TRANSFER COEFFICIENTS OF DISSOCIATED HYDROGEN AT PRESSURES UP TO 1000 BARS AND TEMPERATURES UP TO 10,000°K

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The results of a calculation relating to the viscosity and thermal conductivity of hydrogen at pressures of 1-1000 bars and temperatures of 2000-10,000°K are presented.

At pressures of $10\text{-}10^3$ bars and temperatures of 2000-10,000°K, and also at a pressure of 1 bar and temperatures of 2000-8000°K, hardly any ionization occurs in hydrogen [1]. However, dissociation occurs very considerably over the same range of temperature and pressure.

In this paper we shall calculate the viscosity, thermal conductivity, and diffusion coefficient of dissociated hydrogen over the range in question.

The results of similar calculations (without allowing for ionization) were presented earlier for lower pressures [2].

A reference book on the thermal conductivity of gases and liquids [3] gives an analysis of experimental investigations into the thermal conductivity of hydrogen at high pressures; at 600°K, according to this book, the thermal conductivity of hydrogen changes by only 6% on raising the pressure from 1 to 600 bars, the effect of the real nature of the gas (its nonideal properties) on the thermal conductivity diminishing with increasing temperature.

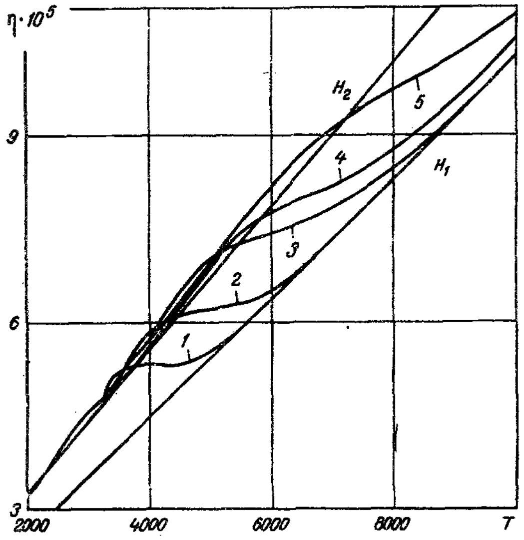

Fig. 1. Viscosity (N · sec/m^2) of dissociated hydrogen: 1) 1 bar; 2) 10; 3) 10^2; 4) $2 \cdot 10^2$; 5) 10^3 bars. T, °K.

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TABLE 1. Molar Proportion x_2 of the Molecular Component for Dissociated Hydrogen

T, K	P, bars						
	100	200	300	400	690	800	1000
2000	0,9998	0,9998	0,9999	0,9999	0,9999	0,9999	0,9999
2200	0,9994	0,9996	0,9996	0,9998	0,9998	0,9998	0,9998
2400	0,9984	0,9988	0,9990	0,9992	0,9994	0,9994	0,9994
2600	0,9962	0,9972	0,9978	0,9980	0,9984	0,9986	0,9988
2800	0,9918	0,9942	0,9952	0,9958	0,9966	0,9970	0,9974
3000	0,9843	0,9889	0,9908	0,9920	0,9934	0,9944	0,9948
3200	0,9722	0,9802	0,9837	0,9859	0,9885	0,9899	0,9910
3400	0,9541	0,9673	0,9732	0,9767	0,9808	0,9833	0,9851
3600	0,9288	0,9489	0,9581	0,9635	0,9701	0,9739	0,9765
3800	0,8950	0,9246	0,9378	0,9459	0,9554	0,9612	0,9650
4000	0,8524	0,8930	0,9117	0,9229	0,9363	0,9444	0,9501
4200	0,8007	0,8543	0,8790	0,8943	0,9124	0,9236	0,9311
4400	0,7408	0,8083	0,8403	0,8598	0,8836	0,8981	0,9080
4600	0,6743	0,7556	0,7952	0,8197	0,8498	0,8681	0,8809
4800	0,6032	0,6978	0,7447	0,7743	0,8109	0,8337	0,8495
5000	0,5305	0,6360	0,6900	0,7246	0,7680	0,7950	0,8141
5200	0,4587	0,5721	0,6323	0,6714	0,7213	0,7528	0,7753
5400	0,3905	0,5080	0,5728	0,6160	0,6718	0,7078	0,7334
5600	0,3280	0,4456	0,5135	0,5597	0,6206	0,6604	0,6892
5800	0,2725	0,3866	0,4557	0,5039	0,5688	0,6119	0,6434
6000	0,2245	0,3323	0,4008	0,4497	0,5172	0,5630	0,5968
6200	0,1842	0,2839	0,3504	0,3994	0,4687	0,5169	0,5530
6400	0,1507	0,2408	0,3038	0,3515	0,4207	0,4698	0,5072
6600	0,1232	0,2035	0,2620	0,3075	0,3753	0,4246	0,4628
6800	0,1010	0,1715	0,2251	0,2679	0,3333	0,3819	0,4202
7000	0,08310	0,1446	0,1931	0,2327	0,2949	0,3422	0,3800
7200	0,06869	0,1221	0,1655	0,2018	0,2601	0,3056	0,3424
7400	0,05712	0,1033	0,1419	0,1749	0,2291	0,2722	0,3078
7600	0,04777	0,08770	0,1219	0,1517	0,2015	0,2421	0,2761
7800	0,04019	0,07471	0,1049	0,1316	0,1772	0,2150	0,2472
8000	0,03404	0,06393	0,09053	0,1144	0,1559	0,1910	0,2212
8200	0,02902	0,05498	0,07843	0,09978	0,1374	0,1697	0,1980
8400	0,02488	0,04749	0,06817	0,08722	0,1212	0,1509	0,1772
8600	0,02147	0,04123	0,05950	0,07650	0,1072	0,1344	0,1587
8800	0,01863	0,03597	0,05215	0,06733	0,09507	0,1199	0,1423
9000	0,01626	0,03152	0,04588	0,05945	0,08449	0,1071	0,1278
9200	0,01426	0,02775	0,04053	0,05268	0,07530	0,09596	0,1150
9400	0,01257	0,02454	0,03596	0,04686	0,06731	0,08616	0,1036
9600	0,01114	0,02180	0,03202	0,04183	0,06034	0,07754	0,09358
9800	0,00991	0,01944	0,02862	0,03747	0,05426	0,06996	0,08470
10000	0,008854	0,01740	0,02567	0,03366	0,04891	0,06327	0,07681

The thermal conductivity of hydrogen was also considered in [4] up to a pressure of 800 bars. Analysis of the latter experimental data, together with all the preceding results, using the method of [3] and extrapolating the relationship between the excess thermal conductivity of hydrogen and its density obtained from the experimental points in the high-temperature direction shows that at 1600°K, for example, the thermal conductivity of hydrogen changes by only 3% on raising the pressure from 1 to 1000 bars.

We may conclude from these data that at T > 2000°K the transfer properties of dissociated hydrogen may be calculated up to pressures of 10^3 bars by simply using the theory of transfer phenomena developed for mixtures of reacting ideal gases. The basic relationships of this theory were given in [5].

The mutual diffusion coefficient of gases 1 and 2 is (to a first approximation) independent of concentration and is determined by the equation

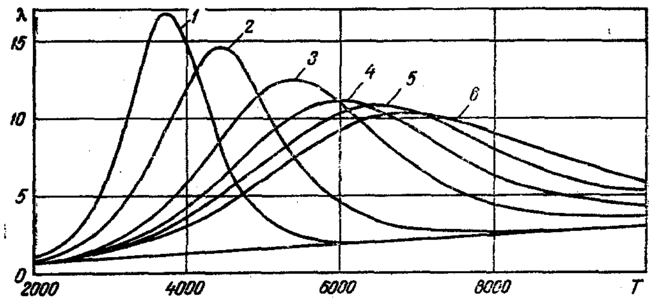

Fig. 2. Thermal conductivity (W/m · deg) of dissociated hydrogen: 1) 1 bar; 2) 10; 3) 10^2; 4) $3 \cdot 10^2$; 5) $6 \cdot 10^2$; 6) 10^3 bars.T, °K.

TABLE 2. Diffusion Coefficient $D \cdot 10^3$ (m^2/sec) of Dissociated Hydrogen at a Pressure of 1 Bar

T, K	D_{11}	D_{22}	D_{12}	T, K	D_{11}	D_{22}	D_{12}
2000	5,74	3,84	6,28	6200	45,3	31,7	54,5
2200	6,84	4,57	7,50	6400	75,2	33,7	58,0
2400	8,05	5,37	8,84	6600	50,6	35,7	61,7
2600	9,35	6,23	10,3	6800	53,4	37,8	65,4
2800	10,7	7,15	11,8	7000	56,3	40,0	69,2
3000	12,2	8,12	13,5	7200	58,7	42,2	73,2
3200	13,8	9,16	15,2	7400	62,1	44,5	77,3
3400	15,4	10,2	17,1	7600	65,3	46,8	81,5
3600	17,1	11,4	19,1	7800	68,8	49,2	85,8
3800	18,9	12,6	21,1	8000	72,4	51,6	90,2
4000	20,8	13,9	23,3	8200	76,0	54,1	94,6
4200	22,7	15,2	25,6	8400	79,7	56,7	99,3
4400	24,7	16,6	28,0	8600	83,5	59,4	104,1
4600	26,7	18,0	30,5	8800	87,4	62,1	108,9
4800	28,8	19,5	33,1	9000	91,3	64,8	114,0
5000	31,0	21,1	35,8	9200	95,4	67,6	119,1
5200	33,2	22,7	38,7	9400	99,6	70,5	124,3
5400	35,4	24,4	41,6	9600	103,7	73,4	129,8
5600	37,8	26,1	44,7	9800	108,1	76,4	135,2
5800	40,2	27,9	47,8	10000	112,6	79,5	140,8
6000	42,7	29,8	51,1				

TABLE 3. Viscosity $\eta \cdot 10^5$ (N · sec/m^2) of Dissociated Hydrogen

T, K	p, bars								
	1	10	100	200	300	400	600	800	1000
2000	3,18	3,18	3,18	3,18	3,18	3,18	3,18	3,18	3,18
2200	3,42	3,42	3,42	3,42	3,42	3,42	3,42	3,42	3,42
2400	3,66	3,66	3,66	3,66	3,66	3,66	3,66	3,66	3,66
2600	3,92	3,90	3,90	3,90	3,90	3,90	3,90	3,90	3,90
2800	4,23	4,18	4,15	4,14	4,14	4,14	4,14	4,14	4,14
3000	4,47	4,42	4,40	4,40	4,39	4,39	4,39	4,39	4,39
3200	4,76	4,69	4,65	4,64	4,64	4,64	4,64	4,64	4,64
3400	5,01	5,00	4,91	4,90	4,89	4,89	4,88	4,88	4,88
3600	5,19	5,25	5,17	5,15	5,14	5,14	5,13	5,13	5,13
3800	5,27	5,51	5,44	5,41	5,40	5,40	5,39	5,38	5,38
4000	5,27	5,75	5,71	5,68	5,66	5,66	5,64	5,64	5,63
4200	5,25	5,93	5,98	5,95	5,93	5,92	5,91	5,90	5,89
4400	5,27	6,05	5,25	6,22	6,20	6,19	6,17	6,16	6,15
4600	5,32	6,11	6,50	6,49	6,47	6,46	6,44	6,42	6,41
4800	5,41	6,14	6,73	6,74	6,73	6,72	6,70	6,69	6,68
5000	5,53	6,15	6,92	6,98	6,99	6,98	6,97	6,95	6,94
5200	5,67	6,18	7,09	7,20	7,22	7,23	7,23	7,22	7,21
5400	5,83	6,23	7,21	7,39	7,44	7,47	7,48	7,48	7,47
5600	5,99	6,30	7,31	7,55	7,64	7,68	7,71	7,72	7,72
5800	6,17	6,41	7,38	7,68	7,80	7,87	7,93	7,95	7,96
6000	6,35	6,54	7,45	7,79	7,95	8,04	8,13	8,17	8,19
6200	6,54	6,69	7,52	7,89	8,08	8,19	8,31	8,38	8,41
6400	6,73	6,85	7,59	7,97	8,19	8,32	8,48	8,56	8,61
6600	6,93	7,03	7,67	8,05	8,28	8,44	8,62	8,73	8,80
6800	7,13	7,21	7,77	8,14	8,38	8,54	8,75	8,88	8,97
7000	7,33	7,39	7,88	8,23	8,47	8,64	8,87	9,02	9,12
7200	7,52	7,58	8,00	8,33	8,56	8,74	8,98	9,15	9,26
7400	7,72	7,76	8,13	8,43	8,66	8,83	9,09	9,26	9,39
7600	7,92	7,96	8,28	8,55	8,76	8,94	9,19	9,38	9,52
7800	8,12	8,15	8,43	8,68	8,88	9,04	9,30	9,49	9,63
8000	8,32	8,34	8,59	8,81	9,00	9,16	9,41	9,60	9,75
8200		8,54	8,75	8,96	9,13	9,28	9,52	9,71	9,86
8400		8,73	8,92	9,10	9,26	9,40	9,64	9,82	9,98
8600		8,93	9,10	9,26	9,41	9,54	9,76	9,94	10,1
8800		9,13	9,28	9,43	9,56	9,68	9,89	10,1	10,2
9000		9,33	9,46	9,60	9,72	9,83	10,0	10,2	10,3
9200		9,53	9,65	9,77	9,88	9,99	10,2	10,3	10,5
9400		9,73	9,84	9,95	10,0	10,1	10,3	10,5	10,6
9600		9,93	10,0	10,1	10,2	10,3	10,5	10,6	10,7
9800		10,1	10,2	10,3	10,4	10,5	10,6	10,8	10,9
10000		10,3	10,4	10,5	10,6	10,6	10,8	10,9	10,0

TABLE 4. Thermal Conductivity λ(W/m·deg) of Dissociated Hydrogen

T, K	p, bars								
	1	10	100	200	300	400	600	800	1000
2000	0,905	0,839	0,816	0,816	0,804	0,804	0,804	0,804	0,804
2200	1,19	0,983	0,914	0,904	0,904	0,893	0,893	0,893	0,893
2400	1,75	1,21	1,04	1,02	1,01	1,00	0,992	0,992	0,992
2600	2,75	1,60	1,21	1,17	1,14	1,13	1,11	1,11	1,10
2800	4,42	2,20	1,46	1,36	1,32	1,30	1,26	1,25	1,23
3000	6,87	3,11	1,80	1,63	1,56	1,51	1,46	1,42	1,41
3200	10,0	4,40	2,28	1,99	1,87	1,79	1,70	1,65	1,61
3400	13,4	6,07	2,90	2,46	2,27	2,15	2,01	1,93	1,87
3600	16,0	8,08	3,69	3,06	2,77	2,60	2,39	2,28	2,19
3800	16,7	10,3	4,64	3,77	3,38	3,14	2,86	2,69	2,58
4000	15,1	12,3	5,74	4,61	4,09	3,78	3,41	3,18	3,02
4200	12,0	13,9	6,95	5,57	4,92	4,52	4,04	3,74	3,54
4400	8,85	14,6	8,22	6,60	5,81	5,33	4,74	4,37	4,12
4600	6,39	14,2	9,46	7,68	6,77	6,20	5,49	5,06	4,75
4800	4,71	13,0	10,6	8,73	7,74	7,10	6,29	5,78	5,42
5000	3,66	11,2	11,4	9,70	8,68	7,99	7,10	6,53	6,13
5200	3,02	9,30	12,0	10,5	9,54	8,84	7,89	7,28	6,83
5400	2,64	7,60	12,2	11,1	10,3	9,59	8,65	8,00	7,53
5600	2,42	6,21	12,0	11,5	10,8	10,2	9,33	8,68	8,19
5800	2,30	5,16	11,5	11,6	11,2	10,7	9,90	9,28	8,80
6000	2,24	4,38	10,7	11,5	11,3	11,0	10,3	9,75	9,29
6200	2,22	3,83	9,85	11,1	11,2	11,1	10,6	10,1	9,73
6400	2,23	3,45	8,92	10,5	10,9	11,0	10,8	10,4	10,1
6600	2,25	3,18	8,01	9,84	10,5	10,8	10,8	10,5	10,3
6800	2,29	3,01	7,18	9,11	9,97	10,4	10,6	10,6	10,4
7000	2,33	2,89	6,45	8,37	9,36	9,90	10,4	10,5	10,4
7200	2,38	2,82	5,83	7,67	8,73	9,36	10,0	10,2	10,3
7400	2,43	2,78	5,32	7,03	8,10	8,80	9,58	9,94	10,1
7600	2,48	2,76	4,91	6,47	7,51	8,23	9,12	9,58	9,83
7800	2,54	2,77	4,57	5,97	6,97	7,69	8,64	9,18	9,51
8000	2,59	2,78	4,30	5,56	6,48	7,19	8,16	8,77	9,15
8200		2,80	4,10	5,20	6,06	6,73	7,70	8,34	8,77
8400		2,84	3,94	4,91	5,69	6,32	7,27	7,93	8,40
8600		2,88	3,81	4,67	5,38	5,97	6,87	7,53	8,02
8800		2,92	3,72	4,48	5,12	5,66	6,52	7,16	7,66
9000		2,97	3,66	4,33	4,90	5,39	6,20	6,83	7,32
9200		3,02	3,62	4,20	4,72	5,17	5,92	6,52	7,00
9400		3,07	3,59	4,11	4,57	4,98	5,68	6,24	6,71
9600		3,12	3,58	4,04	4,45	4,82	5,47	6,00	6,45
9800		3,18	3,58	3,98	4,35	4,69	5,29	5,79	6,21
10000		3,23	3,59	3,95	4,28	4,59	5,17	5,60	6,00

$$D_{12}=\frac{2.6628\sqrt{T^3\dfrac{M_1+M_2}{2M_1M_2}}}{p\,\overline{\Omega_{12}^{(1,1)}}}\;10^{-7}\left(\frac{\mathrm{m}^2}{\mathrm{sec}}\right), \tag{1}$$

where M_1 and M_2 are the molecular weights of components 1 and 2, T is the temperature in °K, p is the total pressure in bars, $\Omega_{12}^{(1,1)}$ is the diffusion collision integral in Å^2. The self-diffusion coefficient is also defined by Eq. (1), allowing for the fact that the components are identical.

The viscosity of the binary mixture may be calculated from

$$\eta_{\mathrm{mix}}=\left[\frac{x_1^2}{H_{11}}+\frac{x_2^2}{H_{22}}-\frac{2x_1x_2H_{12}}{H_{11}H_{22}}\right]\Big/\left[1-\frac{H_{12}^2}{H_{11}H_{22}}\right], \tag{2}$$

where

$$H_{11}=\frac{x_1^2}{\eta_1}+\frac{2x_1x_2}{M_1+M_2}\cdot\frac{RT}{pD_{12}}\left[1+\frac{3M_2A_{12}^*}{5M_1}\right],$$

$$H_{12}=-\frac{2x_1x_2}{M_1+M_2}\cdot\frac{RT}{pD_{12}}\left[1-\frac{3}{5}A_{12}^*\right].$$

H_{22} may be derived from H_{11} by a change of indices; A_{12}^* is a function of the collision integrals; η_1, η_2 are the viscosities of atomic and molecular hydrogen; D_{12} is the first approximation to the mutual diffusion coefficient of H_1 and H_2 at the pressure in question.

The quantities η_1 and η_2 are determined from

$$\eta_i=\frac{2.6693\sqrt{M_iT}}{\overline{\Omega_{ii}^{(2,2)}}}\cdot 10^{-6}\left(\frac{\mathrm{kg}}{\mathrm{m\cdot sec}}\right), \tag{3}$$

where $\overline{\Omega_{ii}^{(2,2)}}$ is the collision integral in Å^2.

TABLE 5. Maximum Values of the Thermal Conductivity λ_{max} (W/m · deg) of Dissociated Hydrogen

p, bars	1,0	10	10^2	$2 \cdot 10^2$	$3 \cdot 10^2$	$4 \cdot 10^2$	$6 \cdot 10^2$	$8 \cdot 10^2$	10^3
T, K	3760	4420	5400	5800	6000	6200	6500	6700	6900
λ_{max}	16,7	14,7	12,2	11,6	11,3	11,1	10,9	10,6	10,5

The thermal conductivity in dissociated gas mixtures may conveniently be expressed as the sum of three components,

$$\lambda_{mix} = \lambda^0_{mix} + \lambda_{in.\,mix} + \lambda_{r\,mix} \tag{4}$$

In this expression λ^0_{mix} is the component of the thermal conductivity of the gas mixture solely due to the progressive motion of the atoms and molecules, i.e., it is here assumed that the mixture consists of different monatomic gases; $\lambda_{in.mix}$ is the component due simply to the presence of internal degrees of freedom (vibrational and rotational) in the molecules; λ_{rmix} is the component of the thermal conductivity of the mixture which allows for heat transfer due to the dissociation reaction.

Let us consider each of the components individually.

For a mixture consisting of two monatomic components the expression for the thermal conductivity of the gases based on the strict kinetic theory takes the form

$$\lambda^0_{mix} = -4\left[\frac{x_1^2}{L_{11}} + \frac{x_2^2}{L_{22}} - \frac{2x_1x_2L_{12}}{L_{11}L_{22}}\right] \Big/ \left[1 - \frac{L_{12}^2}{L_{11}L_{22}}\right], \tag{5}$$

where

$$L_{11} = -\frac{4x_1^2}{\lambda_1^0} - \frac{16}{25} \cdot \frac{x_1x_2}{(M_1+M_2)^2} \cdot \frac{T}{pD_{12}}\left[\frac{15}{2}M_1^2 + \frac{25}{4}M_2^2 - 3M_2^2B_{12}^* + 4M_1M_2A_{12}^*\right],$$

$$L_{12} = \frac{16}{25} \cdot \frac{x_1x_2M_1M_2}{(M_1+M_2)^2} \cdot \frac{T}{pD_{12}}\left[\frac{55}{4} - 3B_{12}^* - 4A_{12}^*\right],$$

L_{22} is obtained from L_{11} by a change of indices; A_{12}^* and B_{12}^* are functions of the collision integrals; λ_i^0 is the first approximation to the thermal conductivity of component i, if this is regarded as a monatomic gas.

The value of λ_i^0 is calculated by means of the equation

$$\lambda_i^0 = \frac{15}{4} \cdot \frac{R}{M_i}\eta_i, \tag{6}$$

where η_i is the viscosity of the pure gas i.

The component $\lambda_{in.mix}$ of the thermal conductivity of dissociated hydrogen (solely due to the presence of internal degrees of freedom) is

$$\lambda_{in.\,mix} = \frac{pD_{22}\left(c_{R2} - \frac{5}{2}R\right)}{RT\left(1 + \frac{x_1}{x_2} \cdot \frac{D_{22}}{D_{12}}\right)}. \tag{7}$$

Equation (7) is valid on assuming that at every point of the mixture the composition is in equilibrium with the temperature, i.e., local chemical equilibrium is maintained.

The component of the thermal conductivity due to the occurrence of the reaction $H_2 \rightleftharpoons 2H_1$ takes the form

$$\lambda_{r\,mix} = \frac{pD_{12}(\Delta H)^2}{R^2T^3}\left[\frac{x_1x_2}{(x_2+1)^2}\right]; \tag{8}$$

where ΔH is the heat of the reaction at constant pressure, referred to 1 mole.

For an ideal gas ΔH is independent of pressure

$$\Delta H = 2(H^0 - H_0^0)_1 - (H^0 - H_0^0)_2 + D_0^0.$$

Here the upper index 0 means that the reaction under consideration is taking place at p = 1 bar; D_0^0 is the hydrogen dissociation energy; $(H^0 - H_0^0)_i$ is the difference between the enthalpies of an ideal gas for a pressure of 1 bar at the current temperature T and at zero temperature T = 0°K, respectively, for the component i.

We see from the relationships presented that the viscosities and thermal conductivities of the gas mixtures depend on their composition; hence, when calculating the transfer coefficients in the region of hydrogen dissociation, allowance must be made for the influence of the real nature of the gas on the composition of the reacting mixture.

Data regarding the composition of dissociated hydrogen (with due allowance for its real nature) up to 6000°K were presented in [1]. For T > 6000°K we calculated the composition on the basis of a reacting mixture of ideal gases, since the influence of the real nature of the gases on the composition is negligibly slight at these high temperatures. Table 1 gives the molar proportion of the molecular component H_2 of the mixture used in the present investigation. Thus the transfer coefficients of dissociated hydrogen were calculated on the basis of the strict kinetic theory of transfer phenomena for mixtures of ideal gases, but allowing for the influence of the real nature of the gas on the composition of the mixture.

The accuracy of the calculations presented below may be estimated at 10%, but close to the sharp thermal-conductivity maxima, 20%, these errors being mainly due to the fact that the potential functions used for the interaction of the atoms and molecules ($H_1 - H_2$) are insufficiently accurate.

The results of our calculations for the self-diffusion coefficients of the atomic component (D_{11}) and the molecular component (D_{22}), as well as the mutual diffusion of the atomic and molecular components of the mixture (D_{12}) at a pressure of 1 bar, are presented in Table 2.

The viscosities and thermal conductivities for various pressures from 1 to 1000 bars are shown in Tables 3 and 4 and Figs. 1 and 2. Table 5 gives the maximum values $\lambda_{\max}$ of the thermal conductivity for corresponding temperatures and pressures.

In the present investigation we also calculated the transfer coefficients without allowing for the effect of the real nature of the gases on the composition of the dissociated hydrogen. On comparing the results of calculations based on the two principles we found that allowing for the effect of the real nature of the components on the composition of the mixture of reacting hydrogen at pressures of 100-1000 bars reduced the thermal conductivity by up to 4%, while the viscosity discrepancy was far smaller.

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