TRANSFER COEFFICIENTS OF MONATOMIC GASES IN THE TEMPERATURE RANGE 100-3000°K

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Viscosity, thermal-conductivity, and self-diffusion coefficients are calculated for monatomic gases at a pressure of 1 bar and temperatures of 100-3000°K for the (12-7) model potential. The calculated results are compared with experimental data.

To calculate the thermophysical properties of gases and liquids it is necessary to know the intermolecular interaction potential. For gases and liquids of spherical nonpolar molecules the most widely used potential until very recently was the Lennard-Jones (12-6) [1]. However, experiments with molecular beams [2-4], spectroscopic studies of dimers [5], and analysis of improved data on the second virial coefficient [6, 7] and viscosity [8-15] performed in recent years have demonstrated convincingly that the true pair potential of monatomic gases is deeper at the minimum and steeper at large distances than the (12-6) potential. It has also been shown [16, 17] that for the Lennard-Jones (n-6), Kikhara (12-6, γ) and Buckingham (exp-6) model potentials, force constants may be chosen such that one or another property of a monatomic gas may be described over some temperature interval. However, these potentials cannot describe in a consistent (with unique constant values for each gas) manner various experimental data over the entire range of measurements; i.e., for these models the law of corresponding states is not fulfilled.

Due to this, in the last ten years a number of new models of the paired-interaction potential have been studied [18-20]. The most varied analytical forms have been used for the repulsive energy, in many cases with a large number of freely variable parameters. For the attractive energy the first (London, $-c_6r^{-6}$) or several first terms of the expansion for dispersion energy [1, 21] are used. The expression

$$\varphi_{\mathrm{disp}}(r) = -c_6r^{-6} - c_3r^{-8} - c_{10}r^{-10} - \ldots \tag{1}$$

is asymptotically valid for large intermolecular distances which are still smaller than the characteristic length $\lambda = (\alpha\Delta\varepsilon)^{-1}$ for delayed forces [22].

Analysis has shown that none of these models in which theoretical values of the coefficients c_6, c_8, and c_{10} are taken [23] has any advantage over the Lennard-Jones, Kikhara, or Buckingham potentials. In particular, as before, it is impossible to consistently describe not only various experimental data, but also the rapid change of the second virial coefficient at low temperatures [20]. This may be because series (1) diverges over the entire distance range where "delay" effects may be neglected [24].

A sufficiently accurate description of heterogeneous experimental data over a wide temperature range can be attained with the (n-6-8) Klein–Hanley potential [25, 26]:

$$\varphi(r) = \varepsilon\left[\frac{6+2\gamma}{n-6}\left(\frac{r_m}{r}\right)^n - \frac{n-\gamma(n-8)}{n-6}\left(\frac{r_m}{r}\right)^6 - \gamma\left(\frac{r_m}{r}\right)^8\right], \tag{2}$$

in which for monatomic gases and methane $n=11$ and $\gamma=3$. In this case the coefficient c_6 in Eq. (2) is three times smaller, while c_8 is seven times larger, than the corresponding theoretical values [23].

In [27, 28] the model potential of Mi (n-m) with $n \geq 9$ and $m = 6, 7, 8$ was considered. Analysis has shown that the (12-7) potential

$$\varphi(r) = 5.104\varepsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^7\right] \tag{3}$$

consistently (i.e., with one and the same constant values) describes the various properties of gases formed of spherical nonpolar molecules over the entire measurement range within the limits of divergence of experimental results of various authors; i.e., for the (12-7) potential the law of corresponding states is satisfied.

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TABLE 1. Force Constants of the (12-7) Potential

Constant	Gas				
	helium	neon	argon	krypton	xenon
$\frac{\varepsilon}{k}$, °K	10,2	45,0	152	214	295
$\sigma \cdot 10^8$, cm	2,537	2,724	3,304	3,511	3,845

TABLE 2. Coefficient of Dynamic Viscosity of Monatomic Gases at a Pressure of 1 bar, $\mu \cdot 10^7$ (Pa · sec)

T, °K	Helium	Neon	Argon	Krypton	Xenon
100	100,0	143,4	81,5	—	—
120	112,6	165,9	97,4	106.1	—
160	135,5	205,9	128,8	140,6	126,0
200	156,3	241,4	159,2	174,7	156.5
240	175,7	273,7	188,1	208,3	187,0
280	193,9	303,7	215,4	241,0	217,4
300	202,7	318,0	228,4	257,0	232,4
320	211,3	331,9	241,1	272,3	247,3
360	227,9	358,7	265,4	302,8	276,7
400	243,8	384,2	288,5	331,9	305,4
500	281,4	444,1	341,8	399,6	373,6
600	316,5	499,5	390,2	461,2	437,0
700	349,6	551,4	434,8	518,0	495.8
800	381,0	600,7	476,7	571,1	550,9
900	411,3	647,8	516,3	621,0	608,7
1000	440,3	693,0	554,0	668,5	651,8
1200	495,6	778,9	624,9	757,4	743,5
1400	547,8	859,7	691,1	839,9	828,1
1600	597,5	936,6	753,7	917,6	907,5
1800	645,2	1010	813,3	991,4	982,5
2000	691,1	1081	870,4	1062	1054
2200	735,4	1149	925,4	1130	1123
2400	778,4	1215	978,4	1195	1189
2600	821,2	1280	1030	1258	1253
2800	860,9	1342	1080	1320	1315
3000	900,7	1403	1129	1380	1375

In the intermediate distance range the (12-7) potential agrees with experimental results on beam scattering in the thermal energy interval. This is indicated by the good agreement of force constants and curvature at the minimum point of the (12-7) potential with values obtained in beam experiments [2-4].

The force constants of the (12-7) potential are presented in Table 1. They are defined from the condition of minimum deviation of calculated values of the second virial coefficient, transfer coefficients (viscosity, thermal conductivity, and self-diffusion), and the compressibility factor from corresponding experimental values. Inclusion of data on compressibility is desirable for two reasons. First, the value of the compressibility factor $Z = PV/RT$ is more sensitive to the value of the force constants of the paired potential (especially the constant σ) than are transfer properties or the second virial coefficient. Second, especially in the case of light gases, measurements of compressibility can be performed with higher accuracy than is the case for any other property. Thus, for helium the divergence in the compressibility factor among the various authors comprises 0.5-2.0% (depending on temperature), while for transfer properties and the second virial coefficient the divergence is 2-10% [29]. It must be noted that previously in [27] data on compressibility were not analyzed, and the influence of quantum effects was not considered in calculating the second virial coefficient. The refined values of the force constants (Table 1) differ from those published previously [27] by a maximum of 2%.

A review and analysis of experimental data on properties of monatomic gases was presented in [16, 17, 26, 29]. In the present study, in determining the force constants of the (12-7) potential, generalized experimental data from [6, 7] were used. The measurements of Smith et al. [8-10] were used for viscosity for temperatures from 120 to 1600°K and those of Guevara et al. [11-15] were used for 1100 to 2100°K. These results encompass the widest temperature range and are used for study of various potential models [18-20]. For the compressibility factor experimental data of [30-35] were used, covering a wide temperature ($T^* = 2$-46) and density ($\rho b_0 \leq 2$, $b_0 = {}^2\!/_3 \pi \tilde{N} \sigma^3$) range and considered the most reliable available [16, 17].

The calculations used standard formulas of the molecular theory of gases [1]. The virial-coefficient values presented for the (12-7) potential were calculated in [36] and the quantum corrections in [37]. The compressibility factor was calculated with a semiempirical equation of state of a dense gas with consideration of nonadditivity and quantum effects [38]. At high normalized temperatures ($T^* \geq 10$), corresponding to com-

TABLE 3. Thermal-Conductivity Coefficient of Monatomic Gases at a Pressure of 1 bar, $\lambda \cdot 10^{-2}$ ($W \cdot m^{-1°} \cdot K^{-1}$)

T, °K	Helium	Neon	Argon	Krypton	Xenon
100	0,780	0,2217	0,0637		
120	0,878	0,2564	0,0760	0,0395	
160	1,056	0,3183	0,1006	0,0523	0,0299
200	1,219	0,3732	0,1244	0,0650	0,0372
240	1,370	0,4231	0,1469	0,0776	0,0444
280	1,512	0,4694	0,1682	0,0897	0,0516
300	1,580	0,4915	0,1784	0,0957	0,0552
320	1,647	0,5130	0,1883	0,1015	0,0588
360	1,776	0,5544	0,2073	0,1127	0,0657
400	1,900	0,5940	0,2254	0,1236	0,0726
500	2,194	0,6865	0,2670	0,1488	0,0888
600	2,467	0,7721	0,3048	0,1717	0,1038
700	2,725	0,8524	0,3396	0,1929	0,1178
800	2,971	0,9286	0,3723	0,2126	0,1309
900	3,206	1,001	0,4032	0,2312	0,1432
1000	3,432	1,071	0,4327	0,2489	0,1549
1200	3,863	1,204	0,4881	0,2820	0,1767
1400	4,270	1,329	0,5398	0,3127	0,1968
1600	4,658	1,448	0,5887	0,3416	0,2156
1800	5,029	1,562	0,6352	0,3691	0,2335
2000	5,387	1,671	0,6798	0,3953	0,2509
2200	5,733	1,777	0,7228	0,4206	0,2668
2400	6,068	1,879	0,7643	0,4449	0,2825
2600	6,394	1,979	0,8045	0,4686	0,2976
2800	6,711	2,075	0,8437	0,4914	0,3124
3000	7,021	2,170	0,8818	0,5137	0,3267

TABLE 4. Self-diffusion Coefficient of Monatomic Gases at a Pressure of 1 bar, D ($cm^2 \cdot sec^{-1}$)

T, °K	Helium	Neon	Argon	Krypton	Xenon
100	0,2684	0,0752	0,0220		
120	0,3632	0,1045	0,0315	0,0164	
160	0,5846	0,1730	0,0553	0,0289	0,0165
200	0,8450	0,2541	0,0850	0,0448	0,0257
240	1,142	0,3466	0,1201	0,0639	0,0368
280	1,472	0,4495	0,1601	0,0859	0,0498
300	1,650	0,5048	0,1818	0,0980	0,0569
320	1,835	0,5624	0,2045	0,1107	0,0646
360	2,228	0,6848	0,2532	0,1382	0,0811
400	2,651	0,8163	0,3057	0,1679	0,0992
500	3,832	1,183	0,4532	0,2523	0,1510
600	5,177	1,599	0,6218	0,3495	0,2115
700	6,678	2,064	0,8099	0,4584	0,2797
800	8,326	2,573	1,016	0,5782	0,3552
900	10,12	3,125	1,240	0,7082	0,4374
1000	12,04	3,719	1,481	0,8481	0,5260
1200	16,19	5,023	2,009	1,156	0,7212
1400	21,00	6,478	2,598	1,498	0,9389
1600	26,20	8,074	3,243	1,874	1,178
1800	31,84	9,806	3,942	2,281	1,437
2000	37,91	11,67	4,693	2,718	1,715
2200	44,39	13,65	5,495	3,185	2,012
2400	51,27	15,76	6,345	3,679	2,326
2600	58,54	17,99	7,242	4,201	2,659
2800	66,19	20,41	8,185	4,471	2,831
3000	74,21	22,78	9,172	5,324	3,372

pressibility measurements in helium, the empirical term in the equation becomes negligibly small. In calculating the transfer coefficients, quantum effects were not considered. Collision integrals for the (12-7) potential are presented in [39, 40]; transfer coefficient corrections to higher approximations may be found in [28].

The force constants of the (12-7) potential determined in this manner were used to calculate the coefficients of viscosity, thermal conductivity, and self-diffusion of monatomic gases in the temperature range 100-3000°K (Tables 2-4).

The calculated results are compared with experimental data on various properties of monatomic gases in Table 5. Aside from the experimental values used in obtaining the force constants, Table 5 presents the results of comparison with data obtained by generalizing viscosity and thermal-conductivity experiments at temperatures to 1300°K [17, 42] and with data from the most recent thermal-conductivity measurements at temperatures up to 2700°K [43-47]. For all gases the divergence between calculated and experimental values is smaller than for the other model potentials.

TABLE 5. Comparison of (12-7) Model Potential Values of Various Monatomic Gas Properties with Experimental Data

Gas	Characteristic	P, bar	T, °K	T^*	Maximum deviation	Mean deviation	Literature cited
Helium	Viscosity coefficient	1	120—1600	11,8—157	6,5 %	3,0 %	[9,10]
	Viscosity coefficient	1	476—2344	46,7—230	3,5 %	1,9 %	[11]
	Viscosity coefficient	1	1100—2100	108—206	8,9 %	7,7 %	[12]
	Viscosity coefficient	1	100—1200	9,8—118	2,6 %	1,5 %	[42]
	Thermal-conductivity coefficient	1	400—2200	39,2—216	5,0 %	2,3 %	[43]
	Thermal-conductivity coefficient	1	400—2300	39,2—226	8,7 %	6,0 %	[47]
	Second virial coefficient	—	100—600	9,8—58,8	0,85 cm^3/mole	0,35 cm^3/mole	[6]
	Compressibility factor	1—1000	113—273	11,1—26,8	0,70 %	0,15 %	[30]
	Compressibility factor	1000—7000	293—423	28,7—41,2	1,2 %	0,60 %	[31]
Neon	Viscosity coefficient	1	120—1600	2,67—35,6	1,6 %	1,1 %	[9,10]
	Viscosity coefficient	1	1100—2100	24,4—46,6	3,5 %	2,8 %	[14]
	Viscosity coefficient	1	100—1300	2,22—28,9	2,2 %	1,0 %	[17]
	Thermal-conductivity coefficient	1	100—1300	2,22—28,9	2,2 %	1,0 %	[17]
	Thermal-conductivity coefficient	1	373—2723	8,30—60,5	2,9 %	1,9 %	[44[
	Second virial coefficient	—	40—1000	0,89—22,2	0,7 cm^3/mole	0,4 cm^3/mole	[6,41]
	Compressibility factor	1—2027	90—130	2,00—2,92	1,0 %	0,55 %	[32]
	Compressibility factor	1—2710	273—423	6,07—9,40	0,35 %	0,15 %	[33]
Argon	Viscosity coefficient	1	120—1600	0,74—10,5	1,1%	0,3%	[8,10]
	Viscosity coefficient	1	1100—2100	6,80—13,8	2,9%	2,6%	[12]
	Viscosity coefficient	1	100—1300	0,66—8,55	2,7%	0,7%	[17]
	Thermal-conductivity coefficient	1	100—1300	0,66—8,55	2,7%	0,7%	[17]
	Thermal-conductivity coefficient	1	350—2500	2,30—16,5	2,1%	1,0%	[45]
	Second virial coefficient	—	80—1000	0,53—6,58	0,6 cm^3/mole	0,3 cm^3/mole	[6]
	Compressibility factor	1—10000	308—673	2,03—4,32	0,75%	0,25%	[17,34]
Krypton	Viscosity coefficient	1	140—1600	0,65—7,48	1,4%	1,0%	[8,10]
	Viscosity coefficient	1	1100—2000	5,14—9,35	0,5%	0,4%	[13]
	Viscosity coefficient	1	120—1300	0,56—6,08	2,5%	1,0%	[17]
	Thermal-conductivity coefficient	1	120—1300	0,56—6,08	2,5%	1,0%	[17]
	Thermal-conductivity coefficient	1	400—2500	1,87—11,7	4,4%	2,0%	[46]
	Second virial coefficient	—	110—1100	0,51—5,14	1,2 cm^3/mole	0,3 cm^3/mole	[6]
	Compressibility factor	1—3040	423	1,98	0,80%	0,40%	[35]
Xenon	Viscosity coefficient	1	160—1600	0,54—5,43	1,1%	0,5%	[8,10]
	Viscosity coefficient	1	1100—2000	3,74—6,78	2,0%	1,7%	[15]
	Viscosity coefficient	1	170—1300	0,58—4,41	2,6%	0,7%	[17]
	Thermal-conductivity coefficient	1	170—1300	0,58—4,41	2,6%	0,7%	[17]
	Second virial coefficient	—	275—1000	0,93—3,37	3,6 cm^3/mole	2,6 cm^3/mole	[6]

NOTATION

D, diffusion coefficient at pressure of 1 bar; k, Boltzmann's constant; P, pressure; T, temperature; V, volume, Z = PV/RT, compressibility factor; r, distance between molecules; $\varphi(r)$, potential energy (potential) of intermolecular interaction; ε and σ, force constants of interaction potential; λ, thermal-conductivity coefficient at pressure of 1 bar; μ, dynamic-viscosity coefficient at pressure of 1 bar.

LITERATURE CITED

1. J. O. Hirschfelder et al., Molecular Theory of Gases and Liquids, Wiley-Interscience (1964).
2. M. Cavallini et al., Chem. Phys. Lett., 7, 303 (1970).
3. P. E. Siska et al., J. Chem. Phys., 55, 5762 (1971).
4. L. Kleinman and M. Wolfsberg, J. Chem. Phys., 61, 4366 (1974).
5. D. Freeman, K. Yoshino, and Y. Tanaka, J. Chem. Phys., 59, 5160 (1973).
6. D. E. Gray (editor), American Institute of Physics Handbook, McGraw-Hill, New York (1971).
7. J. H. Dymond and E. B. Smith, The Virial Coefficients of Gases. A Critical Compilation, Clarendon Press, Oxford (1969).
8. A. G. Clarke and E. B. Smith, J. Chem. Phys., 48, 3988 (1968).
9. A. G. Clarke and E. B. Smith, J. Chem. Phys., 51, 4156 (1969).
10. R. A. Dawe and E. B. Smith, J. Chem. Phys., 52, 693 (1970).
11. F. A. Guevara and W. E. Wageman, Los Alamos Sci. Lab. Rep. LA-3315 (1968) (cf. [16]).
12. F. A. Guevara, B. B. McInteer, and W. E. Wageman, Phys. Fluids, 12, 2493 (1969).
13. M. Goldblatt, F. A. Guevara, and B.B. McInteer, Phys.Fluids, 13, 2873 (1970).
14. F. A. Guevara and G. Stensland, Phys. Fluids, 14, 746 (1971).
15. M. Goldblatt and W. E. Wageman, Phys. Fluids, 14, 1024 (1971).

16. N. V. Tsedeberg, V. N. Popov, and N. A. Morozova, Thermodynamic and Thermophysical Properties of Helium [in Russian], Atomizdat, Moscow (1969).
17. V. A. Rabinovich, A. A. Vasserman, V. I. Nedostup, and L. S. Veksler, Thermophysical Properties of Neon, Argon, Krypton, and Xenon [in Russian], Standartov, Moscow (1976).
18. H. J. Hanley et al., Mol. Phys., 24, 11 (1972).
19. P. D. Neufeld and R. A. Aziz, J. Chem. Phys., 59, 2334 (1973).
20. E. B. Smith, Physica, 73, 211 (1974).
21. M. A. Michels and L. G. Suttorp, Physica, 61, 609 (1972).
22. W. J. Meath and J. O. Hirschfelder, J. Chem. Phys., 44, 3210 (1966).
23. G. Starkschall and R. G. Gordon, J. Chem. Phys., 56, 2801 (1972).
24. R. H. Young, Int. J. Quantum Chem., 9, 47 (1975).
25. M. Klein and H. J. Hanley, J. Chem. Phys., 53, 4722 (1970).
26. H. J. Hanley and M. Klein, J. Phys. Chem., 76, 1743 (1972).
27. R. M. Sevast'yanov and N. A. Zykov, Teplofiz. Vys. Temp., 9, 46 (1971).
28. R. M. Sevast'yanov and N. A. Zykov, Numerical Methods in Mechanics of Continuous Media. Models of the Medium [in Russian], Vol. 7 (1976), p. 150.
29. R. D. McCarthy, Nat. Bur. Stand. Tech. Note No. 631 (1972).
30. N. V. Tsederberg, V. N. Popov, and A. B. Kalenkov, Tr. Mosk. Énerg. Inst., 65, 234 (1975).
31. D. S. Tsiklis, V. Ya. Maslennikova, and S. Ya. Gluvka, Dokl. Akad. Nauk SSSR, 216, 769 (1974).
32. W. B. Street, J. Chem. Eng. Data, 16, 289 (1971).
33. A. Michels, T. Wassenaar, and G. Wolkers, Physica, 31, 237 (1965).
34. S. L. Robertson, S. E. Babb, and J. Scott, J. Chem. Phys., 50, 2160 (1969).
35. N. Trappeniers, T. Wassenaar, and G. Wolkers, Physica, 32, 1503 (1966).
36. R. M. Sevast'yanov and N. A. Zykov, Teplofiz. Vys. Temp., 9, 911 (1971).
37. S. D. Gavrilov, Zh. Fiz. Khim., 48, 1370 (1974).
38. R. M. Sevast'yanov and N. A. Zykov, Teplofiz. Vys. Temp., 14, No. 6 (1976).
39. V. Z. Svoiskii, Uch. Zap. Tsentr. Aero-Gidrodin Inst., 2, No. 5 (1971).
40. B. Schramm, Ber. Bunsenges. Phys. Chem., 73, 1045 (1969).
41. Yu. A. Dedikov, V. A. Medvedev, and M. P. Orlova, Zh. Fiz. Khim., 46, 2669 (1972).
42. I. F. Golubev and N. E. Gnezdilov, Viscosity of Gas Mixtures [in Russian], Standartov, Moscow (1970).
43. D. L. Timrot and A. S. Umanskii, Teplofiz. Vys. Temp., 3, No. 3 (1965).
44. B. J. Jody and S. C. Saxena, Phys. Fluids, 18, 20 (1975).
45. S. H. Chen and S. C. Saxena, Mol. Phys., 29, 455 (1975).
46. P. S. Jain and S. C. Saxena, J. Chem. Phys., 63, 5052 (1975).
47. P. S. Jain and S. C. Saxena, Chem. Phys. Lett., 36, 489 (1976).