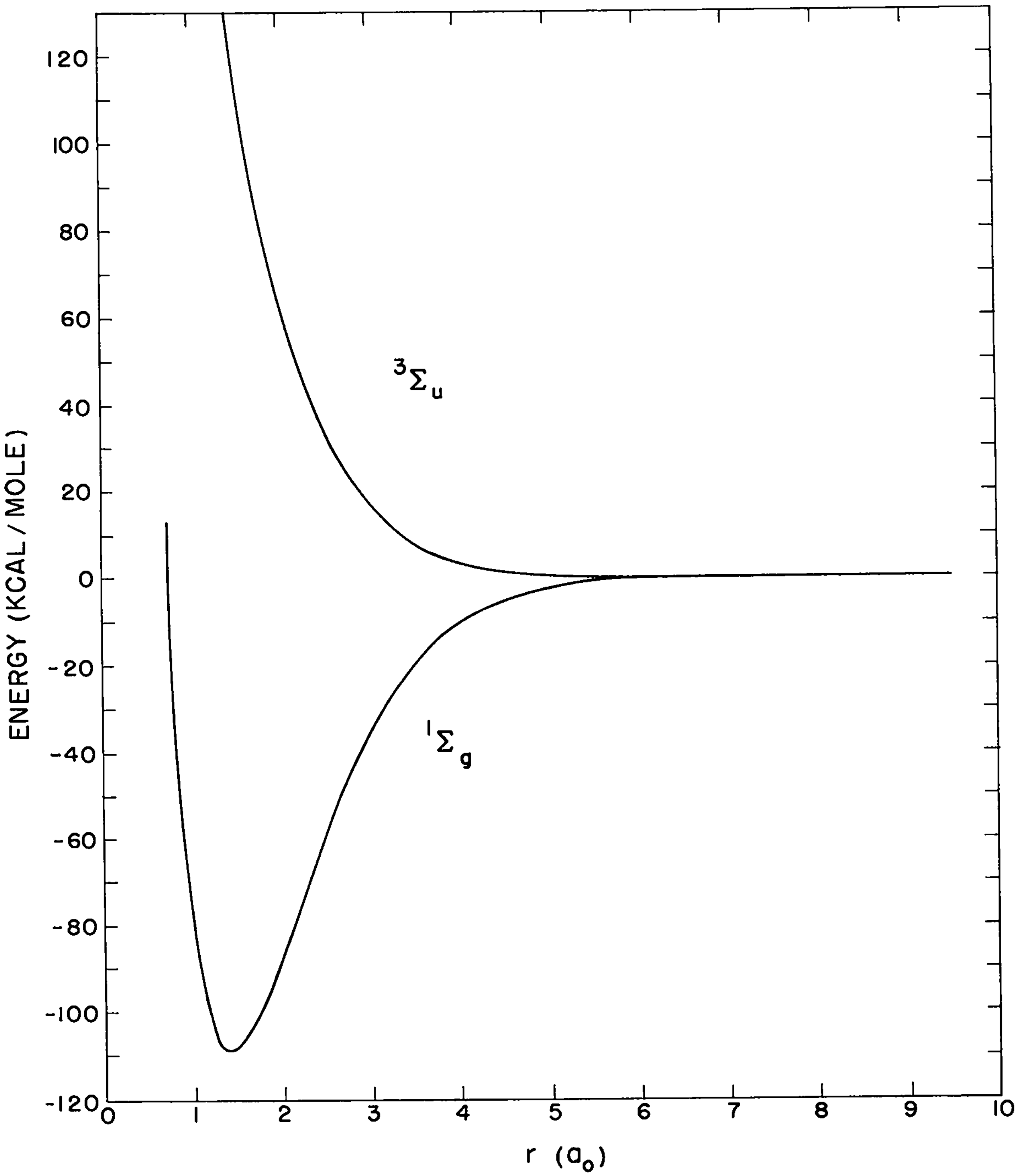

Figure 1 Energy of interaction of two 1s hydrogen atoms as a function of internuclear separation.

demonstrated by those authors for certain inverse-power potentials. The $^3\Sigma_u$ potential curve of H_2 generally follows the shape of an inverse-power repulsive potential, $\varphi(r) = a/r^n$, and the portion of the $^1\Sigma_g$ potential curve to the right of the potential minimum is, in general, in the shape of an inverse-power attractive potential, $\varphi(r) = -b/r^n$. From this consideration of these curves it seems that the Hirschfelder-Eliason method is applicable.

In this method one supposes that for transport processes the effective collision diameter would correspond to a separation such that the intermolecular potential energy is comparable to the average relative kinetic energy, RT. The computation of this effective rigid-sphere collision diameter involves knowing the parameter, n, which gives the best inverse-power type $[\varphi(r) = a/r^n$ or $-b/r^n]$ of fit to the appropriate potential energy curve in the range where the potential energy is comparable to the average relative kinetic energy. This is obtained by finding $d\varphi/dr$ when $\varphi(r) = RT$; and then the effective $n = -(r/\varphi)(d\varphi/dr)$. Knowing this best effective n, one then obtains from the tables provided by Hirschfelder and Eliason (for both inverse-power attractive and repulsive potentials) a factor θ_{visc}. Then using the appropriate potential energy curve, one finds the value of r for which $\varphi(r) = \theta_{visc} RT$. This value of r is the effective collision diameter, σ, which, when substituted into Equation (13), will give the correct coefficient of viscosity appropriate to the corresponding collision considered.

The values of RT, n, and θ_{visc} used in this work are listed in Table 1 for both the $^3\Sigma_u$ and $^1\Sigma_g$ potential curves. In practice, exploded versions of Figure 1 were used to obtain these parameters. The n's are given to the nearest integer. Included in this table are the σ's determined for each potential curve and temperature and the effective weighted average, σ^2.

It should be noted that only certain portions of the two potential curves were actually used in these determinations, since the method employs only

Table 1

Parameters Used in the Hirschfelder and Eliason Analysis for $[\eta_1]_1$

T (°K)	RT (kcal/mole)	$^3\Sigma_u$ State			$^1\Sigma_g$ State			$\sigma^2_{\mathrm{av\ rig\ sph}}$ $(\mathrm{\AA}^2)$ (weighted av)
		n	θ_{visc}	$\sigma_{\mathrm{rig\ sph}}$ (Å)	n	θ_{visc}	$\sigma_{\mathrm{rig\ sph}}$ (Å)	
1000	1987.19	11	0.838	2.196	6	0.5831	2.963	5.812
1500	2980.79	12	0.831	2.106	6	0.5831	2.801	5.288
2000	3974.38	11	0.838	2.056	6	0.5831	2.675	4.958
2500	4967.98	9	0.854	2.008	6	0.5831	2.580	4.688
3000	5961.57	10	0.846	1.969	6	0.5831	2.507	4.481
3200	6359.01	9	0.854	1.955	6	0.5831	2.480	4.404
3500	6955.17	8	0.863	1.934	6	0.5831	2.447	4.303
3700	7352.60	8	0.863	1.921	6	0.5831	2.425	4.238
4000	7948.76	7	0.891	1.894	6	0.5831	2.394	4.125
4200	8346.20	7	0.891	1.884	6	0.5831	2.376	4.073
4500	8942.36	7	0.891	1.868	6	0.5831	2.350	3.997
5000	9935.95	7	0.891	1.826	6	0.5831	2.311	3.835

those portions of the curves corresponding to potential energy ranges comparable with RT. The ranges of the interatomic separation corresponding to these potential energy intervals are about 4 to 6 a_o (Bohr orbitals) and 3.5 to 6 a_o for the $^1\Sigma_g$ and $^3\Sigma_u$ states, respectively. The potential energies of these two states over these ranges of interatomic separation have been computed by Dalgarno and Lynn.[11] See Appendix B.

Another significant feature considered in these computations is that the a priori probability of interaction in accordance with the $^3\Sigma_u$ curve is 3/4, whereas for the $^1\Sigma_g$ curve it is 1/4; therefore, to obtain an over-all value for $\sigma_{\text{rig sph}}$ to compute a corresponding over-all effective viscosity, η, these two possible interactions must be weighted properly.

Konowalow, Hirschfelder, and Linder,[14] and Mason, Vanderslice, and Yos[15] have shown that when molecules or atoms interact in accordance with more than one potential energy function and if a given collision has the a priori probability, p_i, of occurring in accordance with the ith potential energy, $\Phi_i(r)$, then the collision cross sections, Q_i, for any type of process are additive such that

$$Q = \sum_i p_i Q_i \quad . \tag{10}$$

Since the collision cross sections are proportional to the collision diameters squared, σ_i^2, it follows that the mean value of the collision diameter is given by

$$\sigma^2 = \sum_i p_i \sigma_i^2 \quad . \tag{11}$$

Accordingly, for the two potential curves for the H-H interaction, one obtains

$$\sigma^2_{\text{av rig sph}} = \frac{3}{4}\sigma_3^2 + \frac{1}{4}\sigma_1^2 \quad , \tag{12}$$

where σ_3 = effective rigid-sphere collision diameter for the ${}^3\Sigma_u$ state,

σ_1 = effective rigid-sphere collision diameter for the ${}^1\Sigma_g$ state.

Following the procedure outlined above, one obtains the effective weighted average rigid-sphere collision diameter for the H-H interaction at a chosen temperature. Upon inserting this quantity into the following equation[1] the viscosity of a gas obeying the interactions of the H-H system are obtained.

$$[\eta_1]_1 \times 10^7 = 266.93 \frac{\sqrt{MT}}{\sigma^2_{\text{av rig sph}}} \text{ gm/cm-sec} . \tag{13}$$

The coefficient of viscosity of a gas with particle interactions corresponding to the H-H_2 interactions was calculated using an "average" Lennard-Jones (12-6) potential function.

Two limiting cases arise for the interaction of a hydrogen atom and a hydrogen molecule. The atom may approach the molecule perpendicular to the line of the nuclei ($\perp$) or the approach may be parallel to the line of the nuclei ($\parallel$). A quantum mechanical calculation of the energy as a function of distance of separation for these two cases has been made by Margenau.[3] These values are also listed in MTGL. A plot of these calculated potential energy values versus internuclear distance was made for the two directions of approach ($\perp$ and $\parallel$), and the necessary parameters to fit these curves to a Lennard-Jones (12-6) potential function were taken from the plot. See Figure 2. The values obtained are:

$$\epsilon/k(\perp) \quad 37.9°\text{K}, \qquad \sigma_\perp = 2.63\text{Å}, \tag{14}$$

$$\epsilon/k(\parallel) \quad 23.4°\text{K}, \qquad \sigma_\parallel = 3.00\text{Å}. \tag{15}$$

In order to obtain a single "average" potential function for the H-H_2 system, and from a very general consideration of the geometry of the system,

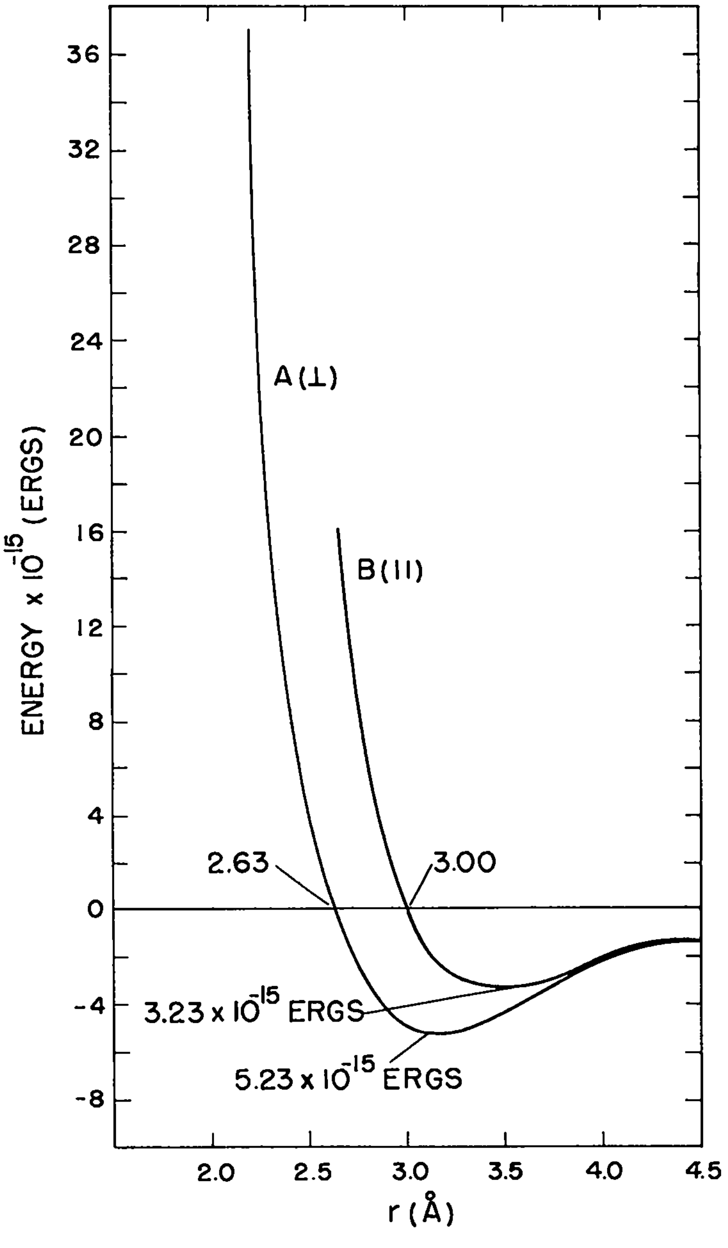

Figure 2 Potential of interaction between a hydrogen atom and a hydrogen molecule for perpendicular and parallel orientations.

the two sets of parameters corresponding to the above two potential curves were averaged by weighting the perpendicular (⊥) approach two times and the parallel (||) approach one time. Using these weights, an arithmetic average for the σ's and a geometric average for the ε/k's was made.[1]

$$\sigma_{12\ av} = \frac{2\sigma_{\perp} + \sigma_{\parallel}}{3} = 2.75\mathring{A}\ , \tag{16}$$

$$\left(\epsilon_{12}/k\right)_{av} = \left(\frac{\epsilon_{\perp}}{k}\,\frac{\epsilon_{\perp}}{k}\,\frac{\epsilon_{\parallel}}{k}\right)^{1/3} = 32.27°K. \tag{17}$$

Use was then made of these numbers as parameters for an "average" Lennard-Jones (12-6) potential function, which was applied to Equation (18) to compute the viscosity corresponding to the H-H_2 interaction:

$$\left[\eta_{12}\right]_1 \times 10^7 = \frac{266.93\sqrt{2M_1M_2T/\left(M_1 + M_2\right)}}{\sigma_{12}^2\,\Omega_{12}^{(2,2)*}\left(T_{12}^*\right)}\ \text{gm/cm-sec}, \tag{18}$$

where T = temperature in °K,

T_{12}^* = kT/ϵ_{12} = reduced temperature,

M_1, M_2 = molecular weights of H and H_2 respectively,

$\sigma_{12}, \epsilon_{12}/k$ = parameters of the potential function; 2.75A, and 32.27°K, respectively,

$\Omega_{12}^{(2,2)*}\left(T_{12}^*\right)$ = parameter as defined by MTGL.

The three coefficients of viscosity, η_2, η_1, and η_{12}, corresponding to the three interactions, H_2-H_2, H-H, and H-H_2, respectively, were calculated using the methods described above. These calculations were made for a number of temperatures from 1000°K to 5000°K. The results obtained are listed in Table 2.

The coefficient of viscosity of the dissociated hydrogen mixture was calculated using Equation (1). The appropriate values of the coefficients of

Table 2

Coefficient of Viscosity for Interactions in Dissociating Hydrogen System

	$[\eta_2]_3 \times 10^7$ gm/cm-sec	$[\eta_1]_1 \times 10^7$ gm/cm-sec	$[\eta_{12}]_1 \times 10^7$ gm/cm-sec
T (°K)	H_2-H_2	H-H	H-H_2
1000	2013	1458	1855
1500	2643	1963	2409
2000	3207	2417	2902
2500	3722	2858	3351
3000	4202	3276	3769
3200	4387	3443	3934
3500	4655	3685	4150
3700	4829	3847	4291
4000	5096	4109	4503
4200	5270	4264	4642
4500	5523	4498	4850
5000	5926	4942	5192
Method:	Modified Buckingham (exp-6) Potential	Hirschfelder and Eliason	Lennard-Jones (12-6) Potential

viscosity were taken from Table 2, and the appropriate values for the mole fractions of the species in the mixture were taken from Table A-2. Because of the pressure dependency of the dissociation of hydrogen, the resulting coefficients of viscosity for partially dissociated hydrogen show a pressure dependency. These coefficients of viscosity of the mixture are listed in Table 3 for the appropriate temperatures and pressures. Figure 3 is a plot of these coefficients of viscosity versus temperature for various pressures.

Coefficients of Diffusion

The formula for the coefficient of diffusion of a binary mixture as given in MTGL and used here is:

$$[D_{12}]_1 = 2.628 \times 10^{-3} \frac{\sqrt{T^3(M_1 + M_2)/2M_1M_2}}{p\sigma_{12}^2 \Omega_{12}^{(1,1)*}\left(T_{12}^*\right)}, \tag{19}$$

where D_{12} = diffusion coefficient in cm^2/sec,
p = pressure in atmospheres,
T = temperature in °K,
$T_{12}^* = kT/\epsilon_{12}$,
M_1, M_2 = molecular weights of H and H_2, respectively,
$\sigma_{12}, \epsilon_{12}/k$ = intermolecular potential energy parameters characteristic of the H-H_2 interaction in Å and °K, respectively.

The parameters σ_{12}, and ϵ_{12}, which were used in conjunction with Equation (19) to obtain the $[D_{12}]_1$ were the parameters for the "average" Lennard-Jones (12-6) potential function discussed in the section on viscosity. These values are:

$$\sigma_{12\ av} = 2.75\text{Å}, \tag{20}$$

$$\left(\epsilon_{12}/k\right)_{av} = 32.27°K. \tag{21}$$

Table 3

Coefficient of Viscosity of Dissociating Hydrogen

	$\eta_{mix} \times 10^7$ gm/cm-sec							
T (°K)	0.1 atm	0.2 atm	0.5 atm	1 atm	2 atm	10 atm	50 atm	100 atm
1500	2643	2643	2643	2643	2643	2643	2643	2643
2000	3205	3206	3206	3206	3206	3207	3207	3207
2500	3695	3703	3711	3714	3717	3720	3721	3722
3000	3983	4049	4108	4137	4157	4182	4195	4196
3200	3995	4103	4208	4263	4301	4350	4371	4376
3500	3962	4089	4258	4365	4448	4564	4615	4627
3700	3997	4094	4259	4388	4502	4679	4763	4782
4000	4164	4210	4314	4426	4554	4815	4966	5004
4200	4293	4320	4387	4471	4585	4876	5079	5133
4500	4510	4521	4553	4600	4675	4949	5218	5300
5000	4945	4948	4957	4971	4997	5144	5412	5527

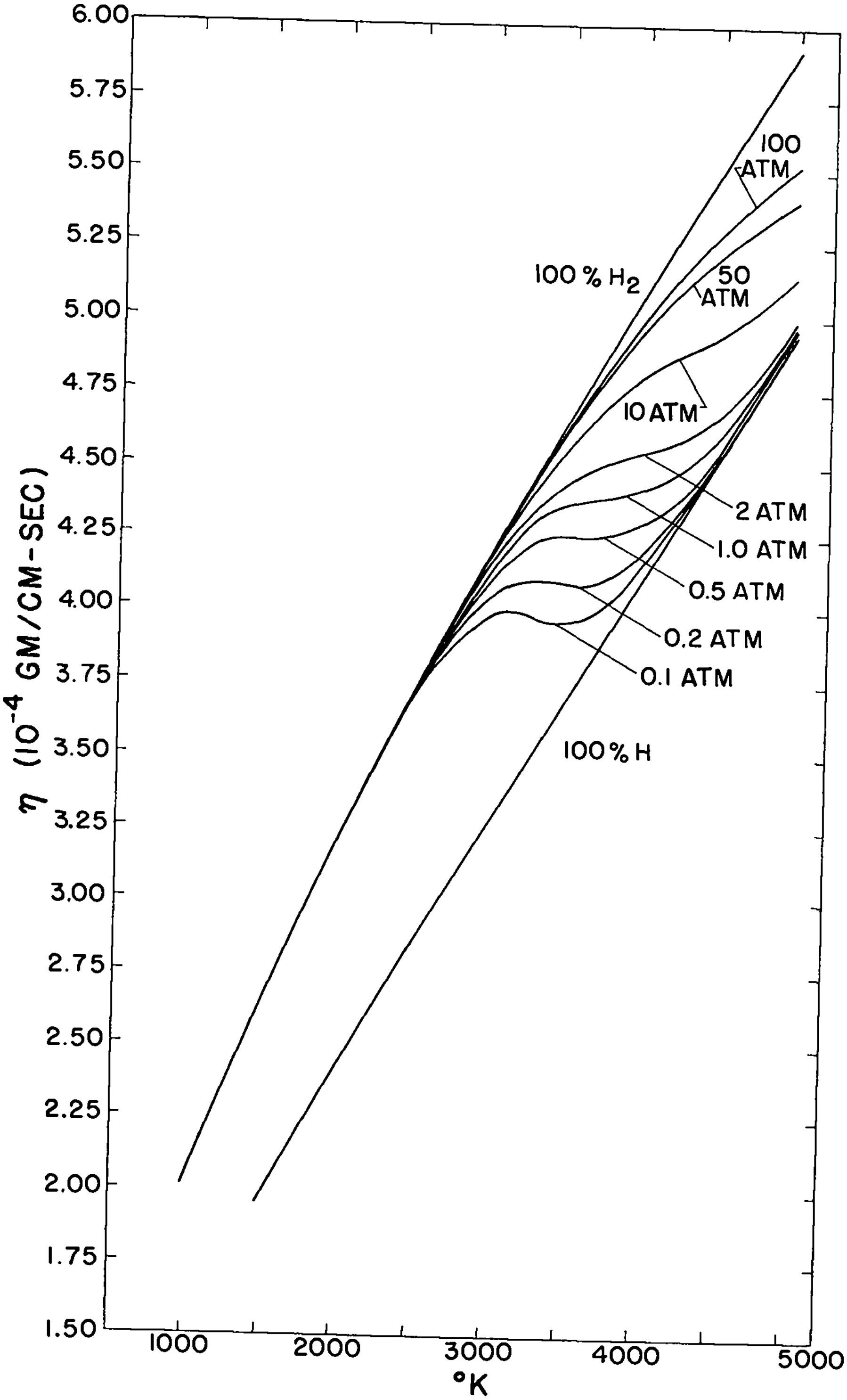

Figure 3 Coefficient of viscosity of dissociating hydrogen.

Applications of these parameters and Equation (19) gave the results listed in Table 4 in the form of $p[D_{12}]_1$.

The formula for the coefficient of self-diffusion for a system obeying a modified Buckingham (exp-6) potential as given by Mason and Rice[4] is:

$$(22) \qquad [D_{22}]_1 = \frac{2.628 \times 10^{-3} \sqrt{T^3/M}}{p r_m^2 \Omega_{2,2}^{(1,1)*}(\alpha, T^*)},$$

where $[D_{22}]_1$ = coefficient of self-diffusion in $\mathrm{cm}^2/\mathrm{sec}$,

p = pressure in atmospheres,

T = temperature in °K,

T^* = kT/ϵ,

M = molecular weight (in this case for H_2),

$\Omega_{2,2}^{(1,1)*}(\alpha, T^*)$ = dimensionless function which may be obtained from Reference 9,

ϵ = depth of potential energy minimum,

r_m = position of the potential energy minimum.

Equation (22) and the parameters for the modified Buckingham (exp-6) potential for the H_2-H_2 interaction (see the section on viscosity) were used to obtain the coefficient of self-diffusion for H_2. The values of these parameters are:

$$(23) \qquad \alpha = 14.0,$$

$$(24) \qquad r_m = 3.337\text{Å},$$

$$(25) \qquad \epsilon/k = 37.3\text{°K}.$$

The results of these calculations are given in Table 4, in the form of $p[D_{22}]_1$.

Table 4

Coefficients of Diffusion

T (°K)	$p[D_{12}]_1$ (atm cm^2/sec)	$p[D_{11}]_1$ (atm cm^2/sec)	$p[D_{22}]_1$ (atm cm^2/sec)
1000	15.276	15.662	11.244
1500	29.880	31.701	22.343
2000	48.132	52.670	36.351
2500	69.643	78.595	53.011
3000	94.373	111.49	72.122
3200	105.54	125.29	80.432
3500	121.96	147.48	93.547
3700	133.35	164.05	102.71
4000	151.24	189.91	117.35
4200	163.64	208.57	127.55
4500	183.24	237.93	143.44
5000	217.92	291.94	171.41

The formula for the coefficient of self-diffusion for a system obeying the rigid-sphere type potential as given in MTGL is:

$$[D_{11}]_1 = 2.628 \times 10^{-3} \frac{\sqrt{T^3/M}}{p\sigma^2}, \tag{26}$$

where $[D_{11}]_1$ = coefficient of self-diffusion in cm^2/sec,

T = temperature in °K,

p = pressure in atmospheres,

M = molecular weight (in this case for H),

σ = rigid-sphere collision diameter.

In order to employ Equation (26) to obtain the self-diffusion coefficient for the H-H system it is necessary to have a value for the rigid-sphere collision diameter, σ. As stated in the section on viscosity, there are two potential energy curves for the H-H interaction, $\left({}^3\Sigma_u \text{ and } {}^1\Sigma_g\right)$. If one applies the method of Hirschfelder and Eliason[2] to each of these potential energy curves, one obtains an effective rigid-sphere collision diameter for the interaction curve considered and the temperature considered. Since the degeneracy of the two curves are 3 and 1, by the same reasoning as outlined in the section on viscosity, these rigid-sphere diameters are weighted and averaged to obtain the appropriate "effective" rigid-sphere diameter at any one temperature.

In the description of the method of Hirschfelder and Eliason in the section on viscosity, it is seen that a specific procedure is used to obtain a factor, θ_{visc}, which is then used in the evaluation of the effective rigid-sphere collision diameter. For the case of diffusion, essentially the same procedure is used; however, one now obtains a factor, θ_{diff}, which is then used to get the effective rigid-sphere collision diameter for the diffusion process. This procedure is explained more fully in the article by Hirschfelder and Eliason.

The values of RT, n, and θ_{diff} used in the work presented here to obtain the collision diameters are given in Table 5. Also in Table 5 are the σ's for each potential curve and the effective weighted average value for $\sigma^{2'}$.

Substituting these values of the effective rigid-sphere collision diameters into Equation (26) gives the coefficient of self-diffusion for the H-H system. These results are listed in Table 4 in the form of $p[D_{11}]_1$.

Coefficient of Thermal Conductivity

It has been shown by Butler and Brokaw[6] that the coefficient of thermal

Table 5

Parameters Used in the Hirschfelder and Eliason Analysis for $[D_{11}]_1$

T (°K)	RT (kcal/mole)	$^3\Sigma_u$ State			$^1\Sigma_g$ State			$\sigma^2_{\text{av rig sph}}$ (Å^2) (weighted av)
		n	θ_{diff}	$\sigma_{\text{rig sph}}$ (Å)	n	θ_{diff}	$\sigma_{\text{rig sph}}$ (Å)	
1000	1987.19	11	1.841	2.026	6	-0.5979	2.950	5.285
1500	2980.79	12	1.846	1.951	6	-0.5979	2.787	4.797
2000	3974.38	11	1.841	1.887	6	-0.5979	2.664	4.445
2500	4967.98	9	1.807	1.830	6	-0.5979	2.570	4.163
3000	5961.57	10	1.844	1.751	6	-0.5979	2.496	3.858
3200	6359.01	9	1.807	1.734	6	-0.5979	2.471	3.782
3500	6955.17	8	1.759	1.709	6	-0.5979	2.436	3.675
3700	7352.60	8	1.759	1.686	6	-0.5979	2.416	3.591
4000	7948.76	7	1.727	1.660	6	-0.5979	2.383	3.487
4200	8346.20	7	1.727	1.640	6	-0.5979	2.365	3.416
4500	8942.36	7	1.727	1.613	6	-0.5979	2.340	3.321
5000	9935.95	7	1.727	1.568	6	-0.5979	2.303	3.170

conductivity of a dissociating gas may be expressed as follows:

$$\lambda_e = \lambda_f \left[1 + \delta \left(\frac{\hat{C}_{pe}}{\hat{C}_{pf}} - 1 \right) \right] . \tag{27}$$

In this equation λ_e = effective thermal conductivity of the dissociating mixture in cal/cm-sec-°K,

λ_f = thermal conductivity of the "frozen" mixture, or the thermal conductivity due to molecular collisions in cal/cm-sec-°K,

$\hat{C}_{pe}$ = equilibrium heat capacity of the mixture at constant pressure in cal/°K-gm of mix,

$\hat{C}_{pf}$ = heat capacity of the mixture at constant pressure and constant composition in cal/°K-gm of mix,

$\delta = \frac{D_{12}\rho\hat{C}_{pf}}{\lambda_f}$ = dimensionless quantity which is a function of the reaction under consideration. See Ref. 6,

or

$$\delta = \frac{D_{12}nC_{pf}}{\lambda_f} ,$$

where D_{12} = coefficient of binary diffusion in cm^2/sec,

n = number of moles of gas mixture/cm^3

C_{pf} = "frozen" composition constant pressure heat capacity per mole of gas mixture per °K.

The ratio $\hat{C}_{pe}/\hat{C}_{pf}$ is the same as the ratio C_{pe}/C_{pf}, where the latter quantities are for the total mixture.

For a better understanding of C_{pe} and C_{pf}, consider the following steps. The enthalpy of the mixture at a given composition is:

$$H = \sum_i n_i H_i , \tag{28}$$

where n_i = number of moles of ith species,

H_i = enthalpy per mole of the ith species.

Then the equilibrium heat capacity at constant pressure is:

$$(29) \qquad C_{pe} = \left(\frac{\partial H}{\partial T}\right)_p = \sum_i n_i \left(\frac{\partial H_i}{\partial T}\right)_p + \sum_i \left(\frac{\partial n_i}{\partial T}\right)_p H_i \, .$$

The "frozen" heat capacity at constant pressure, or the constant pressure heat capacity at constant composition, is:

$$(30) \qquad C_{pf} = \sum_i n_i \left(\frac{\partial H_i}{\partial T}\right)_p = \sum_i n_i C_{pi} \, .$$

These two heat capacities, computed for dissociating hydrogen as a function of temperature and pressure, are listed in Appendix A in Table A-3. The Lewis number, δ, of Equation (27) varies with composition for a mixture of two gases. Butler and Brokaw[6] made estimates of the variation of δ for the dissociation of a diatomic molecule, and they suggest that δ varies from about 1.4 (gas composed entirely of diatomic molecules) to about 0.6 (gas composed entirely of atoms). These authors also state that for rough estimates, δ is of the order of unity, and therefore one may make the approximation,

$$(31) \qquad \frac{\lambda_e}{\lambda_f} \sim \frac{C_{pe}}{C_{pf}} \, .$$

Thus, the use of either Equation (27) or Equation (31) will give two methods of computing λ_e with varying degrees of approximation.

The term λ_f in the above equations is the coefficient of thermal conductivity of the mixture when no reaction is considered; however, since the mixture contains H_2 and H, it may be thought of as a polyatomic gas mixture of two components. Henceforth this term, λ_f, will be called the coefficient of thermal conductivity of the "frozen" polyatomic gas mixture, $\lambda_{\text{poly mix}}$.

Hirschfelder[7] has shown that the coefficient of thermal conductivity for a polyatomic gas mixture of two components is given by:

$$\lambda_{\text{poly mix}} \doteq \lambda_{\text{mon mix}} + x_1\left(x_1 + x_2\frac{D_{11}}{D_{12}}\right)^{-1}\left(\lambda_1 - [\lambda_1]_{\text{mon}}\right) + x_2\left(x_2 + x_1\frac{D_{22}}{D_{12}}\right)^{-1}\left(\lambda_2 - [\lambda_2]_{\text{mon}}\right), \tag{32}$$

where for our case:

$\lambda_{\text{poly mix}}$ = coefficient of thermal conductivity of the polyatomic gas gas mixture (cal/cm-sec-°K),

$\lambda_{\text{mon mix}}$ = the coefficient of thermal conductivity the mixture would possess if the molecules were all monatomic (cal/cm-sec-°K),

x_1, x_2 = mole fraction of H and H_2, respectively,

D_{11}, D_{22} = coefficients of self-diffusion of H and H_2, respectively (cm^2/sec),

D_{12} = coefficient of diffusion in a binary mixture of H and H_2 (cm^2/sec),

$\lambda_1 = [\lambda_1]_{\text{mon}}$ = coefficient of thermal conductivity of H atoms (cal/cm-sec-°K),

λ_2 = coefficient of thermal conductivity of H_2, where the generalized Eucken correction has been made for the internal degrees of freedom (cal/cm-sec-°K). See Equation (34),

$[\lambda_2]_{\text{mon}}$ = coefficient of thermal conductivity of H_2 if it is considered to be monatomic (cal/cm-sec-°K).

Equation (32) is used to obtain the term λ_f for Equations (27) and (31).

In order to obtain the terms $[\lambda_1]_{mon}$ and $[\lambda_2]_{mon}$ the following equation from MTGL is used:

$$(33) \qquad [\lambda_{mon}]_1 \times 10^7 = \frac{15}{4}\frac{R}{M}[\eta]_1 \times 10^7 ,$$

where $[\lambda_{mon}]_1$ = 1st approximation to the thermal conductivity (cal/cm-sec-°K),

R = gas constant (cal/mole, °K),

M = molecular weight,

$[\eta]_1$ = coefficient of viscosity (gm/cm-sec).

To obtain the term λ_2 of Equation (32), the following equation as given by Hirschfelder[7] is used:

$$(34) \qquad \lambda_2 = [\lambda_2]_{mon} + n[D_{22}]_1\left(C_p(H_2) - \frac{5R}{2}\right),$$

where λ_2 = coefficient of thermal conductivity of the polyatomic gas, H_2, where the generalized Eucken-type correction has been made (cal/cm-sec-°K),

$[\lambda_2]_{mon}$ = coefficient of thermal conductivity of H_2 when it is considered monatomic. See Equation (33),

n = number of moles of the gas mixture per cm^3,

D_{22} = self-diffusion coefficient of H_2 (cm^2/sec),

$C_p(H_2)$ = constant pressure heat capacity of H_2 (cal/mole, °K),

R = gas constant (cal/mole-°K).

The term $\lambda_{mon\ mix}$ of Equation (32) is the thermal conductivity of the mixture if it is considered to be a mixture of monatomic gases. The following equations for a binary mixture of monatomic gases as given in MTGL were used:

$$\frac{1}{[\lambda_{mix}]_1} = \frac{X_\lambda + Y_\lambda}{1 + Z_\lambda} , \tag{35}$$

$$X_\lambda = \frac{x_1^2}{[\lambda_1]_1} + \frac{2x_1x_2}{[\lambda_{12}]_1} + \frac{x_2^2}{[\lambda_2]_1} , \tag{36}$$

$$Y_\lambda = \frac{x_1^2}{[\lambda_1]_1} U^{(1)} + \frac{2x_1x_2}{[\lambda_{12}]_1} U^{(Y)} + \frac{x_2^2}{[\lambda_2]_1} U^{(2)} , \tag{37}$$

$$Z_\lambda = x_1^2 U^{(1)} + 2x_1x_2 U^{(Z)} + x_2^2 U^{(2)} , \tag{38}$$

$$U^{(1)} = \frac{4}{15} A_{12}^* - \frac{1}{12}\left(\frac{12}{5} B_{12}^* + 1\right)\frac{M_1}{M_2} + \frac{1}{2}\frac{\left(M_1 - M_2\right)^2}{M_1M_2} \tag{39}$$

$$U^{(2)} = \frac{4}{15} A_{12}^* - \frac{1}{12}\left(\frac{12}{5} B_{12}^* + 1\right)\frac{M_2}{M_1} + \frac{1}{2}\frac{\left(M_2 - M_1\right)^2}{M_1M_2} , \tag{40}$$

$$U^{(Y)} = \frac{4}{15} A_{12}^* \left(\frac{\left(M_1 + M_2\right)^2}{4M_1M_2}\right)\frac{[\lambda_{12}]_1^2}{[\lambda_1]_1[\lambda_2]_1} - \frac{1}{12}\left(\frac{12}{5} B_{12}^* + 1\right) - \frac{5}{32A_{12}^*}\left(\frac{12}{5} B_{12}^* - 5\right)\frac{\left(M_1 - M_2\right)^2}{M_1M_2} , \tag{41}$$

$$U^{(Z)} = \frac{4}{15} A_{12}^* \left[\left(\frac{\left(M_1 + M_2\right)^2}{4M_1M_2}\right)\left(\frac{[\lambda_{12}]_1}{[\lambda_1]_1} + \frac{[\lambda_{12}]_1}{[\lambda_2]_1}\right) - 1\right] - \frac{1}{12}\left(\frac{12}{5} B_{12}^* + 1\right) , \tag{42}$$

where x_1, x_2 = mole fraction of H and H_2, respectively,

M_1, M_2 = molecular weight of H and H_2, respectively,

A^*_{12}, B^*_{12} = functions of $T^*_{12} = kT/\epsilon_{12}$ defined in Equations 8.2-15 and 8.2-16 of MTGL,

$[\lambda_1]_1, [\lambda_2]_1, [\lambda_{12}]_1$ = coefficients of thermal conductivity corresponding to the H-H, H_2-H_2, and H-H_2 interactions, respectively,

$[\lambda_{mix}]_1$ = coefficient of thermal conductivity of the binary monatomic mixture.

All of the terms in these equations except the term $[\lambda_{12}]_1$ have been explained. The term $[\lambda_{12}]_1$ was obtained from the following equation taken from MTGL:

$$[\lambda_{12}]_1 = \frac{15}{4} R \frac{(M_1 + M_2)}{2M_1 M_2} [\eta_{12}]_1 , \tag{43}$$

where $[\lambda_{12}]_1$ = coefficient of thermal conductivity of a hypothetical gas, the molecules of which have a molecular weight of $2M_1M_2/(M_1 + M_2)$ and interact according to a potential curve specified by the parameters σ_{12} and ϵ_{12} as used to determine $[\eta_{12}]_1$ (cal/cm-sec-°K),

M_1, M_2 = molecular weights of H and H_2, respectively,

$[\eta_{12}]_1$ = coefficient of viscosity as discussed in the section on viscosity (gm/cm-sec),

R = gas constant (cal/mole, °K).

Table 6 presents the values of $[\lambda_1]_1$, $[\lambda_{2\ mon}]_1$, and $[\lambda_{12}]_1$ as obtained from the above equations, the values for $[\eta_1]_1$ and $[\eta_{12}]_1$ as given in Table 2, and the value of $[\eta_2]_1$ which was used to get the third approximation, $[\eta_2]_3$, to the viscosity of H_2.

Table 6

Coefficients of Thermal Conductivity for the Systems H-H, $H\text{-}H_2$, and $H_2\text{-}H_2$, Considering Each System as Monatomic (cal/cm-sec-°K)

T (°K)	$[\lambda_1]_1 \times 10^7$ H-H	$[\lambda_{12}]_1 \times 10^7$ $H\text{-}H_2$	$[\lambda_2]_1 \times 10^7$ $H_2\text{-}H_2$
1000	10,780.	10,283.	7,389.9
1500	14,512.	13,356.	9,702.2
2000	17,870.	16,088.	11,773.
2500	21,130.	18,579.	13,664.
3000	24,219.	20,900.	15,423.
3200	25,451.	21,813.	16,100.
3500	27,240.	23,008.	17,084.
3700	28,440.	23,794.	17,722.
4000	30,379.	24,969.	18,700.
4200	31,526.	25,737.	19,337.
4500	33,249.	26,890.	20,265.
5000	36,533.	28,787.	21,741.

Table 7 gives the values of $\lambda_{\text{mon mix}}$ obtained from Equation (35) using the appropriate mole fractions and the results given in Table 6.

Table 8 gives the values of the coefficient of thermal conductivity of H_2, λ_2, when the generalized Eucken-type of correction has been made. See Equation (34). Also listed in this table are the factors $\left(\lambda_2 - [\lambda_2]_{\text{mon}}\right)$ which are used in Equation (32) to obtain $\lambda_{\text{poly mix}}$.

Table 9 lists the values of the coefficient of thermal conductivity of the mixture when no reaction is considered but the Eucken-type correction for the polyatomic gas is applied. This is $\lambda_{\text{poly mix}}$.

Equation (31) gives the first and roughest approximation to the thermal conductivity of the reacting mixture, λ_e or λ_{reac}. In arriving at this approximation, the term δ of Equation (27) was assumed to be unity. The values of C_{pe} and C_{pf} which are necessary for Equation (31) are given in Table A-3 of Appendix A.

Table 10 gives the results for λ_{reac} as obtained from Equation (31).

Equation (27) is the more exact expression for the coefficient of thermal conductivity for the reacting mixture. This expression involves δ, which is defined as follows:

$$(44) \qquad \delta = \frac{D_{12} n C_{pf}}{\lambda_f} ,$$

where the symbols have the significance given above. The values of δ as computed and used in this work are given in Table 11.

The final results for the coefficient of thermal conductivity for the reacting mixture of dissociating hydrogen as obtained from the more exact expression, Equation (27), are given in Table 12 and graphed in Figure 4.

The recommended "best" values for the coefficient of thermal conductivity of the dissociating mixture are those given in Table 12 and Figure 4. The values given in Table 10 are more approximate.

Table 7

Coefficient of Thermal Conductivity for the Dissociating Hydrogen Mixture When it is Considered a Binary Mixture of Monatomic Gases

	$\lambda_{\text{mon mix}} \times 10^7$ (cal/cm-sec-°K)						
T (°K)	p = 0.1 atm	p = 0.5 atm	p = 1.0 atm	p = 2.0 atm	p = 10 atm	p = 50 atm	p = 100 atm
1500	9,702.4	9,702.2	9,702.2	9,702.2	9,702.2	9,702.2	9,702.2
2000	11,803.	11,786.	11,783.	11,780.	11,776.	11,775.	11,774.
2500	14,164.	13,955.	13,830.	13,778.	13,715.	13,687.	13,680.
3000	18,450.	16,917.	16,518.	16,198.	15,777.	15,583.	15,536.
3200	21,007.	18,725.	18,032.	17,504.	16,750.	16,395.	16,310.
3500	24,893.	22,075.	20,923.	19,957.	18,461.	17,717.	17,534.
3700	27,083.	24,563.	23,225.	21,973.	19,838.	18,707.	18,425.
4000	29,798.	28,167.	26,923.	25,474.	22,370.	20,457.	19,959.
4200	31,195.	30,117.	29,134.	27,808.	24,315.	21,796.	21,109.
4500	33,097.	32,541.	31,946.	30,992.	27,515.	24,108.	23,069.
5000	36,480.	36,273.	36,026.	35,573.	33,076.	28,810.	27,088.

Table 8

Coefficient of Thermal Conductivity for H_2 with the Eucken-Type Correction Included

T (°K)	$[\lambda_2]_1 \times 10^7$ (cal/cm-sec-°K)	$\left(\lambda_2 - [\lambda_2]_{mon}\right) \times 10^7$ (cal/cm-sec-°K)
1000	10,472.	3,081.7
1500	14,685.	4,982.8
2000	18,877.	7,103.6
2500	22,858.	9,194.3
3000	26,623.	11,200.
3200	28,098.	11,998.
3500	30,194.	13,110.
3700	31,585.	13,863.
4000	33,656.	14,956.
4200	35.007.	15,670.
4500	37,023.	16,758.
5000	40,211.	18,470.

Table 9

Coefficient of Thermal Conductivity for the "Frozen" Polyatomic Gas Mixture [Equation (32)]

T (°K)	$\lambda_{\text{poly mix}} \times 10^7$ (cal/cm-sec-°K)						
	p = 0.1 atm	p = 0.5 atm	p = 1.0 atm	p = 2.0 atm	p = 10 atm	p = 50 atm	p = 100 atm
1500	14,685.	14,685.	14,685.	14,685.	14,685.	14,685.	14,685.
2000	18,879.	18,878.	18,877.	18,877.	18,877.	18,877.	18,877.
2500	22,814.	22,903.	22,850.	22,849.	22,854.	22,857.	22,857.
3000	25,977.	26,324.	26,427.	26,473.	26,555.	26,593.	26,602.
3200	26,889.	27,493.	27,661.	27,785.	27,956.	28,034.	28,053.
3500	27,948.	28,763.	29,090.	29,364.	29,791.	30,007.	30,061.
3700	28,812.	29,506.	29,882.	30,243.	30,888.	31,251.	31,344.
4000	30,495.	30,836.	31,117.	31,466.	32,329.	32,966.	33,149.
4200	31,584.	31,783.	32,054.	32,262.	33,156.	33,979.	34,239.
4500	33,272.	33,358.	33,455.	33,622.	34,367.	35,368.	35,746.
5000	36,536.	36,548.	36,562.	36,592.	36,824.	37,539.	37,974.

Table 10

Coefficient of Thermal Conductivity for the Dissociating Hydrogen Mixture Using the Equation:

$$\lambda_{reac} = \lambda_{poly\ mix} \frac{C_{pe}}{C_{pf}}$$

$\lambda_{reac} \times 10^7$ (cal/cm-sec-°K)

T (°K)	p = 0.1 atm	p = 0.5 atm	p = 1.0 atm	p = 2.0 atm	p = 10 atm	p = 50 atm	p = 100 atm
1500	14,753.	14,716.	14,706.	14,700.	14,692.	14,688.	14,688.
2000	23,270.	20,841.	20,265.	19,859.	19,316.	19,073.	19,017.
2500	73,423.	45,748.	38,989.	34,264.	27,965.	25,144.	24,475.
3000	246,050.	135,300.	104,830.	82,425.	51,849.	37,948.	34,638.
3200	318,230.	196,130.	151,930.	117,770.	69,186.	46,624.	41,215.
3500	292,580.	280,880.	233,550.	185,760.	105,320.	64,563.	54,602.
3700	206,580.	295,360.	273,740.	231,690.	135,820.	80,258.	66,272.
4000	105,880.	232,320.	268,670.	268,840.	185,820.	109,140.	87,975.
4200	71,968,	170,090.	224,230.	256,460.	215,020.	130,980.	104,870.
4500	49,635.	101,990.	146,550.	197,230.	237,680.	164,570.	132,600.
5000	40,895.	57,175.	75,197.	104,910.	201,550.	205,120.	176,010.

Table 11

Values of δ as Computed from the Expression:

$$\delta = \frac{D_{12} n C_{pf}}{\lambda_f}$$

T (°K)	p = 0.1 atm	p = 0.5 atm	p = 1.0 atm	p = 2.0 atm	p = 10 atm	p = 50 atm	p = 100 atm
1500	1.277	1.277	1.277	1.277	1.277	1.277	1.277
2000	1.266	1.268	1.268	1.268	1.269	1.269	1.269
2500	1.228	1.245	1.253	1.257	1.262	1.264	1.264
3000	1.078	1.170	1.195	1.215	1.243	1.256	1.259
3200	0.9903	1.112	1.152	1.184	1.230	1.252	1.258
3500	0.8707	0.9978	1.054	1.104	1.185	1.228	1.239
3700	0.8192	0.9220	0.9806	1.038	1.144	1.205	1.221
4000	0.7738	0.8325	0.8796	0.9367	1.070	1.161	1.187
4200	0.7593	0.7959	0.8284	0.8785	1.016	1.127	1.159
4500	0.7463	0.7638	0.7836	0.8141	0.9358	1.069	1.113
5000	0.7238	0.7296	0.7365	0.7494	0.8232	0.9620	1.023

Table 12

Coefficient of Thermal Conductivity for the Dissociating Hydrogen Mixture from the Equation:

$$\lambda_{reac} = \lambda_{poly\ mix}\left[1 + \delta\left(\frac{C_{pe}}{C_{pf}} - 1\right)\right]$$

$\lambda_{reac} \times 10^7$ (cal/cm-sec-°K)

T (°K)	p = 0.1 atm	p = 0.5 atm	p = 1.0 atm	p = 2.0 atm	p = 10 atm	p = 50 atm	p = 100 atm
1500	14,772.	14,725.	14,711.	14,704.	14,694.	14,689.	14,689.
2000	24,438.	21,366.	20,637.	20,122.	19,434.	19,126.	19,054.
2500	84,946.	51,341.	43,071.	37,196.	29,302.	25,748.	24,903.
3000	263,220.	153,790.	120,110.	94,472.	57,992.	40,853.	36,719.
3200	315,400.	215,090.	170,850.	134,280.	78,657.	51,310.	44,605.
3500	258,360.	280,340.	244,650.	202,010.	119,300.	72,443.	60,463.
3700	174,440.	274,620.	269,010.	239,420.	150,970.	90,298.	73,976.
4000	88,826.	198,580.	240,070.	251,930.	196,590.	121,430.	98,200.
4200	62,246.	141,850.	191,250.	229,210.	217,930.	143,300.	116,130.
4500	45,483.	85,774.	122,080.	166,810.	224,630.	173,490.	143,570.
5000	39,691.	51,597.	65,018.	87,788.	172,420.	198,750.	179,240.

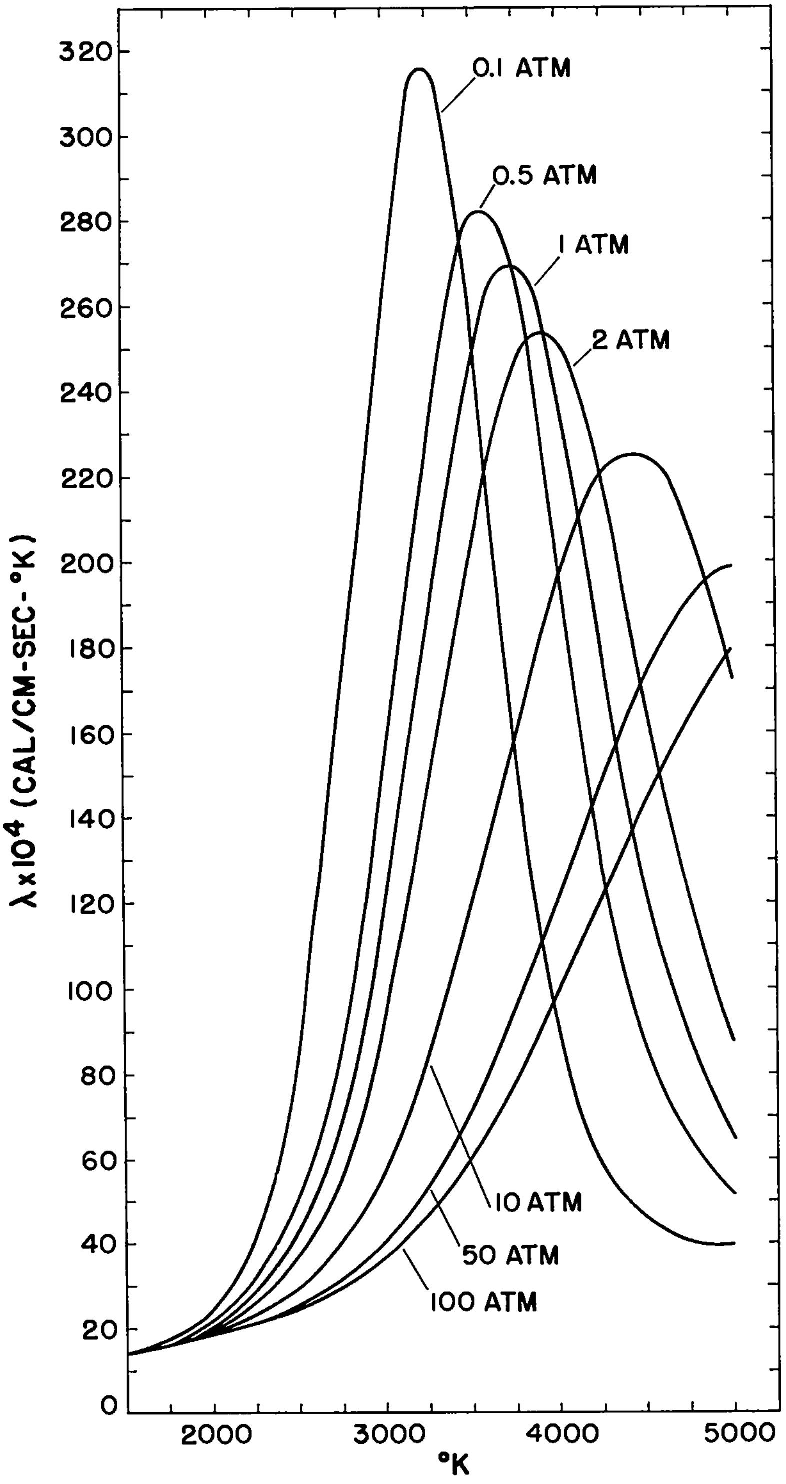

Figure 4 Coefficient of thermal conductivity of dissociating hydrogen.

APPENDIX A

In the calculations of the coefficients of viscosity and the coefficients of thermal conductivity of dissociating hydrogen for various temperatures and pressures, it is necessary to have the equilibrium composition of the mixture, the equilibrium heat capacity at constant pressure, and the constant pressure, "frozen" composition, heat capacity.

The following analysis of this equilibrium was used:

A.1 $$H_2 \rightleftharpoons 2H,$$

A.2 $$(1 - \alpha) \rightleftharpoons 2\alpha,$$

A.3 $$n_1 = 2\alpha = \text{number of moles of H},$$

A.4 $$n_2 = 1 - \alpha = \text{number of moles of } H_2,$$

A.5 $$x_1 = \frac{2\alpha}{1 + \alpha} = \text{mole fraction of H},$$

A.6 $$x_2 = \frac{1 - \alpha}{1 + \alpha} = \text{mole fraction of } H_2,$$

A.7 $$K_p = \frac{4\alpha^2 p}{1 - \alpha^2} = \text{thermodynamic equilibrium constant},$$

A.8 $$\ln K_p = \ln \frac{4\alpha^2}{1 - \alpha^2} + \ln p = -\frac{\Delta F^\circ}{RT}.$$

In equation A.1 consider 1 mole of originally undissociated H_2 to be at equilibrium at a given temperature and pressure. In equation A.2 the α represents the degree of dissociation. It is the fraction of the originally undissociated H_2 which has dissociated. In equation A.8 the $\Delta F°$ represents the change in the standard Gibbs free energy for the reaction, R equals the gas constant, T is the temperature in °K, and p is the pressure in atmospheres.

An IBM 704 computer program which solves for the composition of multicomponent systems was used to solve the above equilibrium. For the convenience of handling, the thermodynamic data used as input data for the program were fit to polynomials in temperature. The form of these expressions is:

A.9 $$-\frac{F°}{RT} = a \ln T + bT + \frac{cT^2}{2} + \frac{dT^3}{3} + \frac{eT^4}{4} + k - \frac{H_0°}{RT},$$

A.10 $$C_p = a + bT + cT^2 + dT^3 + eT^4,$$

A.11 $$\left(\frac{H° - H_0°}{T}\right) = a + bT + cT^2 + dT^3 + eT^4.$$

The basic data used to evaluate the constants in the above equations were obtained from Reference 8. The constants for the fits are tabulated in Table A-1. For further details of the IBM program and the handling of the thermodynamic data, see Reference 16.

Using the program described, the degree of dissociation, α, the mole fractions, x, and the number of moles, n, of the components were calculated for the hydrogen dissociation equilibrium for the temperatures and pressures of interest to these calculations. The degree of dissociation and mole fraction of H are listed in Table A-2.

Table A-1

Constants for Polynomial Fits of Thermodynamic Data

		a	b	c	d	e	k	H_0°	Temp Range
$H_2(g)$	$-\frac{F^\circ}{RT}$	3.4426017 00	-5.6229289-05	1.4891164-07	-3.4545064-11	2.5711512-15	-7.3150000 00		1000° to 5000°K
	C_p	5.9285929 00	1.3850613-03	-8.8392668-08	-3.0634184-11	4.1311159-15			1000° to 5000°K
	$\frac{H^\circ-H_0^\circ}{T}$	6.8407357 00	-1.1112171-04	2.9554909-07	-6.8555066-11	5.1012020-15			1000° to 5000°K
$H(g)$	$-\frac{F^\circ}{RT}$	2.5000018 00	-2.3828664-09	5.4167994-13	2.4203764-16	-7.4527263-20	-2.9593000 00	5.1620000-04	1000° to 5000°K
	C_p	4.9681000 00							1000° to 5000°K
	$\frac{H^\circ-H_0^\circ}{T}$	4.9681000 00							1000° to 5000°K

Table A-2

Degree of Dissociation and Mole Fraction of H for Dissociated Hydrogen

	p = 0.1 atm		p = 0.2 atm		p = 0.5 atm		p = 1.0 atm	
T (°K)	α	x_H	α	x_H	α	x_H	α	x_H
1500	2.78×10^{-5}	5.56×10^{-5}	1.97×10^{-5}	3.93×10^{-5}	1.24×10^{-5}	2.49×10^{-5}	8.79×10^{-6}	1.76×10^{-5}
2000	2.57×10^{-3}	5.12×10^{-3}	1.82×10^{-3}	3.63×10^{-3}	1.15×10^{-3}	2.29×10^{-3}	8.12×10^{-4}	1.62×10^{-3}
2500	0.03967	0.07632	0.02806	0.05460	0.01775	0.03489	0.01255	0.02480
3000	0.24194	0.38962	0.17364	0.29589	0.11082	0.19954	0.07861	0.14576
3200	0.40561	0.57713	0.29939	0.46081	0.19465	0.32588	0.13896	0.24402
3500	0.68207	0.81099	0.55056	0.71015	0.38497	0.55592	0.28290	0.44103
3700	0.82001	0.90110	0.71168	0.83156	0.53949	0.70086	0.41268	0.58425
4000	0.92946	0.96344	0.87202	0.93163	0.74792	0.85578	0.62313	0.76781
4200	0.96177	0.98051	0.92762	0.96245	0.84354	0.91513	0.74314	0.85265
4500	0.98371	0.99179	0.96820	0.98384	0.92571	0.96142	0.86585	0.92810
5000	0.99523	0.99761	0.99052	0.99524	0.97680	0.98826	0.95514	0.97706

Table A-2 (continued)

Degree of Dissociation and Mole Fraction of H for Dissociating Hydrogen

	p = 2.0 atm		p = 10 atm		p = 50 atm		p = 100 atm	
T (°K)	α	x_H	α	x_H	α	x_H	α	x_H
1500	6.21×10^{-6}	1.24×10^{-5}	2.77×10^{-6}	5.56×10^{-6}	1.24×10^{-6}	2.49×10^{-6}	8.79×10^{-7}	1.76×10^{-6}
2000	5.74×10^{-4}	1.15×10^{-3}	2.57×10^{-4}	5.14×10^{-4}	1.15×10^{-4}	2.30×10^{-4}	8.12×10^{-5}	1.62×10^{-4}
2500	8.88×10^{-3}	0.01760	3.97×10^{-3}	7.91×10^{-3}	1.78×10^{-3}	3.55×10^{-3}	1.26×10^{-3}	2.51×10^{-3}
3000	0.05567	0.10547	0.02493	0.04864	0.01115	0.02205	7.88×10^{-3}	0.01565
3200	0.09874	0.17973	0.04433	0.08490	0.01984	0.03891	0.01403	0.02767
3500	0.20417	0.33910	0.09287	0.16995	0.04168	0.08002	0.02948	0.05728
3700	0.30509	0.46754	0.14182	0.24841	0.06394	0.12020	0.04526	0.08660
4000	0.49084	0.65847	0.24431	0.39268	0.11197	0.20138	0.07942	0.14715
4200	0.61762	0.76362	0.33136	0.49778	0.15516	0.26864	0.11038	0.19882
4500	0.77435	0.87283	0.48009	0.64873	0.23774	0.38415	0.17053	0.29138
5000	0.91582	0.95606	0.71403	0.83316	0.41497	0.58655	0.30694	0.46971

The two heat capacities necessary for the thermal conductivity calculations were obtained from the following formulations as an extension of the previously mentioned computer program.

Consider the total enthalpy of the dissociated mixture.

A.12 $$H^\circ_{(tot)} = n_1 H^\circ_1 + n_2 H^\circ_2 ,$$

where n_1, n_2 = number of moles of H and H_2, respectively,

H°_1, H°_2 = enthalpy per mole of H and H_2, respectively.

Therefore, from A.3, A.4, and A.12,

A.13 $$H^\circ_{(tot)} = 2\alpha H^\circ_1 + (1 - \alpha) H^\circ_2 ,$$

A.14 $$C_{pe} = \left(\frac{\partial H^\circ_{(tot)}}{\partial T}\right)_p = 2\alpha C_{p1} + (1 - \alpha) C_{p2} + \left(2H^\circ_1 - H^\circ_2\right)\left(\frac{\partial \alpha}{\partial T}\right)_p ,$$

where C_{p1}, C_{p2} = constant-pressure heat capacity per mole for H and H_2, respectively,

C_{pe} = equilibrium constant pressure heat capacity of the mixture,

$2H^\circ_1 - H^\circ_2 = \Delta H^\circ$ = standard enthalpy change for the reaction at T

It follows that,

A.15 $$\left(\frac{\partial \alpha}{\partial T}\right)_p = \left(\frac{\partial \alpha}{\partial \ln K_p}\right)_p \cdot \left(\frac{\partial \ln K_p}{\partial T}\right)_p ,$$

A.16 $$\left(\frac{\partial \ln K_p}{\partial T}\right)_p = \frac{\Delta H^\circ}{RT^2} ,$$

and from A.8

A.17 $$\left(\frac{\partial \alpha}{\partial \ln K_p}\right)_p = \frac{\alpha\left(1 - \alpha^2\right)}{2} ;$$

therefore,

A.18 $$\left(\frac{\partial \alpha}{\partial T}\right)_p = \frac{\Delta H^\circ \alpha\left(1 - \alpha^2\right)}{2RT^2} ,$$

A.19 $$C_{pe} = 2\alpha C_{p1} + (1 - \alpha)C_{p2} + \frac{\Delta H^{\circ 2} \alpha\left(1 - \alpha^2\right)}{2RT^2} ,$$

and

A.20 $$C_{pf} = 2\alpha C_{p1} + (1 - \alpha)C_{p2} ,$$

where C_{pf} = the constant pressure heat capacity for "frozen" composition.

The values of C_{pe} and C_{pf} computed with the IBM computer using these formulas and the appropriate data for the temperatures and pressures of interest are given in Table A-3.

The above reported values of C_{pe} and C_{pf} are the heat capacities in terms of cal/°K for the mixture.

In the computation of δ in Equation (27), the quantity C_{pf}, the "frozen" composition constant pressure heat capacity per mole of mixture, is necessary. Table A-4 gives the number of moles of mixture and C_{pf} per mole of mixture, as computed from the data in Tables A-2 and A-3.

Table A-5 gives the values of C_{pH_2} which were used in Equation (34) to obtain λ_2, the coefficient of thermal conductivity of H_2 with the Eucken-type correction applied.

Table A-3

Equilibrium and "Frozen" Heat Capacities for Dissociated Hydrogen (cal/°K)

T (°K)	p = 0.1 atm		p = 0.5 atm		p = 1 atm		p = 2 atm		p = 10 atm		p = 50 atm		p = 100 atm	
	C_{pe}	C_{pf}	C_{pe}	C_{pf}	C_{pe}	C_{pf}	C_{pe}	C_{pf}	C_{pe}	C_{pf}	C_{pe}	C_{pf}	C_{pe}	C_{pf}
1500	7.761	7.725	7.741	7.725	7.736	7.725	7.733	7.725	7.728	7.725	7.726	7.725	7.726	7.725
2000	10.07	8.171	9.018	8.168	8.768	8.168	8.592	8.167	8.357	8.167	8.251	8.167	8.226	8.166
2500	27.61	8.578	17.07	8.547	14.57	8.539	12.80	8.534	10.43	8.527	9.377	8.524	9.126	8.523
3000	85.93	9.072	45.86	8.922	35.24	8.885	27.58	8.859	17.23	8.824	12.57	8.809	11.47	8.805
3200	110.2	9.311	64.85	9.090	49.60	9.031	38.10	8.989	22.10	8.932	14.81	8.906	13.08	8.900
3500	100.9	9.639	91.41	9.360	74.38	9.265	58.15	9.191	32.12	9.087	19.45	9.039	16.40	9.028
3700	70.12	9.780	95.45	9.535	86.34	9.425	71.49	9.331	40.41	9.189	23.43	9.121	19.25	9.105
4000	34.31	9.881	73.37	9.738	83.24	9.641	81.48	9.537	53.70	9.343	30.59	9.239	24.45	9.214
4200	22.58	9.908	52.56	9.821	68.19	9.748	76.76	9.656	61.26	9.446	35.91	9.316	28.44	9.284
4500	14.81	9.926	30.23	9.887	43.14	9.847	57.41	9.787	66.34	9.592	43.88	9.431	34.82	9.387
5000	11.12	9.934	15.53	9.924	20.39	9.912	28.36	9.891	53.54	9.782	52.57	9.621	44.32	9.562

Table A-4

Number of Moles of Mixture and C_{pf} (cal/mole of mix-°K)

	p = 0.1 atm		p = 0.5 atm		p = 1 atm		p = 2 atm		p = 10 atm		p = 50 atm		p = 100 atm	
T (°K)	No. moles mix	C_{pf}	No. moles mix	C_{pf}	No. moles mix	C_{pf}	No. moles mix	C_{pf}	No. moles mix	C_{pf}	No. moles mix	C_{pf}	No. moles mix	C_{pf}
1500	1.00003	7.7247	1.00001	7.7248	1.00001	7.725	1.00001	7.7248	1.00000	7.7248	1.00000	7.7248	1.00000	7.7248
2000	1.00257	8.1498	1.00115	8.1588	1.00081	8.161	1.00057	8.1625	1.00026	8.1645	1.00011	8.1655	1.00008	8.1656
2500	1.03967	8.2503	1.01775	8.3975	1.01255	8.433	1.00888	8.4590	1.00397	8.4934	1.00178	8.5089	1.00126	8.5126
3000	1.24194	7.3045	1.11082	8.03020	1.07861	8.237	1.05567	8.3920	1.02493	8.6096	1.01115	8.7114	1.00788	8.7358
3200	1.40561	6.6245	1.19465	7.6086	1.13896	7.929	1.09874	8.1810	1.04433	8.5525	1.01984	8.7326	1.01403	8.7767
3500	1.68207	5.7302	1.38497	6.7586	1.28290	7.222	1.20417	7.6328	1.09287	8.3147	1.04168	8.6774	1.02948	8.7691
3700	1.82001	5.3734	1.53949	6.1939	1.41268	6.672	1.30509	7.1499	1.14182	8.0478	1.06394	8.5732	1.04526	8.7109
4000	1.92946	5.1211	1.74792	5.5714	1.62313	5.940	1.49084	6.3969	1.24431	7.5087	1.11197	8.3091	1.07942	8.5360
4200	1.96177	5.0506	1.84354	5.3275	1.74314	5.592	1.61762	5.9691	1.33136	7.0947	1.15516	8.0649	1.11038	8.3606
4500	1.98371	5.0035	1.92571	5.1342	1.86585	5.277	1.77435	5.5157	1.48009	6.4806	1.23774	7.6199	1.17053	8.0193
5000	1.99523	4.9787	1.97680	5.0201	1.95514	5.070	1.91582	5.1627	1.71403	5.7070	1.41497	6.7991	1.30694	7.3166

Table A-5

Constant Pressure Heat Capacity of H_2

T (°K)	C_{pH_2} (cal/mole-°K)
1500	7.713
2000	8.175
2500	8.526
3000	8.791
3200	8.885
3500	8.993
3700	9.066
4000	9.151
4200	9.202
4500	9.282
5000	9.389

APPENDIX B

The data used to plot Figure 1, the potential energy curves for the $^1\Sigma_g$ and $^3\Sigma_u$ states of the H-H interaction, and the source of these data are listed in Tables B-1 and B-2. As stated in the text, the method of Hirschfelder and Eliason when applied to these interaction curves utilizes only a portion of the curves. The particular portion of the curves used here corresponds only to the range of values of the potential energies which were computed by Dalgarno and Lynn.[11]

Table B-1

Binding Energy for $^1\Sigma_g$ State of Hydrogen

r (a_0)	Binding energy (kcal/mole)	Source
0.78	14.38	Rydberg Experimental Values as given in MTGL, pp. 1060-1061
0.79	20.14	
0.81	26.68	
0.83	33.91	
0.85	41.84	
0.88	50.46	
0.92	59.70	
0.96	69.57	
1.01	80.13	
1.09	91.32	
1.23	103.20	
1.40	109.32	
1.68	103.20	
1.94	91.32	
2.15	80.13	
2.32	69.57	
2.49	59.70	
2.66	50.46	
2.84	41.84	
3.05	33.91	
3.28	26.68	
3.51	20.14	
3.73	14.38	
4.0	10.372	Reference 11
5.0	2.48	
6.0	0.568	
7.0	0.137	
8.0	0.0386	
10.0	0.0058	
12.0	0.0016	

Table B-2

Repulsion Energy for the $^3\Sigma_u$ State of Hydrogen

r (a_0)	Energy of repulsion (kcal/mole)	Source
1.0	245	Reference 12
1.25	166	
1.50	119	
1.75	88.8	
2.00	68.0	
2.5	30.45	Reference 13
3.0	16.35	
3.5	8.45	
4.0	2.378	Reference 11
5.0	0.295	
6.0	- 0.0100	
7.0	- 0.0317	
8.0	- 0.0195	
10.0	- 0.0053	
12.0	- 0.0016	

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