TEMPERATURE DEPENDENCE OF THE DIFFUSION COEFFICIENTS OF GASES

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The use of empirical power laws to calculate the diffusion coefficients of gases is considered. The method of similitude is used to obtain generalized relations which permit the calculation of the diffusion coefficients of gases in temperature ranges not covered by experiment.

A number of equations have been recommended by various authors for calculating the diffusion coefficient in binary mixtures of gases. Some of these equations have a sound theoretical basis, some are semiempirical in character, and some are obtained by generalizing experimental results.

Rigorous kinetic theory [1, 2] leads to the relation

$$D = 0.002628\,\frac{\sqrt{T^3 (M_1+M_2)/2M_1M_2}}{P\sigma_{12}^2\,\Omega_{12}^{(1,1)*}(T_{12}^*)}\,. \tag{1}$$

Since collision integrals have been tabulated for several spherically symmetric intermolecular interaction potentials it is possible to calculate the diffusion coefficients for a number of nonpolar gases to adequate accuracy. It is very difficult to evaluate the collision integrals for nonsymmetric potential functions which depend on the angle of impact. Therefore the theory still does not permit the calculation of the diffusion coefficients of gases with polar and linear molecules.

The main limitations and assumptions of this theory are discussed in detail in [2], where it is noted, for example, that Eq. (1) is obtained rigorously for monatomic gases by taking account only of binary collisions of molecules. In spite of this it should be regarded as the most consistent at the present time, based on modern concepts of the nature of molecular processes.

The simplest and therefore the most satisfactory of the empirical equations is the familiar Winkelman relation

$$D = D_0 \left(\frac{T}{T_0}\right)^n \frac{P_0}{P}\,. \tag{2}$$

It follows from (1) and (2) that

$$n = \frac{3}{2} - \frac{\partial \lg \Omega_{12}^{(1,1)}}{\partial \lg T} = \frac{3}{2} - \frac{\partial \lg \Omega_{12}^{(1,1)*}}{\partial \lg T_{12}^*}\,. \tag{3}$$

Thus in any region where n = const we should expect a linear relation between the logarithm of the collision integral and the logarithm of the reduced temperature.

Such log–log graphs are shown in Fig. 1 for several models of the intermolecular interaction potential. Since the graphs are not straight lines the rigorous kinetic theory of gases does not permit us to consider n constant. Furthermore, for all models at high (and at very low) reduced temperatures, beginning approximately with T* = 5, these graphs can be considered straight lines with far greater justification. Therefore under these conditions Eq. (2) with constant n can be extrapolated with confidence.

Of course these conclusions apply only to those gases which can be described by spherically symmetric potential models.

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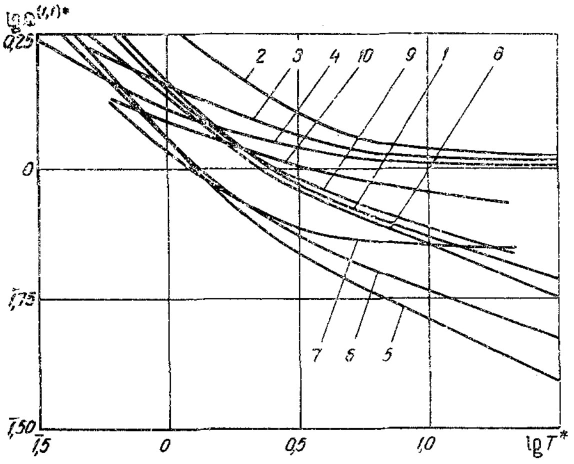

Fig. 1. Logarithm of reduced collision integral as a function of the logarithm of the reduced temperature: 1) Lennard–Jones model (6-12) [2]; 2) potential well model with 1/R = 0.4 [2]; 3) the same for 1/R = 0.6 [2]; 4) Sutherland model with attractive term proportional to the sixth power [2]; 5) modified Buckingham model with α = 12 [3]; 6) the same with α = 15 [3]; 7) Guggenheim–McGlashan model [4]; 8) Morse model with C = 6 [5]; 9) Kihara model with γ = 0.1 [4]; 10) the same with γ = 0.6 [4].

TABLE 1. Values of the Coefficients a and b in Eq. (5)

Binary mixture	a	b	S_1/R	Average spread of points, %
Monatomic gases	0,306	0,000	18,56	±3,5
Monatomic and diatomic gases	0,246	0,00079	19,46	3,5
Diatomic gases	0,209	0,00158	23,50	2,5
Diatomic and triatomic gases	0,175	0,0063	27,06	4,0
Certain polyatomic gases	0,185	0,0087	25,00	4,0

It is of interest to investigate the temperature dependence of the diffusion coefficients of gases by the similitude method. When this method is applied to molecular diffusion processes it leads to a functional relation convenient for generalization [6, 7]:

$$\frac{D}{D_{S_1}} = \varphi\left(\frac{S - S_1}{R}\right). \tag{4}$$

This relation was used to generalize the experimental data on the diffusion and self-diffusion coefficients of gases. The results of the generalization are shown in Fig. 2 as graphs of $\log D/D_{S_1}$ vs $(S - S_1)/R$. They show that Eq. (4) can be expressed in the form (Table 1):

$$\lg \frac{D}{D_{S_1}} = a\,\frac{S - S_1}{R} - b\left(\frac{S - S_1}{R}\right)^2. \tag{5}$$

If Eq. (4) is written in a form analogous to (2)

$$D = D_{S_1}\left(\frac{T}{T_{S_1}}\right)^n, \tag{6}$$

we obtain for the exponent

$$n = a\,\frac{2.3\mu c_{p_m}}{R} - b\left(\frac{2.3\mu c_{p_m}}{R}\right)^2 \lg \frac{T}{T_{S_1}}. \tag{7}$$

From other considerations a similar relation was obtained in [8] for monatomic gases

$$n = \alpha - \beta \lg T, \tag{8}$$

where α and β are constants.

Comparison shows that (8) is a special case of (7) when μc_{p_m} = const.

The generalized relations obtained were used to calculate the diffusion and self-diffusion coefficients of gases in temperature ranges not covered by experiment. A portion of these calculations can be approximated to ±3-4% by power laws of type (2). These are listed in Table 2. It is clear from the table

TABLE 2. Values of D_0, T_0, and n of Eq. (2) for P = 1 atm Obtained by Using the Generalized Relations

Gases		T_0, °K	D_0, cm^2/sec	n	Calculated temperature, °C
Monatomic and diatomic gases	He— air	273	0,630	1,71	—50— 700
Diatomic gases	H_2—air	273	0,660	1,74	—50—1000
		1273	9,86	1,91	1000—2700
	H_2—O_2	273	0,700	1,79	—50—1000
		1273	11,4	1,90	1000—2300
	H_2—N_2	273	0,700	1,74	—50—1000
		1273	10,4	1,91	1000—2500
	H_2—CO	273	0,651	1,75	—50—1000
		1273	9,85	1,89	1000—2500
	N_2—N_2	273	0,188	1,72	—50—1100
	O_2—O_2	273	0,187	1,75	—50— 600
	CO—CO	273	0,175	1,72	—50— 800
	N_2—CO	273	0,192	1,72	—50— 900
	O_2—N_2	273	0,181	1,72	—50— 800
	O_2— air	273	0,178	1,72	—50— 800
Diatomic and triatomic gases	N_2—CO_2	273	0,142	1,82	—50— 500
		773	0,952	1,60	500—1500
	O_2—CO_2	273	0,145	1,79	—50— 500
		773	0,888	1,59	500—1300
	CO—CO_2	273	0,137	1,74	—50— 500
		773	0,855	1,57	500—1500
	O_2—H_2O	273	0,232	1,78	0— 500
		773	1,43	1,56	500—1900
	Air—H_2O	273	0,229	1,87	0— 500
		773	1,56	1,59	500—2500

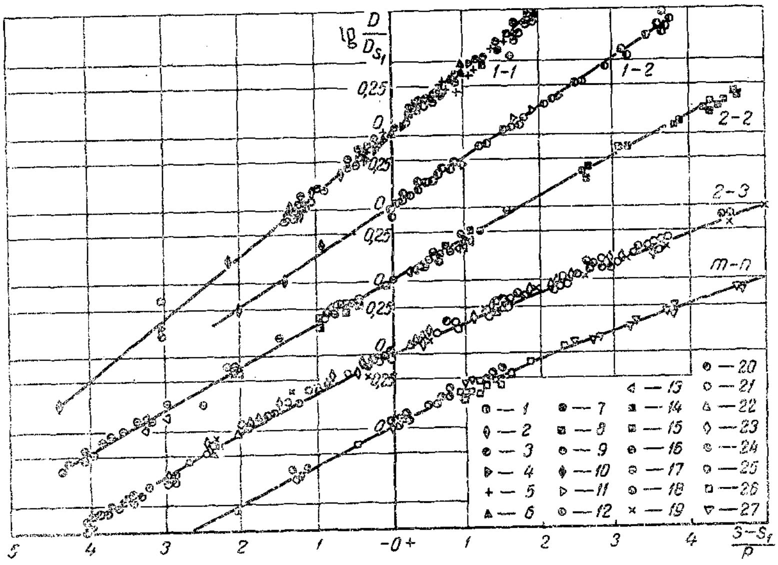

Fig. 2. Generalized relations for diffusion and self-diffusion coefficients of gases: 1-1) monatomic gases, $S_1/R = 18.56$; 1-2) monatomic and diatomic gases, $S_1/R = 19.46$; 2-2) diatomic gases, $S_1/R = 23.50$; 2-3) diatomic and triatomic gases, $S_1/R = 27.06$; m-n) certain polyatomic gases, $S_1/R = 25.00$: 1) Ne–Kr; 2) Ne–Ne; 3) Ar–Ar; 4) Ne–Kr; 5) Ar–Kr; 6) Kr–Kr; 7) Xe–Xe; 8) Ar–Xe; 9) He–Ar; 10) Ar–H_2; 11) Ar–N_2; 12) He–N_2; 13) H_2–O_2; 14) CO–O_2; 15) N_2–N_2; 16) O_2–O_2; 17) H_2–N_2; 18) CO_2–N_2; 19) CO_2–air; 20) H_2O–air; 21, 23) CO_2–N_2; 22) H_2O–O_2; 24) CO_2–CO_3; 25) CH_4–CH_4; 26) CO_2–N_2O; 27) CH_4–O_2.

that the temperature range in which n can be considered constant decreases as the molecular structure of the gases becomes more complex.

NOTATION

D is the diffusion coefficient, cm^2/sec;
P is the pressure, atm;

T	is the temperature, °K;
M_1, M_2	are the molecular weights of the component gases;
$\Omega_{12}^{(1,1)*}(T_{12}^*)$	is the reduced collision integral;
$T_{12}^* = kT/\varepsilon_{12}$	is the reduced temperature;
σ_{12}, ε_{12}/k	are the interaction potential parameters with units Å and °K, respectively.
D_0, T_0, P_0	are the scale values of the corresponding parameters under normal conditions;
D_{S_1}	is the scale diffusion coefficient corresponding to the scale value of the entropy S_1;
S	is the molar entropy, kJ/kmole · °C;
a, b	are parameters depending on the molecular structure of the diffusing gases;
μc_{p_m}	is the mean molar heat capacity, kJ/kmole · °K.

LITERATURE CITED

1. S. Chapman and T. Cowling, The Mathematical Theory of Nonuniform Gases Cambridge University Press, New York (1952).
2. J. O. Hirschfelder, C. F. Curtiss, and R. B. Bird, Molecular Theory of Gases and Liquids Liquids, Wiley, New York (1954).
3. E. A. Mason, J. Chem. Phys., 22, 169 (1954).
4. J. A. Barker, W. Fock, and F. Smith, Phys. Fluids, 7, 897 (1964).
5. J. Smith and R. J. Munn, J. Chem. Phys., 41, 3560 (1964).
6. A. G. Usmanov, in: Heat Transfer and Thermal Simulation [in Russian], Izd. AN SSSR (1959).
7. A. G. Usmanov and É. M. Nafikov, Proceedings of S. M. Kirov Kazan' Institute of Chemical Technology [in Russian], No. 31, 36 (1963).
8. M. J. Holleran, J. Chem Phys., 21, 2184 (1953).