VARIATION OF THE KINETIC COEFFICIENTS OF RAREFIED GASES AS FUNCTIONS OF TEMPERATURE

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We consider the possibilities of describing the variation of the viscosity and thermal conductivity of gases as functions of temperature by means of mutually consistent equations.

According to the Chapman–Enskog theory for monatomic gases, thermal conductivity and viscosity are related by the simple formula [1]

$$\frac{\lambda M}{\eta c_v} = f = 2.5. \tag{1}$$

This equation enables us to calculate the thermal conductivity if we have information on the viscosity and heat capacity of the gas.

The value of f (this is often called the Aiken factor) for polyatomic gases is less than 2.5. The theory attributes this property to the effect of the internal degrees of freedom of complex molecular structures [1]. Aiken proposed calculating the factor f for molecules consisting of more than one atom by means of the equation

$$f = 1 + \frac{9R}{4c_v}. \tag{2}$$

According to Hirschfelder,

$$f = L + \frac{3R}{2c_v}\left(\frac{5}{2} - L\right), \tag{3}$$

where

$$L = \rho D/\eta.$$

In [2] Mason and Monchick developed an approach which can be used to take account of the exchange of energy between the translational and internal degrees of freedom in the case of inelastic collisions of polyatomic molecules. The contribution of the energy exchange is characterized in the Mason–Monchick theory by the numbers of collisions necessary to establish equilibrium between the translational and the various internal degrees of freedom for inelastic collisions. Very little experimental information is available for the numbers of collisions, while theoretical methods of calculating them are far from being fully developed.

In addition to the above equations, widespread attention has been given to empirical modifications which can be used to establish the interrelationship between the Aiken factor and other physical and physicochemical characteristics of gases [3].

In the present study we analyzed the behavior of the Aiken factor for a group of substances which are halogen derivatives of methane and ethane and are widely used as refrigerants (they are known in the literature as Freons). We carried out an experimental investigation of the thermal conductivity of these gases at atmospheric pressure. We used an absolute variant of the stationary heated-wire method described in [4]. Taking account of the results of this experiment and the generalization of published experimental data on the transfer properties [4-6], we determined the values of the Aiken factor (Table 1). In addition, the table includes the values of f calculated by Eqs. (2) and (3). The complex L in (3) was calculated in accordance with the recommendations of [1]. Since there are no experimental data on the numbers of collisions for these substances, we did not carry out any calculations by the Mason–Monchick theory. An analysis of the results shown in Table 1 enabled us to establish the following:

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TABLE 1. Experimental and Calculated Values of the Aiken Factor for Freons

Freon	T, K	$\lambda \cdot 10^5$, W/(m·K)	C_v, J/mole·K	f_{ex}	f by Eq. (2)	f by Eq. (3)
11	300	826	70,8	1,455	1,264	1,528
M=137,39	330	955	73,9	1,463	1,253	1,519
T_{cr}=471,15 K	360	1084	76,6	1,468	1,244	1,512
	390	1213	79,1	1,471	1,237	1,506
	420	1337	81,1	1,471	1,231	1,502
	450	1461	83,0	1,471	1,225	1,497
12	300	974	64,8	1,476	1,289	1,547
M=120,92	320	1075	67,2	1,481	1,279	1,539
T_{cr} =385,15 K	350	1227	70,3	1,486	1,266	1,529
	370	1329	72,3	1,489	1,259	1,524
	400	1477	74,7	1,493	1,250	1,517
	430	1624	77,0	1,494	1,243	1,511
21	300	883	53,5	1,501	1,349	1,595
M=102,92	330	1031	56,4	1,508	1,332	1,581
T_{cr}=451,65 K	360	1182	57,4	1,508	1,316	1,569
	390	1336	61,7	1,507	1,303	1,558
	420	1489	64,1	1,501	1,292	1,550
	450	1643	66,3	1,495	1,282	1,542
113	320	995	122,7	1,381	1,152	1,440
M=187,39	350	1138	127,6	1,388	1,147	1,435
T_{cr}=487,30 K	380	1280	132,0	1,390	1,142	1,432
	420	1469	136,0	1,389	1,136	1,427
	450	1607	140,4	1,388	1,133	1,425
114	300	1021	108,6	1,409	1 172	1,456
M=170,99	320	1127	112,2	1,414	1,167	1,451
T_{cr} =418,84 K	340	1240	116,0	1,418	1,161	1,447
	360	1355	119,8	1,420	1,156	1,443
	380	1471	123,5	1,421	1,152	1,439
115	240	825	89,9	1,373	1,208	1,484
M=154,48	280	1052	98,1	1,384	1,191	1,470
T_{cr} =353,16 K	320	1299	106,3	1,395	1,176	1,458
	360	1561	114,4	1,402	1,164	1,449
	400	1836	122,4	1,407	1,153	1,440
	420	1976	126,3	1,408	1,148	1,436

1) there is a reduction in the Aiken factor in the group of substances considered here as the molecular mass of the gas increases;

2) the experimental values of the Aiken factor lie between the calculated values obtained by Eqs. (2) and (3). The Aiken factor values calculated by Hirschfelder's equation are closer to the experimental data;

3) within the limits of error of the initial data and within the values of 0.6-1.3 for the reduced temperatures, the Aiken factor is practically independent of temperature.

It must be emphasized that the conclusions arrived at were obtained for a small group of compounds in a limited range of temperatures, and for other molecular structures appropriate checks must be carried out. Of greatest interest in this connection is the conclusion that the values of the Aiken factor are constant. If this is confirmed for other compounds as well, then there must exist a unique function of temperature which describes the generalized transfer coefficients:

$$\eta^* = \Phi(\tau), \tag{4}$$

$$\varkappa = \Phi(\tau), \tag{5}$$

where we may take

$$\eta^* = \eta/\eta_{cr} \tag{6}$$

as the reduced viscosity, and

$$\varkappa = \frac{\lambda/c_v}{(\lambda/c_v)_{cr}} \tag{7}$$

as the generalized thermal conductivity.

TABLE 2. Values of the Thermal Conductivity and Viscosity of Gases in Reduced Scales of Units

Methane			Propane			CO_2		
τ	$\varkappa$	η^*	τ	$\varkappa$	η^*	τ	$\varkappa$	η^*
0,489	0,487	0,501	0,703	0,683	0,712	0,723	0,723	0,731
0,909	0,909	0,912	0,811	0,816	0,817	0,920	0,934	0,923
1,538	1,479	1,472	1,027	1,025	1,027	1,479	1,407	1,426
2,378	1,999	2,056	1,243	1,195	1,228	1,972	1,799	1,790
CCl_4			Argon			Ethane		
τ	$\varkappa$	η^*	τ	$\varkappa$	η^*	τ	$\varkappa$	η^*
0,539	0,534	0,551	0,729	0,744	0,737	0,764	0,753	0,771
0,719	0,714	0,727	0,862	0,868	0,866	0,895	0,883	0,898
0,899	0,895	0,902	2,320	2,066	2,019	1,157	1,141	1,150
1,078	1,075	1,076	4,971	3,698	3,429	1,419	1,360	1,377
CF_4			Helium			Nitrogen		
τ	$\varkappa$	η^*	τ	$\varkappa$	η^*	τ	$\varkappa$	η^*
0,659	0,659	0,669	0,385	0,379	0,398	0,634	0,657	0,644
0,835	0,842	0,840	0,578	0,588	0,589	1,584	1,538	1,508
1,099	1,089	1,096	0,963	0,971	0,964	3,168	2,701	2,520
1,319	1,271	1,294	6,744	3,578	3,326	7,921	4,687	4,689
n-Butane			n-Hexane			Dichloromethane		
τ	$\varkappa$	η^*	τ	$\varkappa$	η^*	τ	$\varkappa$	η^*
0,706	0,686	0,715	0,788	0,776	0,795	0,590	0,590	0,595
0,823	0,820	0,829	0,886	0,878	0,890	0,688	0,670	0,692
0,941	0,939	0,943	1,083	1,090	1,081	0,983	0,981	0,983
1,176	1,160	1,168	1,181	1,196	1,172	1,180	1,223	1,175
Methyl chloride			Freon 13 VI			Cyclohexane		
τ	$\varkappa$	η^*	τ	$\varkappa$	η^*	τ	$\varkappa$	η^*
0,649	0,638	0,648	0,688	0,658	0,697	0,687	0,668	0,696
0,817	0,824	0,817	0,768	0,745	0,775	0,814	0,809	0,820
1,201	1,172	1,200	0,907	0,909	0,910	0,904	0,899	0,907
1,874	1,825	1,798	1,141	1,135	1,136	1,139	1,163	1,134

The approximation (4) is well known in the literature [7, 8] and, according to the results of comparisons of independent generalizations made by different authors, as shown in [7], leads to practically identical results. Equation (5), which derives from the ideas of the molecular-kinetic theory, was used earlier for generalizing and harmonizing data on the thermal conductivity of gaseous Freons [4].

In Table 2 the values of the generalized kinetic characteristics are calculated for 15 gases, of which methane, ethane, propane, carbon dioxide, helium, nitrogen, argon, and carbon tetrafluoride, in our opinion, are most representative in the sense of completeness and reliability of data concerning the transfer properties of these substances. The initial values of the thermal conductivity, viscosity, and heat capacity are taken from [9, 10]. To calculate the reduced viscosity, we used the functions proposed in [8].

An analogous comparison was carried out for ethylene, propylene, krypton, xenon, air, Freons 13, 12VI, 502, 152a, 142, C-318, and 218, and a number of other gases. These calculations are not shown in Table 2, since they are entirely consistent with the indicated trends, on the one hand, and on the other hand, for some of the substances (for example, Freons), unlike the compounds mentioned in Table 2, the required high degree of consistency between the independent measurements has not yet been achieved, a fact attributable to the scarcity of accurate data not only on the transfer properties but also on the heat capacity of these gases.

As can be seen from Table 2, at subcritical temperatures the values of the generalized characteristics coincide quite satisfactorily. In the region of supercritical temperatures we find some divergences, but even these are, as a rule, not beyond the tolerance limits of

TABLE 3. Values of the Coefficient K in Eq. (8)

Substance	CH_4	$CFCl_3$	CF_2Cl_2	CF_3Cl	CF_4	$CHFCl_2$
K	85,93	87,74	84,23	83,36	88,56	87,60
Substance	CHF_2Cl	CHF_3	C_2H_6	$C_2F_3Cl_3$	$C_2F_4Cl_2$	C_2F_5Cl
K	85,30	83,20	78,83	85,70	85,80	81,46
Substance	C_3H_8	C_4H_{10}	C_6H_{14}	NH_3	CCl_4	CO_2
K	77,95	78,86	80,62	83,56	85,10	88,80
Substance	CH_2Cl_2	$C_2H_3F_2Cl$	C_3F_8	C_4F_8	H_2O	$C_{12}H_{26}$
K	88,20	86,40	81,88	80,96	87,40	87,70
Substance	N_2	He	Kr	Air	Xe	Ar
K	96,38	146,4	143,1	94,00	151,9	127,0

the recommended values of nonequilibrium properties in this interval, which are usually greater [10].

The results obtained do not contradict, in the temperature ranges considered, the assumptions made concerning the character of the temperature dependency of the generalized kinetic coefficients and are of interest because they indicate the direction for seeking criteria of the estimates of quality of the data concerning transfer properties and improving the reliability of the recommended tabular data. Other aspects are also desirable. Several of them are listed below:

1) interconsistency of the transfer properties and caloric properties;

2) the determination of the time-dependent variation of one of the coefficients on the basis of the known function for another; extrapolation of the data to low-temperature and high-temperature regions;

3) prediction of the thermal conductivity of rarefied gases.

Let us consider the last item in more detail. In order to estimate the thermal conductivity, it is proposed that we use a dimensional empirical relation connecting the normalized thermal conductivity, at a temperature equal to the critical temperature, with the Kamerlingh Onnes parameter and the molecular mass:

$$\left(\frac{\lambda}{c_v}\right)_{cr} \cdot 10^5 = KSM^{-0.12}, \tag{8}$$

$$S = \frac{M^{1/2}P_{cr}^{2/3}}{T_{cr}^{1/6}}. \tag{9}$$

The values of K are shown in Table 3. The critical parameters are taken from [9].

It is noteworthy that K in formula (8) depends on the number of atoms in a molecule of the gas. For the largest class of gases, whose molecules consist of three or more atoms, the value of K varies from 77.95 for propane to 88.20 for dichloromethane; in this range this value was found for polar gases and cyclic compounds. Within the homologous series, for compounds obtained by successive displacement of one atom, for example that of chlorine, by other atoms, such as fluorine, K varies much less. Equation (8), from the viewpoint of the theory of similarity, cannot claim any depth, since it is a dimensional equation. Nevertheless, an analysis of the data of Table 3 shows that Eq. (8) may be useful in *a priori* calculations of thermal conductivity, for example in homologous series of compounds, where K is taken to be constant or equal to the value for a similar chemical compound, say, with a nearly equal value of the Filippov parameter [7]. It should be noted in this connection that the number of fluorine–chlorine derivatives of the methane series alone is 15, while the numbers for ethane, propane, and butane, counting isomers, are 55, 332, and over 1,000.

It is also worth noting that Eq. (8) can be used for expert estimates of data when there are substantial divergences within a small group of experimental results on thermal conductivity.

For calculations using Eq. (8), we must have data on heat capacity. If no such data are available, we can use the known calculation methods of [11]. The variation of the thermal conductivity with temperature can be determined in this case from known data for the viscosity of the gas, or from the temperature-dependent variation of the kinetic coefficients of a chemically similar compound, or else calculated from known functional relationships [4, 5, 7, 8].

The proposed approach has been used in considering only a small number of compounds; it is even possible that in other cases the results will prove less optimistic; however, even in less favorable situations, we believe, the above recommendations may prove useful in expert estimates and predictions of the properties of promising working fluids for power generation, refrigeration, cryogenics, and chemical technology.

NOTATION

λ, thermal conductivity; η, dynamic viscosity; M, molecular mass; c_v, heat capacity at constant volume; τ, reduced temperature; T_{cr}, critical temperature; P_{cr}, critical pressure; S, Kamerlingh Onnes parameter; R, universal gas constant; ρ, density; D, coefficient of self-diffusion.

LITERATURE CITED

1. J. O. Hirschfelder, C. Curtiss, and R. Bird, Molecular Theory of Gases and Liquids, Wiley (1964).
2. E. A. Mason and L. Monchick, "Heat conductivity of polyatomic and polar gases," J. Chem. Phys., 36, No. 6, 1622-1639 (1962).
3. V. E. Lyusternik and R. A. Mustafaev, "The Aiken factor and the role of internal degrees of freedom in transfer phenomena in polyatomic hydrocarbon molecules," Inzh.-Fiz. Zh., 31, No. 4, 704-709 (1976).
4. O. B. Tsvetkov, Yu. A. Laptev, and N. A. Polyakova, "Thermal conductivity of gaseous refrigerants," in: Machines and Apparatuses in Refrigeration, Cryogenics, and Air Conditioning [in Russian], No. 3, LTI im. Lensoveta, Leningrad (1978), pp. 129-131.
5. A. V. Kletskii, O. B. Tsvetkov, and N. G. Sagaidakova, "Generalization of experimental data on the viscosity of gaseous freons at atmospheric pressure," Theses of Reports of the Traveling Meeting of the Scientific Council of the USSR Academy of Sciences, Grozny, November 9-13, 1975 [in Russian], pp. 59-60.
6. O. B. Tsvetkov, "Thermal conductivity of gaseous difluorochloromethane," Inzh.-Fiz. Zh., 16, No. 3, 510-515 (1969).
7. L. P. Filippov, Similarity of the Properties of Substances [in Russian], Moscow State Univ. (1978).
8. I. F. Golubev and N. E. Gnezdilov, Viscosity of Gaseous Mixtures [in Russian], Standartov, Moscow (1971).
9. N. B. Vargaftik, Tables on the Thermophysical Properties of Liquids and Gases, Halsted Press (1975).
10. N. B. Vargaftik, L. P. Filippov, L. A. Tarzimanov, and E. E. Totskii, Thermal Conductivity of Gases and Liquids [in Russian], Standartov, Moscow (1978).
11. R. Reid and T. Sherwood, Properties of Gases and Liquids [Russian translation], Khimiya, Leningrad (1971).