USE OF THE LAW OF CORRESPONDING STATES TO GENERALIZE THE THERMODIFFUSION FACTOR OF INERT GAS MIXTURES

A. F. Zolotukhina, M. V. Sagarda, and E. A. Shashkov

UDC 536.23

The law of corresponding states is used to study the temperature and concentration dependence of the thermodiffusion factor α_t of six inert gas mixtures: He–Ne, He–Ar, He–Kr, He–Xe, Ne–Kr, Ne–Xe.

The main source of information on the thermodiffusion factor is experiment. Up to the present a large amount of experimental material on thermodiffusion in various gas systems has been published. The number of such studies continues to increase, but, considering the disparate character of the studies, orienting onself within such a large flow of information becomes ever more difficult. Moreover, analysis of data on the thermodiffusion factor available in the literature reveals that for the overwhelming majority of gas mixtures there has been no systematic study of α_t.

In order to systematize and generalize experimental results, similarity methods are often used. According to [1, 2] dimensionless description of the temperature dependence of transport coefficients from the viewpoint of phenomenological thermodynamic similarity theory is based on expressions of the form

$$\frac{Y}{Y^*} = f(\tau), \tag{1}$$

where Y is the value of the transport coefficient, Y* is a parameter with the dimensions of Y, composed of critical data or molecular parameters, and $\tau = T/T_{cr}$ ($\tau = \mathrm{T}k/\varepsilon$).

This method of reduction with molecular parameters was applied successfully in [1] to inert gases, and to other groups of gases whose molecules are chemically similar, since they satisfy the major assumption of the method — that the molecules are spherical and nonpolar.

In [3], on the basis of Eq. (1), the present authors considered an expression for generalizing the thermodiffusion mixture of inert gas mixtures of the form

$$\alpha_t^* = \frac{\alpha_T}{\alpha_{t_{ss}} \overline{M}^n} = f(T^*), \tag{2}$$

where $\alpha_{t_{ss}}$ is the theoretical value of the thermodiffusion factor calculated for the solid sphere model:

$$\overline{M} = \frac{M_1 - M_2}{M_1 + M_2}; \; T^* = \frac{\overline{T}}{(\varepsilon_{12}/k)}.$$

The gas mixtures could be divided into two groups by the value of the exponent n. For mixtures with $\overline{M} > 0.5$, the exponent $n = 0.25$, while for $\overline{M} < 0.25$, $n = 0.125$.

In the present study we will consider generalized expressions for the thermodiffusion factor of inert gases with $\overline{M} > 0.5$, i.e., He–Ne, He–Ar, He–Kr, He–Xe, Ne–Kr, Ne–Xe.

In generalizing the experimental data of various researchers on the thermodiffusion factor of such gas mixtures, the data of Taylor [4] were used as a reference, since his is one of the latest studies offering the most complete investigation of the thermodiffusion factor in inert gases as a function of concentration over a quite wide temperature range, as compared to earlier studies.

According to [3], the dependence of the dimensionless thermodiffusion coefficient on dimensionless temperature is described by a family of parallel curves for concentrations of

---

Applied Physics Institute, Academy of Sciences of the Belorussian SSR, Minsk. Translated from Inzhenerno-Fizicheskii Zhurnal, Vol. 48, No. 6, pp. 966-971, June, 1985. Original article submitted July 26, 1984.

0022-0841/85/4806-0702$09.50

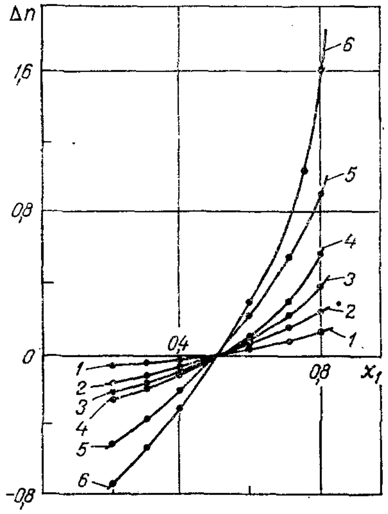

Fig. 1. Concentration dependence of Δn for various gas mixtures: 1) $\bar{M} = 0.61$ (Ne—Kr); 2) 0.67 (He—Ne); 3) 0.73 (Ne—Xe); 4) 0.83 (He—Ar); 5) 0.91 (He—Kr); 6) 0.97 (He—Xe).

TABLE 1. Values of $\bar{M}^k$ for Various Concentration Ranges

Mixture	x_1 (light component)		
	0,2—0,3	0,4—0,6	0,7—0,8
Ne—Kr	0,91	0,88	0,83
He—Ne	0,95	0,90	0,825
Ne—Xe	0,97	0,92	0,83
He—Ar	1,00	0,95	0,87
He—Kr	1,02	0,98	0,91
He—Xe	1,02	0,98	0,90

TABLE 2. Comparison of Experimental and Calculated Values for Limiting Concentrations at $\bar{T} = 300$°K

Mixture	Concn. of lighter component	α_{t_e}	α_{t_c}	$\delta = \frac{\alpha_{t_e} - \alpha_{t_c}}{\alpha_{t_e}} \cdot 100\%$
Ne—Xe	0,8	0,443	0,435	2
	0,2	0,259	0,248	4
Ne—Kr	0,8	0,362	0,357	1,5
	0,2	0,238	0,223	6
He—Xe	0,8	0,698	0,690	1
	0,2	0,355	0,317	11
He—Kr	0,8	0,619	0,641	3,5
	0,2	0,344	0,321	7
He—Ar	0,8	0,531	0,558	5
	0,2	0,316	0,320	1
He—Ne	0,8	0,367	0,345	6
	0,2	0,277	0,266	4

0.2, 0.4, 0.5, 0.6, 0.8. Since these curves may be superposed by changing the exponent n, we will introduce in Eq. (2) in place of $\bar{M}^n$ the expression $\bar{M}^{n+\Delta n}$ (or $\bar{M}^k$, $k = n + \Delta n$). The dependence of Δn on concentration for various gas mixtures is shown in Fig. 1. Superposition was performed relative to the curve for the equimolar concentration. It is evident from the figure that the absolute value of Δn increases with increase in $\bar{M}$.

Table 1 presents averaged values of $\bar{M}^k$ for various gas mixtures in concentration ranges of 0,2-0.3, 0.4-0.6, 0.7-0,8. The averaging was performed because of slight differences in the values of $\bar{M}^k$ over the indicated concentration ranges.

The dimensionless thermodiffusion factors were processed as functions of temperature by the method of least squares, using the polynomial

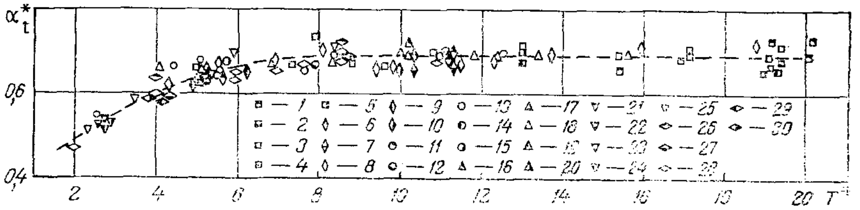

Fig. 2. Dimensionless thermodiffusion factor vs. dimensionless temperature for inert gas mixtures: 1-5) He—Ne at concentrations of 0.2, 0.4, 0.5, 0.6, 0.8, respectively; 6-10) He—Ar; 11-15) He—Kr; 16-20) He—Xe; 21-25) Ne—Kr; 26-30) Ne—Xe at same concentrations.

TABLE 3. Values of $\alpha_{t_{ss}}$ for Various Inert Gas Mixtures

Mixture	x_1 (light component)								
	0,9	0,8	0,7	0,6	0,5	0,4	0,3	0,2	0,1
Ne—Kr	0,8177	0,7105	0,6290	0,5650	0,5134	0,4709	0,4354	0,4052	0,3792
He—Ne	0,6734	0,6136	0,5645	0,5233	0,4885	0,4586	0,4328	0,4103	0,3906
Ne—Xe	1,0867	0,8920	0,7575	0,6588	0,5834	0,5239	0,4757	0,4359	0,4021
He—Ar	1,0746	0,8907	0,7612	0,6652	0,5910	0,5320	0,4839	0,4440	0,4104
He—Kr	1,2848	1,0172	0,8423	0,7189	0,6272	0,5563	0,4999	0,4539	0,4157
He—Xe	1,4954	1,1303	0,9087	0,7599	0,6530	0,5725	0,5097	0,4594	0,4181

TABLE 4. Coefficients a and b for Various Gas Mixtures

Mixture	a	b	Mixture	a	b
Ne—Kr	2,8241	—1,7676	He—Ar	2,6298	—1,8825
He—Ne	2,7095	—1,3451	He—Kr	2,6103	—2,0337
Ne—Xe	2,6871	—1,9556	He—Xe	2,6078	—2,1537

$$\alpha^*_t = \frac{\alpha_t}{\alpha_{t_{ss}} \bar{M}^k} = \sum_{i=1}^{m} C_i (T^*)^{i-1} \tag{3}$$

which allowed description of the data with an error of 3-10% (six of 140 points have an error exceeding 10%) by a single generalized curve (Fig. 2) with the following coefficients:

i	1	2	3	4	5
C_i	0,260	0,128	—0,013	0,00058	—0,0000087

Thus, by using a fourth-order polynomial with the coefficients presented above, the thermodiffusion factor of any of the inert gas mixtures considered can be described over the temperature range 160-800°K at concentrations of 0.2-0.8 with Eq. (3).

Table 2 compares results of calculating α_t for the limiting concentrations of 0.2 and 0.8 with the experimental data of [5].

Table 3 presents values of $\alpha_{t_{ss}}$ calculated for various inert gas mixtures. The solid sphere diameters required for calculation of $\alpha_{t_{ss}}$ were determined from the experimental viscosity values taken from [7]. Lennard-Jones (12-6) potential force constants ε/k [1] were used to calculate the dimensionless temperatures.

Since according to [6] $1/\alpha_t$ varies linearly with concentration, for $1/\alpha_{t_{ss}}$ we may write

$$\frac{1}{\alpha_{t_{ss}}} = a + bx, \tag{4}$$

where x is the concentration of one of the mixture components. Table 4 presents values of a and b obtained from Eq. (4) for the gas mixtures considered, with which $\alpha_{t_{ss}}$ for any concentration may easily be determined.

TABLE 5. Comparison of Experimental and Calculated Values of Thermodiffusion Factor for Inert Gas Mixtures

Mixture	M concn. of light component	T_1	T_2	$\overline{T}$	α_{t_e}	α_{t_c}	$\varepsilon = \frac{\alpha_{t_e} - \alpha_{t_c}}{\alpha_{t_e}} \times 100\%$	Ref. for exptl. data
He—Ne	0,538	293	93	156,3	0,3025	0,3107	3	[7]
		369	293	328,8	0,3150	0,3176	1	
		609		413,6	0,3247	0,3375	4	
	0,21			426	0,290	0,294	1,5	[8]
				462	0,290	0,287	1	
	0,197			325	0,266	0,2830	6,5	[4]
	0,359				0,289	0,2926	1	
	0,494				0,306	0,3180	4	
	0,794				0,353	0,368	4	
He—Ar	0,185	384	290	328,9	0,2951	0,2888	2	[9]
		523		382,6	0,2885	0,2879	0,5	
	0,512	293	93	156,3	0,3558	0,3468	2,5	[10]
			147	203,0	0,3686	0,3713	1	
			233	262,9	0,3798	0,3882	2,5	[10]
	0,20	373	288	331,6	0,2981	0,2924	2	[11]
	0,30				0,3138	0,3187	2	
	0,40				0,3375	0,3503	4	
	0,50				0,3720	0,3891	5	
	0,488	293	596,2	407,91	0,377	0,382	1,5	[14]
		293	694,0	436,09	0,379	0,380	0,5	
		294	795,4	466,39	0,377	0,379	0,5	
		291,5	909,3	489,11	0,383	0,378	1,5	
He—Kr	0,55	293	117	178,5	0,4259	0,3920	8	[10]
			233	262,9	0,4570	0,4330	5,5	
		585		406,9	0,4477	0,4548	2	
	0,30	373	288	333,1	0,3229	0,3353	4	[11]
	0,40				0,3554	0,3731	5	
	0,50				0,4000	0,4206	5	
	0,60				0,4504	0,4822	7	
	0,70				0,5095	0,5245	3	
He—Xe	0,536	293	185	229,6	0,4286	0,4202	2	[10]
			233	262,9	0,4375	0,4349	0,5	
		369	293	328,8	0,4411	0,4547	3	
		585		406,9	0,4387	0,4652	6	
	0,227			339	0,312	0,3290	5	[4]
	0,386				0,369	0,3737	1,5	
	0,552				0,446	0,4678	5	
Ne—Kr	0,53	293	117	178,5	0,2196	0,2231	2	[10]
			185	229,6	0,2557	0,2438	5	
		369	293	328,8	0,3055	0,2861	6	
		585		406,9	0,3183	0,3020	5	
	0,353			250	0,212	0,2158	2	[4]
	0,498				0,238	0,2439	2,5	
	0,655				0,274	0,2686	2	
Ne—Xe	0,50			328	0,3333	0,3205	4	[12]
				473	0,3448	0,3541	3	
				673	0,3704	0,3707	0,5	
				873	0,3571	0,3710	4	
	0,15			340	0,238	0,2480	4	[13]
	0,579				0,336	0,3570	6	
	0,66				0,362	0,3588	1	

Representation of $1/\alpha_t$ in the form of a linear function of concentration permits extrapolation of calculation results with Eq. (3) to any concentration range with little error.

Results of calculating the thermodiffusion factor with Eq. (3) are compared with some experimental data in the temperature range 160-800°K at concentrations of 0.2-0.8 in Table 5. It is evident that Eq. (3) describes the experimental temperature and concentration dependences of α_t satisfactorily. The divergence between calculated and experimental values of α_t does not exceed 3-8% on the average.

LITERATURE CITED

1. J. O. Hirschfelder, C. Curtis, and R. Bird, Molecular Theory of Gases and Liquids, Wiley (1964).
2. L. P. Filippov, Similarity of Properties of Matter [in Russian], Khimiya, Moscow–Leningrad (1966).
3. A. F. Zolotukhina, M. V. Sagarda, and I. P. Evmenova, "Generalization of experimental data on the thermodiffusion factor of gases within the framework of corresponding states theory," Vestn. Akad. Nauk BSSR, Ser. Fiz.-Energ. Navuk, No. 4, 93-95 (1983).

4. W. L. Taylor, "Thermal diffusion factor for the binary noble gas mixtures," J. Chem. Phys., 79, No. 9, 4973-4984 (1980).
5. R. D. Trengove, H. L. Robjohns, T. N. Bell, M. L. Martin, and P. J. Dunlop, "Thermal diffusion factors at 300°K for seven binary noble gas systems containing helium or neon," Physica, 100A, 488-501 (1981).
6. M. F. Laranjeira, "An elementary theory of thermal and pressure diffusion in gaseous binary and complex mixtures," Physica, 26, No. 26, 406-417 (1960).
7. N. B. Vargaftik, Handbook of Thermophysical Properties of Gases and Liquids [in Russian], Nauka, Moscow (1972).
8. S. K. Deb and A. K. Barua, "Thermal diffusion and intermolecular forces in binary inert gas mixtures," Ind. J. Phys., 41, 646-654 (1967).
9. T. L. Ibbs, "Thermal diffusion measurement," Proc. R. Soc., A107, 470-486 (1925).
10. K. E. Grew, "Thermal diffusion of mixtures of the inert gases," Proc. R. Soc., 189A, No. 1018, 402-410 (1947).
11. B. E. Atkins, R. E. Bastick, and T. L. Ibbs, "Thermal diffusion in mixtures of the inert gases," Proc. R. Soc., 172A, 142-158 (1939).
12. W. L. Taylor, S. Weissman, W. J. Haubach, and P. T. Pickett, "Thermal diffusion factor for the Ne–Xe system," J. Chem. Phys., 50, No. 11, 4886-4898 (1969).
13. J. M. Saviron, C. M. Santamaria, J. A. Carrion, and J. C. Yarza, "Isotopic and nonisotopic thermal diffusion factor from column measurement," J. Chem. Phys., 63, No. 12, 5318-5320 (1975).
14. A. F. Bogatyrev, N. D. Kosov, and E. E. Makletsova, "Study of the dependence of thermodiffusion constant of binary gas mixtures on temperature and concentration," in: Thermophysical Properties of Gases [in Russian], Nauka, Moscow (1973), pp. 33-37.

SECOND VIRIAL COEFFICIENT OF VAPORS

L. P. Filippov, N. L. Veretel'nikova,
and A. D. Okhotsimskii

UDC 533.27

An expression is offered for calculation of the second virial coefficient of vapors of nonassociative materials and their mixtures.

Much data from the literature was systematized and generalized in [1], and it was shown that for normal (nonassociated) materials, in accordance with the most recent generalizations, the second virial coefficient B can be expressed as a three-parameter function [2]:

$$B/V_C = F(T/T_C, A). \tag{1}$$

The structure of Eq. (1) reflects the three-parameter nature of the effective model potentials [3, 4]. It is significant that one and the same parameter A characterizes the individuality of the material in describing the properties of dense media (gases and liquids). This question was discussed in connection with the problem of multiparticle interactions in [1, 5].

Below we will consider the question of the second virial coefficient of vapors of multiatomic mainly organic compounds. In the overwhelming majority of cases for vapor we need deal only with the relatively narrow dimensionless temperature range from 0.6 to 1.2. In this limited range of states the values of B are always negative, and the complex Eq. (1) in log–log coordinates log (–B) – log T is practically a straight line. Therefore, it is possible to approximate Eq. (1) with the following simple expression:

$$-B/V_C = 1{,}241^{-1}(1{,}213T_C/T)^m. \tag{2}$$

M. V. Lomonosov Moscow State University. Institute of Chemical Physics, Academy of Sciences of the USSR, Moscow. Translated from Inzhenerno-Fizicheskii Zhurnal, Vol. 48, No. 6, pp. 971-975, June, 1985. Original article submitted July 4, 1984.