AD 698 517

HEAT AND MASS TRANSFER. VOLUME 7, 1968

A. V. Lykova, et al

Foreign Technology Division
Wright-Patterson Air Force Base, Ohio

20 August 1969

AD698517

FTD-HT-23-820-68 Part 1 of 3

FOREIGN TECHNOLOGY DIVISION

AIR FORCE SYSTEMS COMMAND

HEAT AND MASS TRANSFER

BY

A. V. Lykova, B. M. Smol'kogo

FOREIGN TECHNOLOGY DIVISION

253

FTD-HT-23-820-68
Part 1 of 3

EDITED TRANSLATION

HEAT AND MASS TRANSFER

By: A. V. Lykova, B. M. Smol'kogo

Source: Teplo-I Massoperenos, (Heat and Mass Transfer)
1968, Vol. 7, pp. 1-609

English pages: 1 - 243

Translated Under: F33657-68-D-1287

PREPARED BY:

TRANSLATION DIVISION
FOREIGN TECHNOLOGY DIVISION
WP-AFB, OHIO.

DATA HANDLING PAGE

01-ACCESSION NO. **98-DOCUMENT LOC** TM9001155	**39-TOPIC TAGS** heat transfer, thermal conductivity, temperature coefficient, thermal diffusion, enthalpy, heat capacity, gas viscosity, solid viscosity, fluid viscosity, calculation, thermal analysis method, numeric analysis
09-TITLE HEAT AND MASS TRANSFER	
47-SUBJECT AREA 12, 20	

42-AUTHOR/CO-AUTHORS LYKOVA, A. V. ; 16-SMOL'KOGO, B. M.	**10-DATE OF INFO** -----68
43-SOURCE TEPLO- I MASSOPERENOS (RUSSIAN)	**68-DOCUMENT NO.** FTD-HT-23-820-68
	69-PROJECT NO. 72301-78

63-SECURITY AND DOWNGRADING INFORMATION **UNCL, 0**	**64-CONTROL MARKINGS** **NONE**	**97-HEADER CLASH** **UNCL**

76-REEL FRAME NO. 1889 1657	**77-SUPERSEDES**	**78-CHANGES**	**40-GEOGRAPHICAL AREA** UR	**NO OF PAGES** 649
CONTRACT NO. F33657-68-D-1287	**X REF ACC. NO.** 65-	**PUBLISHING DATE** 94-	**TYPE PRODUCT** **TRANSLATION**	**REVISION FREQ** **NONE**

STEP NO. 02-UR/2862/68/007/000/0001/0609	**ACCESSION NO.**

ABSTRACT

(U) Papers of the All-Union Conference on Heat and Mass Transfer (May 1968, Minsk), devoted to physical parameters of heat and mass transfer, are presented in this book. An examination is made of the present standing of analytical and experimental methods of determining thermophysical properties of compounds, instruments and equipment are described, and results of research on thermal conductivity and on the temperature coefficient of thermal conductivity, heat capacity, thermal diffusion, enthalpy, and viscosity of various systems (solid, liquid, gaseous) are also presented. The book is written for scientific coworkers, graduate students, and engineering and technical workers in heat and mass transfer.

TABLE OF CONTENTS

PART ONE

ANALYSIS OF THERMOPHYSICAL AND TRANSPORT PROPERTIES OF COMPOUNDS

PART TWO

METHODS AND INSTRUMENTS FOR DETERMINING PARAMETERS OF HEAT AND MASS TRANSFER

PART THREE

HEAT AND MASS TRANSFER PARAMETERS

Explanation of Foreign Subscripts and Abbreviations

Cyrillic	Translation	Foreign Word	Meaning
смеси, см	mix	смеси	mixture
ид	ideal	идеальный	ideal
прибл	approx	приближитемьный	approximate
з	froz	замороженный	frozen
отн	rel	относитемьный	relative
шт	rod	штанге	rod
осл	atten	ослабление	attenuation
р (pp. 108-116)	eq	равновесие	equilibrium
р (pp. 127-139)	reac	реакция	reaction
вр	rot	вращение	rotation
кол	vib	колицание	vibration
уд	spec	удельный	specific
ср (pp. 244-249)	med	средный	median
ц (pp. 244-249)	cen	центральный	central
равн	eq	равный	equal
внутр	int	внутренный	interior
внешн	ext	внешный	exterior
рел	relax	релаксация	relaxation
н (pp. 275-279)	htr	нагреватель	heater
эфф	eff	эффективный	effective
и	tr	истинный	true
п	sur	поберхность	surface
ср (pp. 295-end)	av	средный	average
в (pp. 301-308)	rup	выталкибание	repulsion
рас	scat	рассеянный	scattered
п	red	приведенный	reduced
г	hot	горяций	hot
х	cold	холодный	cold
н (pp. 326-349)	inhomogeneities	неравномерность	inhomogeneities
в (pp. 326-349)	v	вакуум	vacuum
г	g	газ	gas
ц	ctr	центр	center
оц	rel-ctr	относительная-центр	relative-center

Explanation of Foreign Subscripts and Abbreviations

Cyrillic	Translation	Foreign Word	Meaning
вх	in	вход	input
вых	out	выход	output
изм	meas	измеренный	measured
пр	cor	приведенный	corrected
дж	j	джуль	joule
э	e	эталон	standard
об	ob	отн-боковой	rel-side
б	b	боковой	side
о.ф.	m-p	однофазный	monophase
д.ф.	t-p	двухфазный	two-phase
кин	kin	кинематический	kinematic
пот	pot	потенцияльный	potential
стац	st	стационарьный	stable
кв	kw	киловатт	kilowatt
град	deg	градус	degree

Papers of the All-Union Conference on Heat and Mass Transfer (May 1968, Minsk), devoted to physical parameters of heat and mass transfer, are presented in this book. An examination is made of the present standing of analytical and experimental methods of determining thermophysical properties of compounds, instruments and equipment are described, and results of research on thermal conductivity and on the temperature coefficient of thermal conductivity, heat capacity, thermal diffusion, enthalpy, and viscosity of various systems (solid, liquid, gaseous) are also presented.

The book is written for scientific coworkers, graduate students, and engineering and technical workers in heat and mass transfer.

Editorial Board for the Volume:

Doctor of Technical Sciences, Professor G. N. Dul'nev, Doctor of Physico-mathematical Sciences, Professor A. F. Chudnovskiy, Candidate of Technical Sciences L. N. Novichyonok, and Candidate of Technical Sciences Yu. Ye. Frayman.

PART ONE

ANALYSIS OF THERMOPHYSICAL AND TRANSPORT PROPERTIES OF COMPOUNDS

V. Ye. Alemasov, A. F. Dregalin, V. I. Bychenok,
and V. N. Trinos

EFFECT OF PARAMETRIC ERRORS IN POTENTIALS ON EQUILIBRIUM COMPOSITION AND PROPERTIES OF MIXTURES OF REAL GASES DETERMINED BY CALCULATION

The virial-form equation of state is widely used in the theoretical determination of properties of multicomponent mixtures.

The molecular-kinetic theory of gases makes it possible to determine virial coefficients for components of a mixture if the inter-molecular potential function of interaction is known. The actual pattern of interaction here is described by an analytical model (potential). But at present reliable data on potential parameters over a wide range of pressures and temperatures are lacking for many compounds. This reduces the reliability of calculated values of thermodynamic properties of gas mixtures.

Difficulties encountered in the direct experimental verification of the validity of a chosen model of interaction are well known for multicomponent reacting mixtures at elevated temperatures (1000-2000°K). Therefore, we have chosen the analytical approach in estimating the influence of errors of potential parameters on thermodynamic properties of gas mixtures.

Most often, the interaction among mixture components is approximated by models of Sutherland, Lennard-Jones (12-6), and Buckingham -- for nonpolar components, and for polar components -- by the Stockmeyer potential. Use any of the potentials cited is governed both by the precision essential for a description of the experimental results, and also by the availability of necessary constants. The latter requirement often determines the choice of model in calculating properties of reacting mixtures.

Convenient models of interaction in this respect are as follows: the Lennard-Jones potential (12-6) for nonpolar molecules:

$$u = 4\varepsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right], \qquad (1)$$

and the Stockmeyer potential for polar molecules

$$u = 4\varepsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right] - \frac{\mu^2}{r^3}\xi \qquad (2)$$

Potential parameters σ and ε/k can be determined from experimental values of viscosity, thermal conductivity, and compressibility. In the absence of necessary data, the following relationships are recommended in [2,6,10]:

$$\sigma = 0{,}561(v_c)^{5/18}, \quad \varepsilon/k = 1{,}77(T_c)^{5/6}, \qquad (3)$$

$$\frac{2}{3}\pi N\sigma^3 = 2{,}0V_B - 5, \quad \varepsilon/k = 1{,}15T_b, \qquad (4)$$

$$\frac{2}{3}\pi N\sigma^3 = 2{,}3v_m, \quad \varepsilon/k = 1{,}92T_m, \qquad (5)$$

where v_c, T_c, v_b, T_b, v_m, and T_m = values of the molar volume and temperature at the following points: critical, boiling, and melting.

As was shown by a verification of the precision of formula (3), undertaken by the authors in [6], the error in determination of σ and ε/k for a homologous carbon series is less than 3.1 and 10 percent, respectively.

In this present study, the properties of a mixture of real gases of average density are determined by use of the potentials (1) and (2). Therefore, only paired interactions were used in the calculation. Potential parameters of interaction of oppositely charged particles are found by empirical combination rules:

$$\sigma_{ij} = \frac{1}{2}(\sigma_i + \sigma_j), \quad (\varepsilon/k)_{ij} = \sqrt{(\varepsilon/k)_i \cdot (\varepsilon/k)_j} \qquad (6)$$

The values of σ and ε/k obtained by different authors [2,7,9,10] based on the methods listed were used in the calculations.

The following causes of errors in calculations stemming from use of potentials are as follows:

1. Force constants of the potentials σ and ε/k were determined in approximate terms for several compounds and can be further refined.

2. Calculations at temperatures higher than 1000°K for most compounds presuppose extrapolation beyond the limit of the experimental determination of the constants σ and ε/k.

3. At high temperatures, we can expect lack of agreement of the shape of the actual potential function with the Lennard-Jones potential and the Stockmeyer potential.

4. For several compounds, the force parameters were obtained based on experimental viscosity data, but these values do not always afford good precision in calculating the second virial coefficient.

All these factors can with some approximation be identified with errors caused by use of "imprecise" values of the constants σ and ε/k. In determining the effect these errors have on the end result of calculation, we can artificially set potential parameters differing from those adopted, calculated the main thermodynamic properties of a mixture of real gases, and find the relative deviations of real gas properties from ideal gas properties. We varied the values of σ and ε/k by ± 10 and ± 30 percent.

The range of variation of σ and ε/k by ± 10 percent for several compounds corresponds to the data in [4,5], where a model with the variable σ and ε/k varying as a function of temperature within the limits ± 10 percent is suggested.

The authors developed the following version of a calculation of chemical equilibrium of real reacting mixtures. As we know, the composition and thermodynamic properties of an equilibrium reacting closed system do not depend on the path followed in reaching this equilibrium. Let us assume that for several given values of p and T the equilibrium composition is determined, and the number of moles of mixture components n_j has been found. From our state with pressure p and temperature T, we can formally advance to the state $p^* \to 0,T$, keeping the mixture composition unchanged. Though for a closed equilibratedly reacting system, such a transition is unrealistic in practical terms, nonetheless it gives us an opportunity to employ relationships that are valid for closed systems. Let us integrate with $T = \text{const}$ and $n_j = \text{const}$ the following equality:

$$dJ = \left[v - T\left(\frac{\partial v}{\partial T}\right)_p\right] dp \qquad (7)$$

We get an expression for the enthalpy of the mixture:

$$J(p,T,n_j) = J^*(p^*,T,n_j) + \int_0^p \left[v - T\left(\frac{\partial v}{\partial T}\right)_p\right] dp, \qquad (8)$$

where the index (*) refers to the function of a mixture of ideal gases.

In a similar way, we can obtain relationships for any thermodynamic functions. We will present the most important of them:

entropy

$$S(p,T,n_j) = S^*(p^*,T,n_j) + \int_0^p \left[\left(\frac{\partial v}{\partial T}\right)_p^* - \left(\frac{\partial v}{\partial T}\right)_p\right] dp, \tag{9}$$

Gibbs' potential

$$\mathcal{G}(p,T,n_j) = \mathcal{G}^*(p^*,T,n_j) + \int_0^p (v - v^*)\,dp, \tag{10}$$

chemical potential

$$\varphi_j = \varphi_j^* + \int_0^p (v_j - v^*)\,dp. \tag{11}$$

We will recall that integration in equations (8) - (11) is carried out at constant composition.

The derivation of equations (8) - (11) is not restricted to any equation of state, therefore we used them to determine thermodynamic functions and properties both of real gases as well as, in a particular gas, for ideal gases.

In deriving equilibrium equations, we will use the procedure suggested by Gibbs; we will consider the closed system as the totality of several open systems. Then the condition of equilibrium at p and T = const can be written as:

$$\sum_j \varphi_j\, dn_j = 0. \tag{12}$$

We take atoms as the base components. In this case, the condition (12) is written in the form:

$$\varphi_j - \sum_i a_{ij} \varphi_i = 0. \tag{13}$$

To determine the composition and properties of the reacting mixture at specified p and T, it is necessary that the system (13) be supplemented by equations of the conservation of matter:

$$\sum_q a_{iq} n_q = M_T\, b_{iT}. \tag{14}$$

As the closing equation we use:

$$\sum_q x_q = 1. \tag{15}$$

Introduction of the number M_T in the equality (14) is founded on the following considerations. From the condition of the conservation of mass we can write:

$$\mu_T M_T = \mu N. \tag{16}$$

Since at given p and T

$$\mu = \sum_i x_i \mu_i = \text{const}, \tag{17}$$

then

$$M_T = \text{const} \cdot N. \tag{18}$$

So, we can select the value M_T such that the following condition is met

$$N = \rho_{\text{смеси}}, \tag{19a}$$

$$n_j = \rho_{j\,\text{ид}}. \tag{19b}$$

The relationship (19b) is especially important since it allows us to introduce into the equation of chemical equilibrium (13) n_j as the unknown number of moles.

The system of equations, consisting of (13) - (15), affords determination of the composition, thermodynamic functions and properties both of real and of ideal reacting gas mixtures.

In calculating the composition and properties of mixtures, the following equations of state are used:

$$pV = NR_0T \tag{20}$$

for ideal gases

$$pV = NR_0T\left(1 + \frac{pB}{R_0T}\right) \qquad (21)$$

for real gases.

TABLE 1

Deviations of $\frac{\phi_{ideal}-\phi_{real}}{\phi_{ideal}}$, percent, at a Pressure of 500 Bars..

quantity Φ	T°K	change in potential parameters, percent σ,+10	ε/κ,+10	σ,-10	ε/κ,-10	σ,+30	ε/κ,+30	σ,-30	ε/κ,-30
J	800	- 1,974	- 1,940	- 1,135	- 1,137	- 3,175	- 2,950	- 0,5996	- 0,4939
	1000	- 1,228	- 1,241	- 0,7174	- 0,6763	- 1,962	- 1,909	- 0,3916	- 0,1906
	1200	- 0,6171	- 0,7067	- 0,3685	- 0,2654	- 0,9951	- 1,205	- 0,2168	0,1195
S	800	2,114	1,913	1,191	1,344	3,434	2,652	0,5991	0,9011
	1000	1,221	1,075	0,6885	0,7939	1,984	1,412	0,3466	0,5536
	1200	0,7093	0,6164	0,3957	0,4616	1,169	0,7925	0,1978	0,3258
C_p	800	- 20,51	- 19,58	- 11,48	- 13,91	- 33,53	- 29,47	- 5,722	- 7,838
	1000	- 7,369	- 6,767	- 4,203	- 4,637	- 11,79	- 9,700	- 2,137	- 2,970
	1200	- 8,373	- 7,261	- 4,763	- 5,620	- 13,33	- 9,212	- 2,391	- 4,233
a	800	- 9,068	- 3,746	4,069	- 8,211	- 17,83	1,824	- 1,216	- 12,39
	1000	- 10,91	- 6,581	- 6,534	- 9,169	- 19,12	- 3,561	- 2,192	- 11,39
	1200	- 11,04	- 7,376	- 5,796	- 8,679	- 18,73	- 5,676	- 2,469	- 10,15

TABLE 2

Mole Fractions of Equilibrium Composition, p = 500 bars, T = 800°K.

	change in potential parameters, percent σ, +10	ε/κ, +10	σ, -10	ε/κ, - 10	σ, +30	ε/κ, +30	σ, -30	ε/κ, -30
CH_4	0,04877	0,04864	0,04831	0,04842	0,04928	0,04888	0,04797	0,04823
CO	0,00148	0,00149	0,00147	0,00145	0,00150	0,00156	0,00145	0,00144
CO_2	0,20499	0,20504	0,20525	0,20520	0,20469	0,20484	0,20544	0,20532
H_2	0,00762	0,00807	0,00929	0,00891	0,00572	0,00711	0,01054	0,00962
H_2O	0,40532	0,40506	0,40413	0,40440	0,40666	0,40670	0,40325	0,40390
N_2	0,33181	0,33174	0,33154	0,33160	0,33213	0,33189	0,33133	0,33149

Table 1 shows the effect of errors in potential functions on I, S, c_p, and a for combustion products of a mixture that has the starting composition $C_2H_8N_2 + 1.6N_2O_4$ [11] at a pressure of 500 bars and a temperature range of 800-1200°K. Table 2 presents mole fractions of the equilibrium composition of a mixture of real gases with change in potential parameters at a pressure of 500 bars and T = 800°K.

The calculations were made on the Ural-4 electronic digital computer. Thermodynamic functions of individual compounds were calculated from polynomials approximating the tables in the handbook [3]. Virial coefficients of nonpolar molecules and also derivatives of the form $T^*(\frac{dB^*}{dT})$, $T^{*2}(\frac{d^2B^*}{dT^2})$ were determined from polynomials approximating the tables in [2]. The program for the electronic digital computer makes it possible to determine the composition and thermodynamic functions and properties for compounds of the classes C, H, F, O, and N -- elements of an arbitrary starting composition.

Based on results obtained, we can draw the following conclusion:

1. The nature of variation in deviations as a function of $\Delta\sigma$ and $\Delta\varepsilon/k$ is practically the same for all thermodynamic functions.

2. With temperature rise, the "imprecision" of values of potential parameters has less and less of an effect on the final result. Evidently, we can expect that at temperatures higher than 2000°K the effect of σ and ε/k will be shown quite insignificantly.

3. If we assume that the error in the values of σ and ε/k of the main components does not exceed 10 percent, then the values of the deviations of properties of real mixtures from those of ideal are determined with an error of 20-30 percent.

4. Variations in potential parameters have a weak effect on the equilibrium composition of the mixture under study.

Symbols

σ, ε/k, and ξ = parameters of potentials; n_j = number of moles of the j-th component; v = specific volume; V = total volume; a = velocity of sound, as well as stoichiometric reaction coefficient; B = second virial coefficient; b_{iT} = number of atoms of the i-th chemical element in the original compound; c_p = specific heat capacity at constant temperature; $\mathcal{Y}$ = Gibbs potential; $\mathcal{J}$ = total enthalpy; i = atomic component of mixture; j = molecular component of mixture;

M_T = arbitrary number of moles of original compound; N = Avogadros number; n_q = total number of moles in mixture; x_j = mole fractions of combustion products; p = pressure; q = number of mixture components; R_0 = universal gas constant; r = inter-molecular distance; S = entropy; T = temperature; T* = reduced temperature; u = potential energy of interaction; μ_T, μ = molecular weight of original compound and molecular weight of combustion products; ϕ_j = chemical potential; in Table 2, the mole fractions are denoted by chemical formulas of the compounds.

References

1. Vukalovich, M. P. and I. I. Novikov, *Uravneniye sostoyaniya real'nykh gazov* (Equation of State of Real Gases), Moscow, 1948.

2. Hirschfelder, J., Charles Curtis, and R. Byrd, *Molekulyarnaya teoriya gazov i zhidkostey* (Molecular Theory of Gases and Liquids), Foreign Literature Publishing House, 1961.

3. Gurvich, L. V., G. A. Khachkuruzov et al., *Termodinamicheskiye svoystva individual'nykh veshchestv, Spravochnik* (Thermodynamic Properties of Individual Compounds. Handbook), Academy of Sciences USSR, Moscow, 1962.

4. Kessel'man, P. M. and A. S. Litvinov, *IFK*, Vol. 10, pp. 385-392, 1966.

5. Kessel'man, P. M. and S. K. Chernyshev, *TVT*, No. 5, pp. 700-707, 1965.
6. Thodos, G. and S. W. Flynn, *Am. I. Chem. Eng. Journal*, Vol. 8, No. 3, 1962.
7. Brokaw, R. S., *Alignment Charts for Transport Properties*, NASA, R-81, 1961.
8. Hadgman, C. E., *Handbook of Chemistry and Physics, 37th ed.*, Cleveland.
9. Monchick, L. and E. A. Mason, *J. Chem. Physics*, Vol. 36, No. 10, 1962.
10. Svehla, R. A., *Estimated Viscosities and Thermal Conductivities of Gas at High Temperatures*, NASA, Rep. 132, 1962.
11. Grolecki, G. J. and S. Tannenbaum, *ARS Journal*, Vol. 32, No. 8, 1962.

Kazan' Aviation Institute

THERMOPHYSICAL PROPERTIES OF COMBUSTION PRODUCTS OF CERTAIN CHEMICAL FUELS

V. Ye. Alemasov and A. F. Dregalin

It is necessary to know several thermophysical properties of a mixture to describe gas dynamic and heat exchange processes occurring at elevated temperatures with a reacting working body: heat capacity at constant pressure and constant volume, velocity of sound, transport properties (coefficients of viscosity and thermal conductivity), and others. Due to the limited number of existing ways of experimenting at elevated temperatures, all the more so for corrosive combustion products of chemical fuels, the avenue of theoretical calculation becomes especially important and at the present time is evidently the main approach in determining the thermophysical properties of a mixture. But when applied in calculating equations of thermodynamics and the molecular-kinetic theory of gases, several simplifying assumptions are employed (for example, in writing the equation of state and in selecting the model for interaction of mixture components). This introduces into the values obtained by calculation some indeterminateness, especially as to the value of the transport coefficients. Therefore, an evaluation of the effect errors in theoretical values of thermophysical quantities have on heat exchange properties is of practical interest and at the same time governs the acceptability of theoretical methods of calculating properties.

This article describes methods of determining thermophysical properties of reacting combustion products of chemical fuels. These methods have been used by the authors in a universal program for the M-20 electronic digital computer in getting calculation data for different mixtures.

The groundwork for calculating thermophysical properties of combustion products is a determination of the equilibrium state and derivatives under different sets of conditions. In most of the cases that are of practical interest, the problem boils down to determining the equilibrium state and its corresponding derivatives at known temperatures and pressures.

The system of equations of thermodynamic equilibrium when atoms are used as the base components is written as follows:

$$\begin{gathered}\sum_i a_{ij} \ln p_i = \ln K_j , \\ \ln\Big(\sum_j a_{ij} n_j + \sum_j a_{ij} n_j^{(k)}\Big) = \ln M_T b_{iT} , \\ \ln \sum_j p_j = \ln p , \end{gathered} \tag{1}$$

where M_T = number of moles of fuel ensuring the equality

$$n_j = p_j , \quad \sum_j n_j = p.$$

Solution of the system (1) by the numerical method in [1] determines the equilibrium composition of the combustion products.

To find the particular derivatives of the form $\left(\frac{\partial \ln n_i}{\partial \ln T}\right)_p, \left(\frac{\partial \ln n_i}{\partial \ln p}\right)_p$ it is necessary to appropriately differentiate the system (1) and substitute calculated values of n_i and n_j.

Now several of the most important properties of the working body can be found from customary thermodynamic relationships:

equilibrium heat capacity at p = const

$$\begin{aligned} C_{pp} = \frac{1}{\mu_T M_T} \Big\{ & \sum_j n_j \Big[c_{pj} + \frac{\mathcal{I}_j}{T} \Big(\frac{\partial \ln n_j}{\partial \ln T} \Big)_p + \\ & + \sum_j n_j^{(k)} \Big[c_{pj}^{(k)} + \frac{\mathcal{I}_j^{(k)}}{T} \Big(\frac{\partial \ln n_j^{(k)}}{\partial \ln T} \Big)_p \Big] - \frac{\mathcal{I}}{T} \Big(\frac{\partial \ln M_T}{\partial \ln T} \Big) \Big\}_p , \end{aligned} \tag{2}$$

equilibrium heat capacity at v = const

$$C_{vp} = C_{pp} - \frac{R_0}{\mu} \frac{\left[1 - \left(\frac{\partial \ln M_T}{\partial \ln T}\right)_p\right]^2}{\left(-\frac{\partial \ln M_T}{\partial \ln p}\right)_T} , \tag{3}$$

equilibrium velocity of sound

$$a_p^2 = \frac{C_{pp}}{C_{vp}} \frac{R_0}{\mu} \frac{T}{\left(\frac{\partial \ln M_T}{\partial \ln p}\right)_T} \tag{4}$$

On the assumption of the constancy of composition for an infinitesimally small variation in temperature and pressure, we can determine the frozen properties: $c_{p\text{-froz}}$, $C_{v\text{-froz}}$ and a^2_{froz}.

The transport coefficients of the mixtures -- viscosity and thermal conductivity -- are found from the formulas of the molecular-kinetic theory [2].

The component of the thermal conductivity coefficient caused by transfer of the heat of chemical reactions, λ_R, is of particular interest. A general formula for determination of λ_R has been advanced in [4]. With a few modifications, this formula was used by us in making practical calculations.

The most difficult task in obtaining transport coefficient by calculation was selecting the potential of interaction among mixture components when they collide. In the case of chemical fuels of the C, H, O, and N class, elements whose combustion products contain differently charged molecules and atoms of the order of 20 species, without bringing in empirical models of interaction this problem cannot at present be solved. The most suitable is the Lennard-Jones potential (12-6), since it describes collisions of molecules both in the field of low as well as of moderately high temperatures. This allows us to use experimental data for determining the corresponding potential constants, first of all, and to make more or less warranted extrapolations, in the second place. Additionally, the constants of the potential (12-6) can be estimated from several physical properties in the absence of experimental data.

Interaction of polar components with applicable precision at elevated temperatures is described by the Stockmeyer potential. We adopted this potential for all four components. In contrast to the values of the collision integrals $\Omega^{l,s}$ recommended in [2], in the present study we used the values of $\Omega^{l,s}$ averaged over all orientations from [5]. We borrowed parameters of the Stockmeyer potential from the same reference.

Parameters of the Lennard-Jones potential for 200 compounds, recommended in [3] as possible components of fuel combustion products, are taken from [6] or are evaluated *de novo* by methods in [6].

Tabled data of collision integrals $\Omega^{1,1*}$ and $\Omega^{2,2*}$ in [2,5] are approximated by power polynomials.

Properties of combustion products of several chemical fuels were evaluated by calculation. In this article, properties of combustion products of the chemical fuel [7] $C_2H_8N_2$ + N_2O_4 are presented by way of illustration (Tables 1-3) for the coefficient α = 0.8 of excess N_2O_4 compared to the stoichiometric concentration.

Analysis of the values of potential parameters determined by different methods showed that these methods are extremely approximate. Therefore, values of potential parameters obtained with the aid of these methods can be employed only in preliminary estimations. Experimental data will serve in possible judgement on the size of the error introduced by imprecise values of potential parameters.

In view of the lack of experimental data on transport properties of the combustion products of chemical fuels, we made a thermodynamic calculation of the chemical fuel $C_2H_8N_2$ + N_2O_4, $\alpha = 0.8$, $p = 0.01$ bar, and $T = 2000\text{-}4800°K$. Here "errors" were artificially introduced into the values of the potential parameters. The changes in potential parameters indicated were made for all components in the same direction (decrease or increase). The results of calculations are shown in Table 4. The magnitude of the change in coefficients of viscosity and thermal conductivity as a function of percent change in σ and ε/k can be roughly approximated by the formula

$$\Delta_{\eta,\lambda}\% \approx 2\Delta_{\sigma}\% + 0{,}1\Delta_{\varepsilon/k}\%. \qquad (5)$$

TABLE 1

Pressure 0.00981 bar

T,°K	(A)	(B)	(C)	(D)	(E)	$\frac{\lambda_e}{\lambda_f}$
800	685,8	1,560	1,128	324,7	0,0991	1,115
1600	823,3	1,788	1,041	545,7	0,1691	1,069
2400	989,1	1,926	5,994	733,0	2,193	8,179
3200	1541	2,056	6,093	861,8	2,328	5,709
4000	1884	2,090	1,625	982,9	0,681	1,422

Key: (A) meters/second; (B) $c_{p\text{-froz}}$, kilojoules/kg·deg;
(C) $c_{\text{const } p}/c_{p\text{-froz}}$; (D) $\eta \cdot 10^5$, nanoseconds/meter^2;
(E) λ_e, watts/meter·deg.

TABLE 2

Pressure: 0.981 bar

T	a	(A)	(B)	$\eta \cdot 10^5$	λ_e	$\frac{\lambda_e}{\lambda_f}$
800	569,0	1,554	1,941	323,9	0,1646	1,903
1600	823,9	1,788	1,031	545,7	0,1637	1,036
2400	966,5	1,925	1,378	728,0	0,3809	1,693
3200	1210	1,994	6,310	897,1	2,902	9,038
4000	1669	2,063	6,369	1010	3,057	6,621

Key: (A) $c_{p\text{-froz}}$; (B) $\frac{c_{\text{const } p}}{c_{p\text{-froz}}}$.

TABLE 3

Pressure: 98.06 bars

T	a	(A)	(B)	$\eta \cdot 10^5$	λ_e	$\frac{\lambda_e}{\lambda_f}$
800	556,8	1,522	1,352	319,2	0,1354	1,851
1600	823,9	1,788	1,031	545,7	0,1627	1,028
2400	1002	1,925	1,039	727,5	0,2394	1,069
3200	1140	2,000	1,719	888,7	0,5778	2,017
4000	1338	2,044	3,353	1042	1,665	4,623

Key: (A) $c_{p\text{-froz}}$; (B) $\frac{c_{\text{const } p}}{c_{p\text{-froz}}}$.

When Δ_σ = 10 percent and $\Delta_{\varepsilon/k}$ = 10 percent, the calculated value of the maximum error is 21 percent. It appears to be of low probability that in the future potential parameters of all components will undergo substantial refinement in the same direction. Potential parameters of atoms and free radicals are the most unreliable. If we assume that for these imprecise values of σ and ε/k introduce an error proportional to the content of atoms and free radicals in the combustion products of the fuel, the actual changes in Δ_η and Δ_λ percent, will be small even for considerable values of Δ_σ and $\Delta_{\varepsilon/k}$ for atoms and free radicals. With this in mind, we must at the present time accept as not possibl the calculated determination of the transport properties of combustion products at errors less than 20-30 percent. This affords grounds in calculations of effective thermal conductivity coefficient λ_e to use approximational formulas, which considerably reduces the necessary machine time and simplifies calculations.

TABLE 4

Effect on Thermophysical Quantities
of Changes in Potential Parameters

T^0K	quantities	$\Delta\varepsilon/k$, -10%	$\Delta\varepsilon/k$, 10%	$\Delta\varepsilon/k$, 30%	$\Delta\sigma$, -10% $\Delta\varepsilon/k$, 10%	$\Delta\sigma$, 10% $\Delta\varepsilon/k$, 10%
		change, in percent				
2000	η	1,389	- 1,493	- 4,184	19,12	- 17,83
	λ_e	1,339	- 1,618	- 4,331	19,67	- 18,15
2400	η	1,323	- 1,460	- 4,024	19,62	- 18,06
	λ_e	1,660	- 1,392	- 3,892	20,81	- 18,58
2800	η	1,302	- 1,413	- 3,845	20,48	- 18,39
	λ_e	1,301	- 1,517	- 4,118	20,81	- 18,64
3200	η	1,276	- 1,369	- 3,736	20,79	- 18,48
	λ_e	1,366	- 1,473	- 3,989	20,90	- 18,56
3600	η	1,271	- 1,369	- 3,726	20,79	- 18,49
	λ_e	1,341	- 1,355	- 3,809	20,67	- 18,51

TABLE 5

Pressure: 98.06 bars

α	0,5	0,7	0,9	1,1	1,3
T^0K	2738	3311	3454	3399	3290
$\frac{\lambda_e \text{ approx}}{\lambda_e}$	0,943	0,991	1,083	1,130	1,124

A formula of the following form is most often proposed for approximate determination of λ_e:

$$\frac{\lambda_e}{\lambda_f} = \frac{c_{pe}}{c_{pf}} \cdot \quad \lambda_e = \lambda_f + \lambda_R . \tag{6}$$

Tables 1-3 illustrate application of the formula in [6]. As we can see, in several cases this formula gives unsatisfactory results in the calculation of λ_e.

Another version of the approximational is the following function

$$\lambda_{e\ \text{прибл}} = \frac{5}{2} \eta c_{vp} \tag{7}$$

Verification of this formula has been made at several points. The corresponding results are given in Table 5, where the ratio $\lambda_{e\text{-approx}}/\lambda_e$ is presented for conditions of equilibrium combustion at different α.

Let us look at the possibility of using estimate values of transport coefficients in calculating convective heat exchange when there is a flow of chemical fuel combustion products in a Laval nozzle. We select as an example a profiled Laval nozzle with the following geometric characteristics: area of critical cross-section F_{cr} = 0.0065 meter^2, ratio of cutoff area to area of critical cross-section is 85.7, pressure at inlet to nozzle is 60 bars, and fuel is products of the combustion of kerosene and oxygen. To determine specific thermal convective fluxes q, we use a typical formula of the form

$$q = \varphi \rho w (J^* - J_{\text{stationary}}) \tag{8}$$

Values of specific convective thermal fluxes at inlet to nozzle, in the critical cross-section, and at the nozzle cutoff are, respectively, ~$10\cdot10^6$, ~$40\cdot10^6$, and ~$0.15\cdot10^6$ watts/meter^2. Similar to the data in Table 4, we vary the values of the viscosity and thermal conductivity coefficients by ± 20 percent. The relative change in specific thermal fluxes for given cross-sections will lie in the limits 4-6 percent. Since theoretical methods allow us to determine the quantity q to a precision of ± 10 percent, estimate values of transport coefficients can be used in calculating heat exchange in Laval nozzles. In a similar way, we can demonstrate the applicability of estimate values of transport coefficients in calculating frictional forces.

We present in the conclusion a number of characteristics of the universal [computer] program employed. The program allows us to determine the composition and thermophysical properties of combustion products of chemical fuels of arbitrary original composition. The fuel can contain up to ten atoms of the 22 most widely distributed [3]. Properties of individual components are calculated from seven-order polynomials approximating the tables in [3].

Symbols

a_{ij} = stoichiometric coefficient; p_j = partial pressure; n_j and $n_j^{(k)}$ = number of moles in gaseous and condensed phases; b_{iT} = number of atoms of the i-th chemical element in the conventional formula of the fuel; M_T = number of moles of fuel; p = pressure; T = temperature; μ_T and μ = molecular weight of fuel and molecular weight of combustion products; c_{pp} and c_{vp} = equilibrium heat capacities at constant pressure and at constant volume; $\mathcal{J}$ = total enthalpy of the mixture; $\mathcal{J}_j$ = total enthalpy of the j-th product; c_{pj} = heat capacity at constant pressure of the j-th product; R_o = universal gas constant; a_p = equilibrium velocity of sound; η = coefficient of viscosity; λ_e = effective coefficient of thermal conductivity; λ_f = coefficient of thermal conductivity of internal and translational degrees of freedom; σ and ε/κ = potential parameters; ρ = density; W = flowrate; $\mathcal{J}^*$ = enthalpy at drag temperature; φ = function of thermophysical properties, flowrate, and geometry of the flow section.

References

1. Alemasov, V. Ye. and A. F. Dregalin, *Trudy KAI*, No. 86, 1965.

2. Hirschfelder, J., C. Kertis [transliterated], and R. Bord, *Molekulyarnaya teoriya gazov i zhidkostey* (Molecular Theory of Gases and Liquids), Foreign Literature Publishing House, 1961.

3. Gurvich, L. V., G. A. Khachkuruzov et al., *Termodinamicheskiye svoystva individual'nykh veshchestv, Spravochnik* (Thermodynamic Properties of Individual Compounds. Handbook), Academy of Sciences USSR, Moscow, 1962.

4. Brokaw, R. S., *Journal of Chemical Physics*, Vol. 32, p. 1005, 1960.

5. Monchick, L. and E. A. Mason, *Journal of Chemical Physics*, Vol. 35, No. 5, 1964.

6. Svehla, R. A., *Report, NASA, R-132*, 1962.

7. Grelecki, G. J. and S. Tannenbaum, *ARS Journal*, Vol. 32, No. 8, 1962.

Kazan' Aviation Institute

ENGINEERING METHODS OF CALCULATING THERMOPHYSICAL PROPERTIES OF SOLUTIONS AND BINARY SYSTEMS

L. A. Bakhtin, N. A. Shakhova and L. S. Aksel'rod

In calculating mass and heat transfer processes in systems containing bicomponent solutions, it is necessary to know their thermophysical properties (viscosity, surface tension, partial pressure of solvent vapor, heats of solution, etc.).

Earlier [1] it was shown that the similarity of the temperature dependence of thermophysical properties of binary systems (solutions) y and of individual components (solvent) y_0 at constant pressures and concentrations makes it possible to obtain the following expression that is taken as the basis of a relatively simple method of calculating different properties of solutions:

$$f(y) = K_y f(y_0) + K_y \cdot b'_y \qquad (1)$$

The form of the function f(y) and $f(y_0)$ is best determined from molecular-kinetic principles. Several thermophysical properties as functions of temperature are determined by an exponential formula. For example, the Ya. I. Frenkel' formula for the viscosity of a liquid: $\mu = a_1 \exp(U/RT)$, and the formula for the vapor tension over liquids [2]:
$P = a_2 \exp(-r/RT)$.

We can write expressions for determination of a sought-for property of a solution y and a sought-for property of the solvent y_0 based on an exponential formula:

$$y = a \exp(Q/RT), \tag{2}$$

$$y_0 = a_0 \exp(Q_0/RT), \tag{3}$$

Solving equations (2) and (3) jointly when $T = T_0$, after uncomplicated transformations we get the equation:

$$\lg y = K_y \lg y_0 + K_y \lg b_y \,, \tag{4}$$

which is a particular case of expression (1) when $f(y) = \log y$, in which the multiplier of the similarity transformation and the increment are as follows:

$$K_y = \frac{Q}{Q_0}; \quad b_y = \frac{a^{Q_0/Q}}{a_0} \,. \tag{5}$$

Equation (4) can be written in a different way:

$$y = (b_y \cdot y_0)^{K_y} \,. \tag{6}$$

When deriving equations (4) and (6), the condition $T = T_0$ was adopted. Hence, points of identical temperatures are the similarity points of the curves depicting the temperature dependence of properties of solution and of solvent in this case.

The method of calculation based on similarity of the temperature dependence of physicochemical properties of a solvent and a solution can be used in determining the vapor tension of water over solutions. Equations (4, 6) take on the following form in this case:

$$\lg P = K_P \lg P_0 + K_P \lg b_P \,. \tag{7}$$

$$P = (b_p \cdot P_0)^{K_p}. \qquad (8)$$

An equation analogous to expression (7) was first derived by V. A. Kireyev [3] in the following form:

$$\lg P = K_p \lg P_0 + B. \qquad (9)$$

Studies of V. A. Kireyev and D. F. Othmer have demonstrated that in logarithmic coordinates log P - log P_0 experimental data on the vapor tensions of water over pure liquids, solutions, and mixtures are satisfactorily approximated by straight lines, which confirms the validity of the principle of similarity of temperature dependence of physicochemical properties of related compounds, including solution and solvents, applicable to saturated vapor tensions.

The form in which the principle of the similarity has been written in equations (7, 8) has an advantage compared to the equation of V. A. Kireyev, since it makes it possible to find the saturated vapor tension as an analytical function of composition for a number of binary systems.

Based on (7) and (9) we can write the expression of the integration constant B:

$$B = K_p \lg b_p \cdot \qquad (10)$$

According to the experimental data of D. F. Othmer [4], based on equation (10) the increment B_p was plotted as a function of concentration for ammonium nitrate solutions and is shown in Figure 1. From inspection of the figure it follows that B_p equals the mole fraction of water X_b

$$b_p = X_b, \qquad (11)$$

When we take (11) into account, equation (8) becomes:

$$\hat{p} = (X_B P_0)^{K_p} \tag{12}$$

D. F. Othmer [4] obtained an equation for determination of the differential heat of solution q_t':

$$q_t' = \frac{\partial q_t}{\partial v} = r_0(1 - k_p) \tag{13}$$

Othmer determined the integral heat of solution q_t by graphic integration of the experimental curve $1 - k_p = f(c)$, where c = concentration period.

The differential heat of swelling (solution) as a function of water content u is given in [5] for cases when water is absorbed by a colloidal body and for the dissolving of sulfuric acid in water:

$$q_t' = \frac{\partial q_t}{\partial u} = \frac{a \cdot b}{(b + u)^2} \tag{14}$$

Bearing in mind that the moisture content u is proportional to the mole ratio v, we combine the solution of equations (13) and (14), to get:

$$1 - k_p = \frac{a_1 b_1}{(b_1 + v)^2} \tag{15}$$

Treatment of experimental data [4, 6] has shown that the coefficients of equation (15) for ammonium nitrate solutions are $a_1 = 0.31$ and $b_1 = 7.8$; then equation (15) becomes

$$1 - k_p = \frac{0.31 \cdot 7.8}{(7.8 + v)^2} \tag{16}$$

Figure 2 presents a graph of k_p as a function of concentration for ammonium nitrate solutions, which shows that the curve calculated from equation (16) satisfactorily agrees with experimental data. Experimental values of k_p have been calculated from data [4, 6] treated by the least-squares method.

Equations (12) and (16) allow us to calculate the vapor tension of water over ammonium nitrate solutions for a wide range of temperatures and concentrations. The discrepancy of experimental [4, 6] and calculated values in the concentration range 0-75 percent does not exceed ±4-6 percent, attaining at high concentrations (89.7 percent) a value of 12 percent (based on data in [6]).

The principle of similarity of the temperature dependence of the saturated vapor tension of a solution and of a solvent allows us to correlate experimental data on vapor tension and on heat of solution.

Substituting (16) in (13), we get equations of the differential heat of solution:

$$q_t' = r_0 \frac{0{,}31 \cdot 7{,}8}{(7{,}8 + v)^2} \tag{17}$$

and the integral heat of solution of ammonium nitrate:

$$q_t = \int r_0 \frac{0{,}31 \cdot 7{,}8}{(7{,}8 + v)^2}\, dv \tag{18}$$

which after integration becomes:

$$q_t = r_0 \frac{0{,}31 \cdot v}{7{,}8 + v} + C \tag{19}$$

The dimensionality of the quantities that enter into equation (19) are as follows: $[r_0]$ = [kcal/kg-mole of water], and $[q_t]$ = [C] = [kcal/kg-mole of NH_4NO_3].

The integration constant C can be determined from the heat of infinite solution. Based on (19), the integral heat of infinite solution of 1 kg-mole of NH_4NO_3 ($v \to \infty$) is determined by the expression:

$$q_{t\infty} = 0{,}31 \cdot r_0 + C \tag{20}$$

Based on data in [7], $q_{t\infty}$ = 6470 kcal/kg-mole; C = 3190 kcal/kg-mole (at a temperature of 18°C). From data in [8], $q_{t\infty}$ = 6160 kcal/kg-mole; C = 2905 kcal/kg-mole (at a temperature of 25°C).

As follows from (19), the integral heat of solution of NH_4NO_3 is made up of two components, one of which depends, and the other does not depend on solution concentration period. As we know, one of the causes of heat effects in the formation of real solutions is the difference in forces of intermolecular attraction in pure solvent and in the solution. How strong this factor is obviously depends on concentration and is taken into account by the first member of the righthand side of equation (19). Further, when crystalline compounds are dissolved the crystal lattice breaks down, occurring with an expenditure of heat, which obviously is taken into account by the integration constant C. Hence, the integration constant equals the sum of heats of transformations from the crystalline modification corresponding to the given temperature to the dissolved (liquid) state. For ammonium nitrate the values of the integration constant C calculated from data in [7] from heats of transformations are as follows:

Temperature, °C	Higher than 170	125-170	83-125	32.3-83	Lower than 32.3
C, kcal/kg-mole of salt	0	1460	2487	2798	3055

The values of C calculated from the heat of infinite solution agree with a precision of ±5 percent with the value of C obtained from data based on heats of transformations in the corresponding temperature range (t < 32.3°).

Figure 2 presents a comparison of experimental and calculated values of the integral heat of solution of ammonium nitrate, showing that the curve calculated from equation (19) at $C = 3055$ kcal/kg-mole satisfactorily agrees with the experimental values.

We can obtain an analytical-graph method of calculating the viscosity of a solution based on the principle of the similarity of the temperature dependence of properties of the solvent and of a solution.

For this case equations (4) and (6) become:

$$\lg \mu = k_\mu \lg \mu_0 + k_\mu \lg b_\mu . \qquad (21)$$

$$\mu = (b_\mu \cdot \mu_0)^{k_\mu} . \qquad (22)$$

In Figure 3 experimental data on viscosity of aqueous solutions of urea are plotted in the coordinates $\log \mu - \log \mu_0$. The temperature scale plotted from experimental values of the viscosity of water, and the lines of saturation and boiling of the solution are also shown. Analyzing Figure 3, it is not difficult to see that in the coordinates $\log \mu - \log \mu_0$ experimental points are satisfactorily approximated by straight lines, which confirms the validity of equations (21, 22). A similar result in logarithmic coordinates is given by treatment of experimental data on viscosity of solutions of ammonium nitrate and of nitric acid. From Figure 3 it is clear that values of k_μ (slopes of lines) and b_μ do not depend on temperature and vary with increase in concentration.

Figure 4 presents the multiplier of the similarity transformation k_μ and the increment of viscosity b_μ as functions of the concentration of solutions of urea and of nitric acid. The values of k_μ and b_μ have been calculated from experimental data treated by the least-squares method. Figure 4 also shows the freezing-point diagrams of the systems under study.

Figure 4 shows that the eutectic points of the freezing-point diagrams correspond to the critical points of the curves of k_μ and b_μ as functions of composition. For the urea-water system, the curve of k_μ as a function of composition has a minimum at a solution concentration corresponding to the eutectic point of the freezing-point diagram. For the HNO_3-water system the eutectic point of the freezing-point diagram at concentration $c \approx 33\%$ corresponds to the minimum on the curve $k_\mu = f(c)$, the eutectic point at $c \approx 53\%$ corresponds to the maximum on the curve $k_\mu = f(c)$, and eutectic point $c \approx 90\%$ corresponds to the inflection point of the curve $k = f(c)$.

Equations (21) or (22) together with the graph of k_μ and b_μ as functions of composition allow us to calculate the viscosity of the solutions in question for a wide range of temperatures and concentrations. (When calculating with the aid of the graphs in Figure 4, the viscosity must be substituted in millipoise.)

Comparison of experimental viscosity values with those calculated from equation (22) with the graphs and Figure 4 shows that the discrepancy for the vast majority of experimental data is not greater than ± 3-5 percent.

The temperature range of applicability of equations (21, 22) is limited by the boiling point of the solvent t°_{bp}. Data on solvent viscosity at $t > t^\circ_{bp}$ have been obtained for $P > 1$ atm abs, and their use in calculating solution viscosity from equations (21, 22) contradicts the condition $P = \text{const}$, adopted in their derivation. Figure 3 shows that the function $\log \mu - \log \mu_0$ is linear both for temperatures up to 100°C as well as higher temperatures. However, at the transition through the 100°C point the nature of the curves of k_μ and b_μ as functions of composition changes sharply, accounted for by the effect of change of pressure on viscosity of water at $t > 100°C$.

It must be noted that the Ya. I. Frenkel' exponential formulas of viscosity, saturated vapor tension, etc. are approximate in view of the assumptions made in their derivation. When deriving equations of the form (7, 8, 21, 22), similar assumptions are adopted for the solution and the solvent. In these equations properties of the solution and the solvent are compared, and the relative quantities k_μ and b_μ come into play, therefore the effect of the above-indicated assumptions is not great and the precision of these equations is higher than that of the initial exponential formulas.

Use of the method set forth above in experimental research on physicochemical properties of solutions and binary systems allows us to reduce to a minimum the essential number of experimental points. In determining the multiplier of the similarity transformation k_μ and the increment b_μ for a solution of concentration c, it suffices to determine the magnitude of the sought-for property of the solution at two temperatures and to have available data on the temperature dependence of the corresponding property of the solvent.

As we know, to calculate surface tension σ of pure liquids the parachor method is used [9], which at temperatures far from the critical is determined by the expression

$$\Pi = \sigma^{1/4} V_{\text{м}} . \tag{23}$$

Table 1. Parachor of Ammonium Nitrate Solutions as Functions of Concentration and Temperature

Concentration, by weight, %	Temperature, °C							Mean Parachor Value
	20	40	60	80	100	120	140	
	Value of Parachor							
0	52,71	52,43	52,23	52,16	52,07	51,98	51,89	52,22
20	57,97	57,98	57,85	57,48	57,33	-	-	57,72
40	66,36	66,40	66,33	66,16	65,89	-	-	66,23
60	80,11	80,15	80,15	79,97	79,66	-	-	80,01
80	-	-	-	105,80	105,50	105,2	-	105,50
90	-	-	-	-	128,80	128,50	128,0	128,50

The parachor of pure liquids Π is almost independent of temperature and its value is determined by additive summation of the component fractions of atoms, groups, and bonds [9].

An attempt has been made in this study to employ the parachor method in calculating surface tension of solutions and of binary mixtures.

Table 2. Parachor of Urea Solutions as a Function of Concentration and Temperature

Concentration, by weight,%	Temperature, °C 20	40	60	80	100	120	140	Mean Parachor Value
	Value of Parachor							
20	58,28	57,90	57,65	57,22	57,11	-	-	57,63
40	66,10	65,69	65,40	64,95	64,57	-	-	65,34
60	-	77,57	77,07	76,63	76,98	-	-	76,81
80	-	-	-	95,83	95,01	94,53	-	95,14
90	-	-	-	-	-	109,20	108,8	109,00
95	-	-	-	-	-	-	117,8	117,80

Using experimental data on surface tension and density, we have calculated the parachor values for solutions of ammonium nitrate and of urea at different concentration (cf. Tables 1 and 2). The data of these tables show that the parachor of solutions, as well as of pure liquids, is almost independent of temperature. Additionally, the concentration of a solution has a considerable effect on the parachor value. The parachor of these solutions as functions of concentration is given in Figure 5. We can see from Figure 5 that the parachor of solutions Π rises linearly with increase in mole fraction of solute X_A and can be determined from the additivity rule:

$$\Pi = \Pi_A X_A + \Pi_B X_B \qquad (24)$$

The parachor of water P_B [B = water] is 52.22 (Table 1). The parachor of a melt of ammonium nitrate and of urea ($X_B = 0$; $X_A = 1$) is 163.5 and 130.4, respectively (Figure 5).

The expressions (23) and (24) allow us to calculate the surface tension σ for any working conditions, if we have determined the values of σ for the original components or for two compositions of the binary system, and if we know its density at the given conditions. The discrepancy of experimental and calculated surface tension values for solutions of ammonium nitrate and of urea do not exceed ±6 percent, wholly satisfactory for engineering calculations. The simplicity of the method of determination and the availability of a great deal of experimental material on density (compared with material on surface tension) accounts for the expediency of use of the parachor method in calculating surface tension of solutions and of binary systems.

Symbols

a and b = coefficient constants; B and C = integration constants; k_y and b'_y = multiplier of similarity transformation and increment of corresponding property; P and P_0 = vapor tension of water over solution and vapor tension of water over pure solvent at identical temperatures; $k_p = \bar{r}/r_0$ = multiplier of similarity transformation equal to the ratio of the partial molar heat of evaporation from solution $\bar{r}$ to the latent heat of evaporation of the pure solvent r_0; u = energy of activation; r = latent molar heat of evaporation; R = gas constant; T = absolute temperature; V_M = molecular volume; $v = x_B/x_A$, ratio of mole fractions of solvent and of solute; Q and Q_0 = energy characteristics of the process for the solution and the solvent, respectively; Π, Π_A and Π_B = parachor of solution, solute, and solvent, respectively; x_A and x_B = mole fraction of solute and solvent, respectively; μ and μ_0 = viscosity of solution and of solvent at identical temperatures; $k_\mu = U/U_0$, multiplier of similarity transformation of viscosity equal to the ratio of the energy of activation of solution and the energy of activation of the solvent.

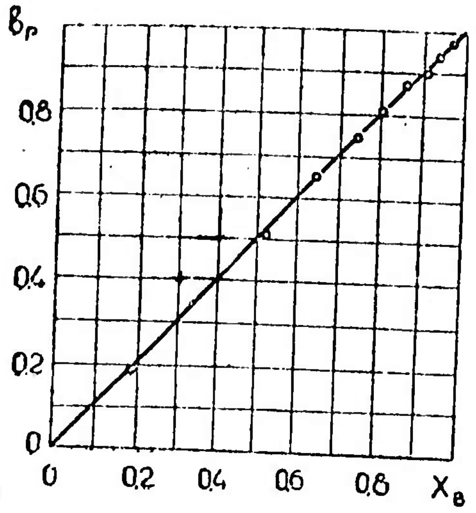

Figure 1. Increment b_p of NH_4NO_3 solutions as a function of concentration

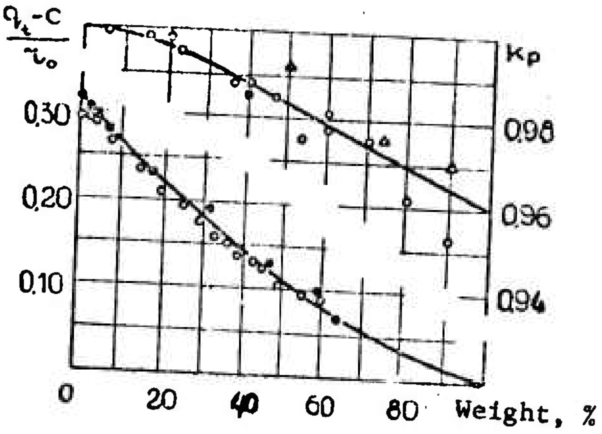

Figure 2. Multiplier of similarity transformation k_p of NH_4NO_3 solutions as a function of concentration (a) and comparison (b) of experimental values of the integral heat of solution with those calculated from equation (19).

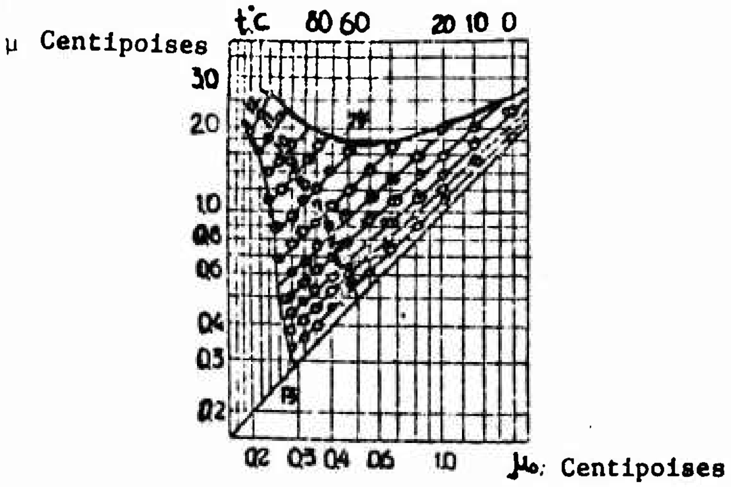

Figure 3. Viscosity of aqueous solutions of urea as a function of temperature and concentration

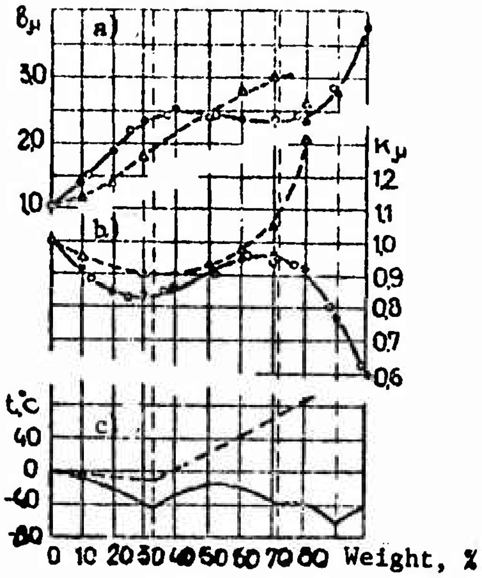

Figure 4. Function of the increment of viscosity (a), multiplier of similarity transformation (b), and freezing-point diagram (c), of solutions of urea (dash lines) and of nitric acid (solid lines)

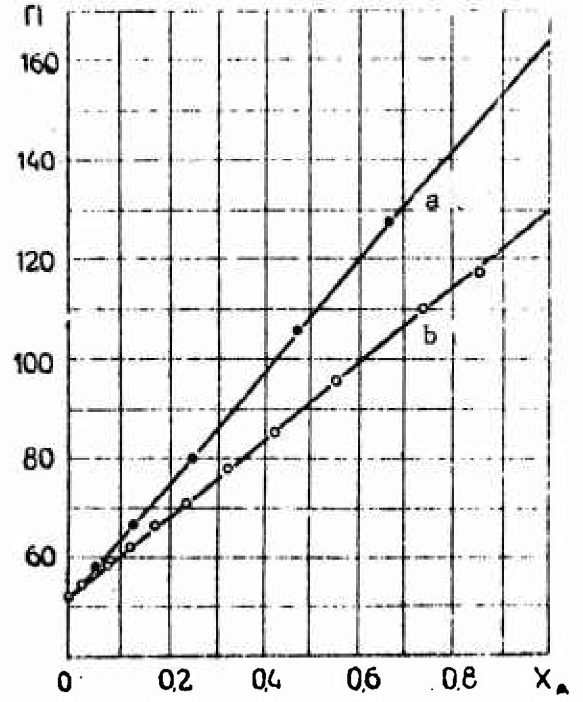

Figure 5. Parachor of solutions of NH_4NO_3 (a) and of urea (b) as a function of concentration

References

1. Bakhtin, L. A., N. A. Shakhova and L. S. Aksel'rod: *Tezisy Dokladov XXVIII Nauchno-tekhnicheskoy Konferentsii MIKhM*, No. 1, p. 3, 1967.

2. Karapet'yants, M. Kh.: *Metody Sravnitel'nogo Rascheta Fiziko-khimicheskikh Svoystv. (Methods of Comparative Calculation of Physicochemical Properties.)* Moscow, Nauka Press, 1965.

3. Kireyev, V. A.: *ZhFKh*, Vol. 2, No. 2, p. 233, 1931.

4. Othmer, D. F. and G. I. Frohlich: *A. I. Ch. E. Journal*, Vol. 6, No. 2, p. 210, 1960.

5. Lykov, A. V.: *Teoriya Sushki. (Theory of Drying.)* Moscow-Leningrad, Godenergoizdat. Press, 1950.

6. Janecke, C. and E. Rahlfs: *Zeitschrift fur anorg, und allg. Chemie*, No. 192, p. 237, 1930.

7. Klavka, V. A. et al.: *Tekhnologiya Azotnykh Udobreniy. (Technology of Nitrogen Fertilizers.)* Moscow, Goskhimizdat. Press, 1963.

8. Baron, N. M. et al.: *Kratkiy Spravochnik Fiziko-khimicheskikh Velichin. (Concise Handbook of Physicochemical Values.)* Leningrad, Khimiya Press, 1965.

9. Bretinsyder, S.: *Svoystva Zhidkostey i Gazov. (Properties of Liquids and Gases.)* Moscow-Leningrad, Khimiya Press, 1966.

EXPERIMENTAL DETERMINATION OF TRANSPORT DIAMETERS IN THE TEMPERATURE RANGE 2000-10,000°K

Yu. N. Belyayev, N. V. Kamyshov, V. B. Leonas and A. V. Sermyagin

Difficulties in determining thermophysical properties of gases at temperatures greater than 1000°K are well known. The customary methods of steady state measurements at these temperatures prove inapplicable, and extrapolation of low-temperature data is unsubstantiated.

However, the kinetic theory allows us to reduce equilibrium and nonequilibrium properties of gases to the same common basis -- forces of intermolecular interaction. These results constitute a reliable foundation for carrying out a broad program of determining equilibrium and nonequilibrium properties by using independent data on molecular forces of interaction.

Determination of these forces in the range that is of interest owing to the existence of thermophysical properties of gases is possible by direct experimentation based on the so-called molecular beam method.

A detailed description of the method and experimental apparatus for investigating elastic scattering of molecular beams is given in [1]. A wide range of systems corresponding to paired combinations of atoms of noble gases [2], the atoms H, N and O, and the molecules H_2, N_2 and O_2 [3, 4] have been investigated on devices of this type since 1964.

In subsequent studies the systems including combinations of the molecules CO, NO and N, atoms N and O, and also CH_4-CH_4 and He-CH_4 have been investigated. Data on transport diameters for the systems listed are given in this present paper.

As we know, the potential of intermolecular forces determines the dynamics of pair collision of particles participating in the transport of a given molecular characteristic (momentum, type of particle, and energy). Kinetic coefficients are associated with forces of intermolecular interaction through the so-called collision integrals $\Omega_{(5)}$ (transport diameters) [35]:

$$\Omega^{(\ell,s)}=\left(\frac{kT}{2\pi\mu}\right)^{1/2}\int_0^\infty e^{-\gamma^2}\gamma^{s+3}Q^{(\ell)}(V_{\text{отн}})\,d\gamma \tag{1}$$

where $\gamma = 1/2\ \mu\ V_{rel}^2/kT$. For the potential $V = k/r^n$, the reduced collision integrals become

$$\Omega^{(1,1)}=\left(\frac{Kn}{kT}\right)^{2/n}\Gamma\left(3-\frac{2}{n}\right)A^{(1)}(n)\ , \tag{2}$$

$$\Omega^{(2,2)}=\frac{1}{2}\left(\frac{Kn}{kT}\right)^{2/n}\Gamma\left(4-\frac{2}{n}\right)A^{(2)}(n), \tag{3}$$

where $\Gamma(x)$ = Euler function, $A^{(1)}(n)$ and $A^{(2)}(n)$ = quantities tabled in [5].

The complex nature of forces of interaction as a function of distance makes the question of how much information we have on these forces essential in making practical calculations nontrivial. This question has been discussed in detail [6, 7]. For calculations in the temperature range 2000-10,000°K, it is necessary to have data on potentials in the range from ~ 0.2 electron volt to ~ 1 electron volt. It is precisely this range of interaction temperatures that has been explored in the present paper.

Parameters of interaction potentials approximated by functions of the type $V = K/r^n$ were obtained from functions of the energy of effective complete scattering cross sections $Q(\theta_0, E)$ at small angles. The measurements were made by the method of scattering beams on gas targets [1].

A compilation of potential parameters of the systems investigated, and also the range of distances within which the values of K are constant are given in Table 1.

The collision intervals $\Omega^{(1.1)}$ and $\Omega^{(2.2)}$, essential in obtaining coefficients of viscosity, diffusion, and thermal conductivity to the first approximation of the kinetic theory of gases, have been calculated for all systems studied in this paper for the temperature range 2000-10,000°K. The results of calculations are given in Tables 2 and 3.

Since the composition of gas mixtures can vary very strongly as a function of conditions, it appeared worthwhile not to calculate the transport coefficients, but to give only tables of collision integrals for the components. The values of $\overline{\Omega}^{(l,s)}$ presented in this paper and also data in [2-4] allow us to calculate the kinetic properties of air and other gas mixtures that are of great practical importance for a wide temperature range.

Table 1. Parameters of Potentials of Systems Studied

System	K (For $A^{0.71}$)	n	Δr [Å]
0 - 0	801	9,00	2,4I - I,89
- 0	379	8,I2	2,38 - I,84
0 - CO	76I	9,30	2,33 - I,80
- CO	I20	6,82	2,25 - I,80
- CO	2038	8,70	2,77 - 2,22
2 - 0	2I6I	8,48	2,85 - 2,28
CO - CO	1965	8,23	2,92 - 2,3I
Hn - CH_4	136	8,00	2,22 - 1,75
CH_4 - CH_4	2765	9,50	2,62 - 2,I4

Table 2. Collision Integrals $\overline{\Omega}^{(2.2)}$, Å^2, for Systems Studied

T °K	Systems								
	N_2-CO	N_2-NO	CO-CO	O-NO	N-NO	O-CO	N-CO	He-CH_4	CH_4-CH_4
2000	8,968	9,548	10,03	6,331	6,799	6,938	6,742	5,910	7,94
3000	8,167	8,675	9,091	5,803	6,211	6,287	5,987	5,27	7,29
4000	7,650	8,108	8,477	5,453	5,826	5,852	5,503	4,895	6,85
5000	7,265	7,691	8,030	5,200	5,546	5,540	5,155	4,63	6,55
6000	6,963	7,367	7,682	5,000	5,325	5,297	4,887	4,43	6,29
7000	6,723	7.105	7,396	4,836	5,146	5,099	4,671	4,25	6,11
8000	6,521	6,887	7,154	4,699	4,995	4,935	4,380	4,12	5,92
9000	6,345	6,694	6,965	4,582	4,867	4,793	4,329	4,00	5,79
10000	6,192	6.532	6,781	4,479	4,753	4,671	4,207	3.895	5,66

Table 3. Collision Integrals $\overline{\Omega}^{(1.1)}$ [Å^2] for Systems Studied

T [°K]	Systems								
	N_2-CO	N_2-CO	CO-CO	O-NO	N-NO	O-CO	〃	He-CH_4	CH_4-CH_4
2000	7,852	8,049	8,414	5,383	5,751	5,796	5,837	5,010	6,780
3000	7,151	7,313	7,627	4,934	5,254	5,253	5,184	4,995	6,220
4000	6,698	6,835	7,112	4,637	4,928	4,889	4,765	4,710	5,920
5000	6,361	6,483	6,736	4,421	4,691	4,628	4,463	4,045	5,600
6000	6,096	6,210	6,445	4,251	4,505	4,425	4,231	3,780	5,370
7000	5,886	5,989	6,205	4,111	4,353	4,260	4,044	3,363	5,217
8000	5,710	5,805	6,002	3,995	4,225	4,123	3,793	3,525	5,060
9000	5,555	5,643	5,835	3,896	4,117	4,005	3,757	3,415	4,951
10000	5,421	5,506	5,689	3,809	4,021	3,902	3,643	3,321	4,840

Symbols

$A^{(l)}(n)$ = numerical coefficients; k = Boltzmann constant; K and n = potential parameters; l and s = 1,2,...; $Q^{(l)}(V)$ = effective transport cross section; r = interatomic distance; T = absolute temperature; V_{rel} = velocity of particles at collision; V(r) = potential of repulsive interaction; $\Gamma(x)$ = Euler γ function; μ = reduced mass; $\overline{\Omega}^{(l,s)}$ = reduced collision integral; $\Omega^{(l,s)}$ = collision integral; θ_o = angular resolution of apparatus.

References

1. Kamnev, A. B. and V. B. Leonas: *Teplo- i Massoperenos*, Vol. 7, Moscow, 1966.

2. Kamnev, A. B. and V. B. Leonas: *TVT*, No. 4, p. 288, 1966.

3. Belyayev, Yu. N. and V. B. Leonas: *TVT*, No. 5, 1967.

4. Belyayev, Yu. N. and V. B. Leonas: *DAN*, Vol. 173, p. 306, 1967.

5. Hirschfelder, J., C. Curtis, and R. Byrd , *Molekulyarnaya Teoriya Gazov i Zhidkostey. (Molecular Theory of Gases and Liquids.)* Foreign Literature Press, 1961.

6. Hirschfelder, J. and A. Eliason: *Ann. N.Y. Acad. Sci.*, Vol. 67, p. 451, 1957.

7. Belyayev, Yu. N. and V. B. Leonas: *Fizika Goreniya i Vzryva*, No. 2, 1967.

DETERMINATION OF VISCOSITY AND THERMAL CONDUCTIVITY OF REAL GASES AND THEIR MIXTURES BY THE SIMILARITY METHOD

A. A. Vasserman and V. I. Nedostup

Similarity methods have found wide acceptance in calculation of viscosity and thermal conductivity of real gases. Generalized equations and diagrams affording determinations from limited data of transport properties of compounds that have been little studied are put forth in [1-4], etc. A shortcoming of these studies is the impossibility of using them for reliable determination of transport coefficients of gas mixtures, since coordinates of the critical point figure as the reduction parameters, but critical states of a mixture and of a pure compound are not corresponding states. Use of so-called pseudocritical points does not insure the requisite precision, since none of these points exist at the surface of the state of a mixture, and moreover different methods of determining their coordinates are not well enough substantiated.

A general method of selecting support points of similarity in investigating thermodynamic properties is put forth in [5, 6]. Since the state of a gas is determined by two independent variables, corresponding states are found from the condition of equality therein of two dimensionless complexes of different designations [5, 6]. These conditions are necessary and sufficient in determining coordinates of reference points* of similarity and afford use of any point of the surface of the state of a real gas as a reference point. However, the simplest and most reliable approach is selection of reference points from curves of the extrema of thermal properties, in particular, from the Boyle curve. Such points, taken from identical values of the compressibility coefficient Z for different gases, have been successfully used in calculating thermodynamic properties of gas mixtures [6, 7].

---

* The terms "support point" and "support curve" should in all instance be read "reference point" and "reference curves" [Tr. editor]

In this paper the principle of selection of support points of similarity described above is applied in generalizing data on transport coefficients of real gases and their mixtures.

The relationship between any thermophysical property of a compound and thermal parameters -- temperature and pressure -- is conveniently depicted in the form of a surface, for whose study the principles of geometric similarity can be employed, if we find a reliable method of determining the support point coordinates. Curves of the viscosity and thermal conductivity minima at isobars exist on the surfaces $\eta = f(p, T)$ and $\lambda = \phi(p, T)$. The following dimensionless complexes can be formed for points on these curves

$$\frac{T}{\eta}\left(\frac{\partial \eta}{\partial T}\right)_p = 0, \qquad (1)$$

$$\frac{T}{\lambda}\left(\frac{\partial \lambda}{\partial T}\right)_p = 0. \qquad (2)$$

The equality (1) or (2) can be employed as one of the conditions of selecting a support point on the corresponding surface.

For transport properties, the role of quantities analogous to ideal-gas properties is played by viscosity and thermal conductivity values at atmospheric pressure which in a temperature range markedly exceeding the critical temperature make a substantial contribution to the quantities η and λ even at increased pressures. Therefore, we selected a ratio of transport coefficients on the minima curves to values at the same temperatures and $P = 1$ atm (η_T and λ_T) as the second dimensionless quantity.

Thus, points on the curves of viscosity and thermal conductivity minima in isobars taken from different gases with the same values η_{min}/η_T (λ_{min}/λ_T) can be chosen as support points of similarity, as satisfying the conditions: for viscosity

$$\frac{T}{\eta}\left(\frac{\partial \eta}{\partial T}\right)_p = 0 = \text{idem},$$

$$\frac{\eta_{min}}{\eta_T} = \text{idem} \qquad (3)$$

for thermal conductivity

for thermal conductivity

$$\frac{T}{\lambda}\left(\frac{\partial\lambda}{\partial T}\right)_p = 0 = \text{idem}$$
$$\frac{\lambda_{min}}{\lambda_T} = \text{idem} \qquad (4)$$

To find coordinates of new support points, we determined the curves of viscosity and thermal conductivity minima and the values of the corresponding properties at atmospheric pressure for several individual gases and gas mixtures. Here, we used table data [8] for nitrogen, oxygen, argon and air; the data in [9] for carbon dioxide, the results of experiments in [10-12] for methane, and those in [12] for natural gas. Using the minima curves, we determined the coordinates of support points T_o, p_o and η_o (λ_o) at the values $\eta_{min}/\eta_T = 1.35$, and $\lambda_{min}/\lambda_T = 1.5$, which are presented in Tables 1 and 2.

Table 1. Coordinates of Support Points of Similarity for Viscosity at the Value $\eta_{min}/\eta_T = 1.35$

Compound	T_0, °K	P_0, bar	$\eta_0 \cdot 10^6$, $\frac{\text{Newtons}\cdot\text{seconds}}{\text{m}^2}$
Nitrogen	246	156	20,70
Oxygen	283	196	26,73
Carbon dioxide	501	249	31,66
Methane	362	197	17,46
Air	243	150	21,09
Natural gas	362	168	17,38

To verify the effectiveness of new support points of similarity, the above-indicated data on viscosity and thermal conductivity were reduced to dimensionless coordinates $\bar{\eta} = \eta/\eta_o$, $\bar{\lambda} = \lambda/\lambda_o$, $\tau_1 = p/p_o$, $\tau = T/T_o$, and then a comparison was made of the values of $\bar{\eta}$ and $\bar{\lambda}$ for different compounds at identical τ_1 and τ. It is clear from Table 3 that dimensionless quantities of viscosities for different compounds agree quite satisfactorily -- mainly within the limits of 1-2 percent. There are large discrepancies for thermal conductivity, reaching 6-7 percent (Table 4). We must bear in mind, however, that the precision of experimental and table values of thermal conductivity as a rule are below the precision of data on viscosity; in particular, the error of the data we used [8] has been evaluated by the authors at 3-4 percent. Thus, the discrepancies observed in Table 4 do not exceed the overall error of original data.

Table 2. Coordinates of Support Points of Similarity for Thermal Conductivity at the Value $\lambda_{min}/\lambda_T = 1.5$

Compound	T_0, °K	P_0, bar	$\lambda_0 \cdot 10^6$, kw/m·degree
Nitrogen	299	214	38,75
Oxygen	321	215	42,48
Argon	324	204	28,26
Air	255	146	34,09

We must note that new support points of similarity are best used not only for mixtures, but also for pure compounds, since in many cases choice of the critical point as a support point introduces substantial errors owing to imprecision of determination of viscosity and thermal conductivity values for it.

Results of the comparison made allow us to recommend the new support points of similarity in determining viscosity and thermal conductivity coefficients of little-studied gases and gas mixtures of constant composition based on data for well-studied compounds. Here, it is enough to have available for the compound under study very limited experimental data affording determination of coordinates of even one point on the minimum curve.

Table 3. Comparison of Dimensionless Values of Viscosity η/η_0 at Identical τ and τ_1

$\tau = T/T_0$	Compound	$\pi = P/P_0$					
		0,5	I,0	I,5	2,0	2,5	3,0
I,0	Nitrogen	0,837	I,000	I,205	I,4I7	I,626	I,830
	Oxygen	0,834	I,000	I,I99	I,4I0	I,620	I,825
	Carbon dioxide	0,832	I,000	I,2I9	I,453		
	Methane	0,84I	I,000	I,205	I,409	I,608	
	Air	0,834	I,000	I,208	I,426	1,638	I,840
	Natural gas	0,839	I,000	I,205	I,385	I,572	
I,5	Nitrogen	I,058	I,I30	I,2I6	I,3I2	I,4I2	I,5I8
	Oxygen	I,062	I,I35	I,238	I,330	I,409	I,508
	Carbon dioxide	I,065	I,I34	I,2I7	I,308		
	Methane	I,066	I,I40	I,224	I,3I7	I,4I2	
	Air	I,066	I,I38	I,225	I,320	I,422	I,526
2,0	Nitrogen	I,275	I,320	I,372	I,430	I,492	I,557
	Oxygen	I,273	I,320	I,374	I,43I	I,492	I,553
	Carbon dioxide	I,28I	I,323	I,375	I,430		
	Air	I,272	I,335	I,387	I,445	I,507	I,572
2,5	Nitrogen	I,457	I,49I	I,529	I,57I	I,6I5	1,664
	Oxygen	I,463	I,498	I,536	I,578	I,622	I,667
	Carbon dioxide	I,473	I,498	I,539	I,579		
	Air	I,488	I,5I2	I,558	I,599	I,643	I,689
3,0	Nitrogen	I,628	I,654	I,685	I,7I7	I,752	I,788
	Oxygen	I,636	1,664	I,694	I,727	I,76I	I,796
	Air	I,67I	I,697	I,726	I,758	I,79I	I,826

Table 4. Comparison of Values of λ/λ_o at Identical τ and τ_1

$\tau = T/T_0$	Compound	$\pi = P/P_0$					
		0,5	I,0	I,5	2,0	2,5	3,0
I,0	Nitrogen	0,810	I,000	I,199	I,378	I,542	I,702
	Oxygen	0,805	I,000	I,187	I,349	I,493	I,624
	Argon	0,825	I,000	I,214	I,410	I,590	I,755
	Air	0,806	I,000	I,217	I,425	I,620	I,805
I,5	Nitrogen	0,998	I,102	I,212	I,320	I,426	I,532
	Oxygen	I,024	I,129	I,237	I,339	I,435	I,525
	Argon	I,007	I,110	I,222	I,334	I,444	I,552
	Air	I,035	I,138	I,231	I,345	I,449	I,552
2,0	Nitrogen	I,197	I,268	I,344	I,421	I,499	I,576
	Oxygen	I,266	I,337	I,413	I,488	I,560	I,630
	Argon	I,201	I,271	I,347	I,426	I,503	I,580
	Air	I,265	I,312	I,403	I,471	I,544	I,615
2,5	Nitrogen	I,391	I,445	I,503	I,562	I,622	I,685
	Oxygen	I,494	I,547	I,605	I,664	I,720	I,778
	Argon	I,381	I,435	I,492	I,552	I,611	I,671
	Air	I,481	I,533	I,580	I,640	I,693	I,746
3,0	Nitrogen	I,584	I,627	I,673	I,722	I,770	I,622
	Oxygen	I,706	I,746	I,793	I,841	I,890	I,936
	Argon	I,546	I,590	I,636	I,684	I,731	I,782
	Air	I,680	I,722	I,765	I,808	I,851	I,894

References

1. Uyehara, O. A. and K. M. Watson: *Nat. Petroleum News. Tech. Ser.*, No. 36, p. 764, 1944.

2. Owens, E. I. and A. I. Thodos: *Ch. E. Journal,* No. 3, p. 455, 1957.

3. Stolyarov, Ye. A.: *ZhFKh.* , No. 24, p. 279, 1950.

4. Bromley, L. A. and G. R. Wilke: *Ind. Eng. Chem.,* No. 43, p. 1641, 1951.

5. Kazavchinskiy, Ya. Z.: *DAN.*, No. 161, p. 1,127, 1965.

6. Kazavchinskiy, Ya. Z.: *IFZh.*, No. 3, p. 9, 1965.

7. Nedostup, V. I.: *IFZh.*, No. 6, p. 10, 1966.

8. Vasserman, A. A., Ya. Z. Kazavchinskiy and V. A. Rabinovich: *Teplofizicheskiye Svoystva Vozdukha i Yego Komponentov. (Thermal Physical Properties of Air and Its Components.)* Moscow, Nauka Press, 1966.

9. Vukalovich, M. P. and V. V. Alutnin: *Teplofizicheskiye Svoystva Dvuokisi Ugleroda. (Thermophysical Properties of Carbon Dioxide.)* Moscow, Atomizdat. Press, 1965.

10. Bicher, L. B. and D. L. Katz: *Ind. Eng. Chem.,* No. 7, p. 35, 1943.

11. Russ, E.: *Z. Angew. Phys.,* H.6, p. 4, 1952.

12. Golubev, I. F.: *Vyazkost' Gazov i Gazovykh Smesey. (Viscosity of Gases and Gas Mixtures.)* Moscow, Fizmatgiz. Press, 1959.

VISCOSITY AND THERMAL CONDUCTIVITY OF LIQUID AIR AND ITS COMPONENTS IN A WIDE RANGE OF TEMPERATURES AND PRESSURES

A. A. Vasserman and V. A. Rabinovich

In spite of the intensive use of liquid nitrogen, liquid oxygen, liquid argon and liquid air in cryogenics, their transport properties have not been adequately studied. An analysis and generalization of experimental data on viscosity and thermal conductivity of liquid air and its components are carried out in the present paper; equations are compiled and detailed tables of transport coefficients are calculated. The report is essentially a continuation of a similar investigation made for the above indicated four compounds in the gaseous state [1].

Dynamic Viscosity

Experimental research on the viscosity of liquid air and its components can be divided into two groups. The first group includes studies [2-12] devoted to determining the viscosity at saturation pressures or near-saturation pressures. Works in the second group contained results of the viscosity measurements in a broader range of parameters. They must first of all include the study [13] in which the viscosity of nitrogen and argon was determined at constant densities and for different temperatures. N. F. Zhdanova [14] measured the viscosity of liquid and gaseous nitrogen in the density range 0.38-0.746 g/cm^3 and the temperature range from the saturation curve to 290°K. The viscosity of nitrogen and argon at low temperatures and high pressures has also been investigated by Robinson [15]. Some data on the viscosity of liquid nitrogen, liquid argon and liquid air have been obtained by G. P. Filippova and I. P. Ishkin [16], experimenting in the temperature range -183 to 0°C up to a pressure of 150 atm. Fairly recently, I. F. Golubev and coworkers [17] carried out an extensive investigation of the viscosity of nitrogen in the temperature range -195.8 to 0°C at pressures up to 500 atm.

For most of the compounds considered, with the exception of nitrogen, experimental data embraces a limited region of parameters and cannot be directly used in compiling tables of viscosity used without entailing calculation methods. In view of the lack of a general theory of the liquid state up to the present time, reliable and theoretically substantiated methods of calculating the viscosity of a liquid have not been developed and a large number of empirical and semi-empirical equations are employed. An analysis of several such equations, in particular, the well known equations of A. I. Bachinskiy [18] and A. S. Prodvoditelev [19], has shown that they satisfy experimental data within experimental precision only for a limited range of temperatures and pressures. Therefore, with the aim of generalizing experimental data on the viscosities of the liquids investigated, we use the dependence of excess viscosity on density proposed by N. B. Vargaftik [20], which has been successfully used for many compounds.

Values of the viscosity of a gas at atmospheric pressure η_T obtained from smoothed experimental data in [1] were used in forming the values of excess viscosity $\Delta\eta$ from viscosity values at given temperatures and pressures $\eta_{p,T}$. We must note that the use of a component of η_T allows us to obtain a single equation for the viscosity of a liquid and the gas, and is justified from the viewpoint of several theories of the liquid state, for example, the theory of essential structures [21]. For temperatures below the normal boiling point values of η_T were obtained by extrapolation of curves plotted from data in [1]; the error of extrapolation cannot substantially affect reliability of $\Delta\eta$ values. Density values at experimental temperatures and pressures were calculated from equations of state that we formulated [22].

In plotting the most precise experimental data on viscosity of liquid nitrogen in the coordinates excess viscosity versus density (Figure 1), the data in [17] embracing a temperature range of 77.35-123.15°K at pressures up to 500 atm agree satisfactorily with experimental results [6] and [4] for the saturation curve. The experimental data in [16] are marked by scatter, however some of them agree with the data given above. Experimental values in [5] and [10] are considerably overstated compared with the results of measurements of other researchers. The data in [9, 13-15], shown only on small-scale graphs, is not plotted in Figure 1.

The support point Δη = f(ρ) for liquid nitrogen in the density range 0.70-0.81 kg/decimeter^3 required points somewhat higher [17] with the aim of insuring a reliable configuration of isobars and good agreement of data for the liquid and the gas. At higher densities, the curve was fitted among experimental points [4, 17] and [6]. At a density value ρ = 0.66 kg/decimeter^3, the support curve fits tightly the curve calculated from the equation Δη = f(ρ) for gaseous nitrogen [1], on which some of the data [17] for the liquid also falls.

Owing to the availability of an equation for calculating excess viscosity of nitrogen for the density interval 0-0.72 kg/decimeter^3, it was recognized as worthwhile to describe the section of the support curve in the range ρ = 0.65-0.90 kg/decimeter^3 using an individual equation:

$$\Delta\eta = \eta_{\rho,T} - \eta_T;[10^{-6}\ \text{н}\cdot\text{сек/м}^2] = 52{,}09 + 253{,}4(\rho - 0{,}65) + 1638(\rho - 0{,}65)^2 - 29438(\rho - 0{,}65)^3 + 283350(\rho - 0{,}65)^4 - 471070(\rho - 0{,}65)^5. \quad (1)$$

For the value ρ = 0.65 kg/decimeter^3, the quantities Δη and the derivative d(Δη)/dρ from equation (1) and the equation given in [1] agree.

Data on the viscosity of liquid oxygen and liquid nitrogen were subjected to similar treatment. For the first compound the support curve is presented from experimental data [4, 11] and fits smoothly at the value ρ = 0.92 kg/decimeter^3, the curve obtained earlier for gaseous oxygen [1]. Experimental points in [5, 7] lie above the support curve, and the points in [12] somewhat lower. The section of the supporting curve for oxygen in the density range 0.92-1.26 kg/decimeter^3 is described by the equation

$$\Delta\eta\,[10^{-6}\ \text{н}\cdot\text{сек/м}^2] = 73{,}66 + 237{,}8(\rho - 0{,}92) + 486(\rho - 0{,}92)^2 + 10695(\rho - 0{,}92)^3 - 79367(\rho - 0{,}92)^4 + 208570(\rho - 0{,}92)^5. \quad (2)$$

The excess viscosity of liquid argon as a function of density was obtained by the present authors, as in the case of oxygen, based on the data in [4, 11], which agree well internally. Experimental points in [10, 12, 16] lie on different sides of the support curve. At the value ρ = 1.08 kg/decimeter^3, the curve presented is congruent with the curve obtained earlier for gaseous argon. In the density range 1.05-1.45 kg/decimeter^3, the values of excess viscosity for argon are represented by the equation

$$\Delta\eta = 65{,}42 + 161{,}5(\rho - 1{,}05) + 225(\rho - 1{,}05)^2 + 7503(\rho - 1{,}05)^3 - 33918(\rho - 1{,}05)^4 + 56905(\rho - 1{,}05)^5. \qquad (3)$$

In view of the limited experimental data on viscosity of liquid air, we used the excess viscosity as a function of density in reduced coordinates $\Delta\eta/\Delta\eta_k = f(\rho/\rho_k)$ [23] and the data for nitrogen, which allows us to calculate the values of excess viscosity of air at densities exceeding 0.6 kg/decimeter^3. The curve obtained $\Delta\eta = f(\rho)$ agrees well with the experimental points [16] for the isotherm -183°C and for a limited number of data [7] for the mixture 80.4 percent N_2 - 19.6 percent O_2. In the density range 0.60-0.93 kg/decimeter^3, the curve is described by the equation

$$\Delta\eta = 34{,}33 + 141{,}9(\rho - 0{,}6) + 350(\rho - 0{,}6)^2 + 4762(\rho - 0{,}6)^3 - 41943(\rho - 0{,}6)^4 + 140530(\rho - 0{,}6)^5. \qquad (4)$$

The viscosity of liquid air and its components at pressures up to 500 bar in the temperature range from the critical point to the triple point was calculated from equations (1)-(4) and from the corresponding equations in the field of lower densities [1]. Starting with the precision of experimental data and the error of their analytical description, we can evaluate the error of the viscosity values obtained at 3 percent for nitrogen and 5 percent for the other compounds.

Thermal Conductivity

In contrast to viscosity, thermal conductivity of liquid nitrogen, liquid oxygen and liquid argon has been investigated chiefly at pressures differing from the saturation pressure.

The thermal conductivity of liquid nitrogen at the saturation state has been investigated by Hamman [24], Ye. Borovik, A. Mateyev, and Ye. Panin [25] and by Powers, Mattox, and Johnston [26]. At higher pressures, the thermal conductivity of this compound was first measured by Ye. Borovik [27] in the temperature range -182.8 to -102.5°C and for pressures of 11.2-99.0 atm. Later, the thermal conductivity of liquid and gaseous nitrogen was investigated by the following: U. Uhlir [28] in the temperature range 76.4-184.3°K and at pressures of 5.8-67.6 atm, by Z. Ziebland and Burton [29] in approximately the same temperature range, but for a wider range of pressures (1-134 atm), and by I. F. Golubev and M. V. Kal'sin [30] in the temperature range -195.6 + 20°C and for pressures from 1 to 485-600 atm.

The thermal conductivity of oxygen has been measured by the following: Hamman [24] at the saturation state, by Ziebland and Burton [31] in the temperature range 79.2-199.8°K and for pressures of 1-135.8 atm, and by N. V. Tsederberg and D. L. Timrot [32] at pressures of 60 and 100 kg/cm^2 and for the temperatures -190 to +25°C. There are even studies [33, 34] in which only individual thermal conductivity values of liquid oxygen are presented.

Quite detailed data on the thermal conductivity of argon has been obtained in the following studies: Yhlir [28] for the temperature range 86.6-193.8°K and the pressures 1-96 atm, by Ziebland and Barton [29] for a temperature range of 93.3-196.1°K and pressures of 1-120 atm, and by Ikenberry and Rice [35], who explored the widest range of parameters (91.6-234.6°K, 1-500 atm). Five experimental thermal conductivity values of liquid argon were obtained by Keyes [34].

There is no experimental data on the thermal conductivity of liquid air in the literature. The lowest temperature at which I. F. Golubev [36] measured the thermal conductivity of air at increased pressures was -77°C, that is, fairly removed from the critical point.

The experimental data cited above were compared by the authors as to isotherms and isobars. The comparison revealed that the data in [30] and in [29] for nitrogen agree within the limits 1-2% and are intermediate when compared with the results of other researchers. For oxygen, the data in [32] and in [31] agree in the main with the same precision, with the exception of the near-critical region, where the discrepancy amounts to 4-5 percent. Data in [35] for argon agree with a considerable fraction of the experimental points in [28, 29] in the limits ±2%, but for individual points the discrepancy amounts to 4-6 percent.

As the result of analysis of equations for thermal conductivity, it was established that the most successful are the equations of A. S. Predvoditelev [37] and N. B. Vargaftik [38], expressing thermal conductivity in the form of the sum of the functions of temperature and density, and taking as the temperature function the thermal conductivity of gas at atmospheric pressure. Thermal conductivity as a function of two variables is more general than as a function solely of density, however, taking cognizance of the good agreement with experimental data for a liquid using the equation $\lambda = B\rho^n$ [37, 39, 40], we deemed it worthwhile to treat the most detailed data for nitrogen and argon both in the coordinates λ and ρ, as well as in the coordinates $\Delta\lambda$, ρ.

Figure 2 presents experimental data for liquid argon in these coordinates. Both coordinate systems allow us to attain approximately the same precision in plotting a generalized curve from the experimental quantities. Most experimental data [29, 35] differ from the curves $\lambda = F(\rho)$ and $\Delta\lambda = f(\rho)$ by not more than 3 percent, but only for several points do the deviations exceed the indicated value. Some of the experimental points [28, 34] reveal somewhat greater deviations from the generalized curves, however these deviations lie within the same limits as in the comparison of experimental data in the customary coordinates λ, p and T. Since a similar state of affairs has been observed also for nitrogen, we used an equation of the type $\lambda_{p,T} = \lambda_T + f(\rho)$ in calculating the thermal conductivity of the liquids under question, allowing us in principle to obtain a single equation for the thermal conductivity of a gas and of a liquid.

The earlier compared [1] equations for calculation of the thermal conductivity of gaseous air and its components even upon their extrapolation satisfactorily describe data for the liquid throughout the entire range of densities under study (dash lines in Figure 2). Nonetheless, for densities higher than 0.76 kg/decimeter^3 for nitrogen and higher than 0.9 kg/decimeter^3 for argon, support curves were corrected by 1-2%, which brought them closer to experimental points.

The absence in the curves $\Delta\lambda = f(\rho)$ of sections with abrupt change in curvature allowed us to describe them in a broad range of densities, including the precritical densities, by the following simple equations:

for nitrogen (in the range ρ = 0-0.9 kg/decimeter^3)

$$\left[\Delta\lambda = \lambda_{p,T} - \lambda_T,\ 10^{-6}\ \text{квт/м·град}\right] = 29,46\rho + 175,67\rho^2 - 305,78\rho^3 + 420,06\rho^4 - 79,16\rho^5; \tag{5}$$

for argon (in the range ρ = 0-1.45 kg/decimeter^3)

$$\Delta\lambda = 18,52\rho + 57,98\rho^2 - 71,53\rho^3 + 57,18\rho^4 - 7,52\rho^5. \tag{6}$$

Thermal conductivity data for liquid oxygen [31, 32, 34] were treated by the authors in the coordinates $\Delta\lambda$, ρ. It turned out that these data in the limits 1-3 percent agree with the curve plotted on the basis of the equation for the thermal conductivity of gaseous oxygen in [1]:

$$\lambda_{p,T} = \lambda_T + 25,45\rho + 192,76\rho^2 - 433,23\rho^3 + 477,84\rho^4 - 156,30\rho^5. \tag{7}$$

Equation (7) has been formulated for the density range 0-1.2 kg/decimeter^3. In calculating the thermal conductivity of liquid to a pressure of 500 bar, it was used by the authors to the value ρ = 1.27 kg/decimeter^3; the error of so slight an extrapolation can hardly prove substantial, if we take into account the good results of extrapolation of similar equations for nitrogen and argon.

The thermal conductivity of liquid air, as noted above, has not been investigated experimentally. Methods of calculating thermal conductivity of liquid mixtures based on data for components, examined in [41, 42], do not insure requisite precision. Therefore, in calculating the thermal conductivity of liquid air we used an equation obtained earlier for gas [1]:

$$\lambda_{p,T} = \lambda_T + 42,16\rho + 56,65\rho^2 + 4,30\rho^3 + 95,98\rho^4. \tag{8}$$

Here it was taken into account that for components of air data on the thermal conductivity of liquid and gas in the coordinates $\Delta\lambda$, ρ forms a single curve, which is described with satisfactory precision by an equation formulated for gas. The equation (8) was extrapolated by us in the course of calculations from the density value 0.7 kg/decimeter^3 to ρ = 0.93 kg/decimeter^3; the reliability of the extrapolation was verified by comparing support curves for nitrogen and air in the reduced coordinates $\Delta\lambda / \Delta\lambda_k$, ρ/ρ_k.

The thermal conductivity of liquid air and its components was calculated from equations (5)-(8) for the same ranges of temperatures and pressure, as was the viscosity, with the exception of the near-critical region where an appreciable deviation of experimental data from the function $\Delta\lambda = f(\rho)$ was observed [1]. Taking account of the slight deviations of the most reliable experimental data from support data and the high precision of the analytical description of the latter, we can evaluate the error of calculated values of the coefficient of thermal conductivity of nitrogen and argon as 3 percent, for oxygen 4 percent, and for air 5-6 percent.

In conclusion, we note that much of the temperature and pressure range for which tables of transport properties of liquid air and its components have been prepared have not been investigated experimentally.

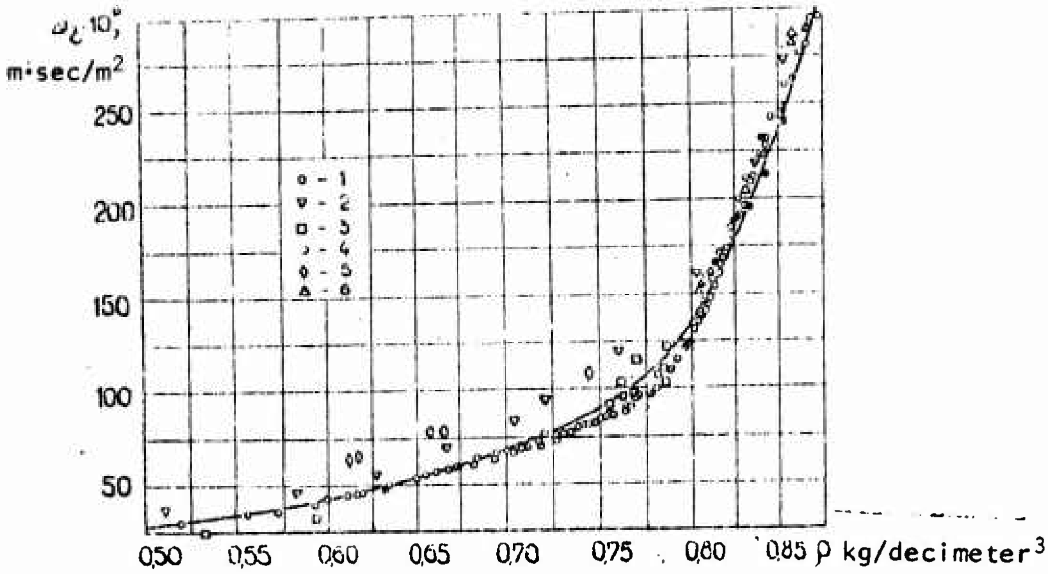

Figure 1. Excess viscosity of liquid nitrogen as a function of density based on the experimental data: 1, I. F. Golubev et al. [17]; 2, Forster [10]; 3, G. P. Filippova and I. P. Ishkin [16]; 4, S. F. Gerf and G. I. Galkov [6]; 5, I. S. Rudenko [5]; 6, N. S. Rudenko and L. V. Shubnikov [4].

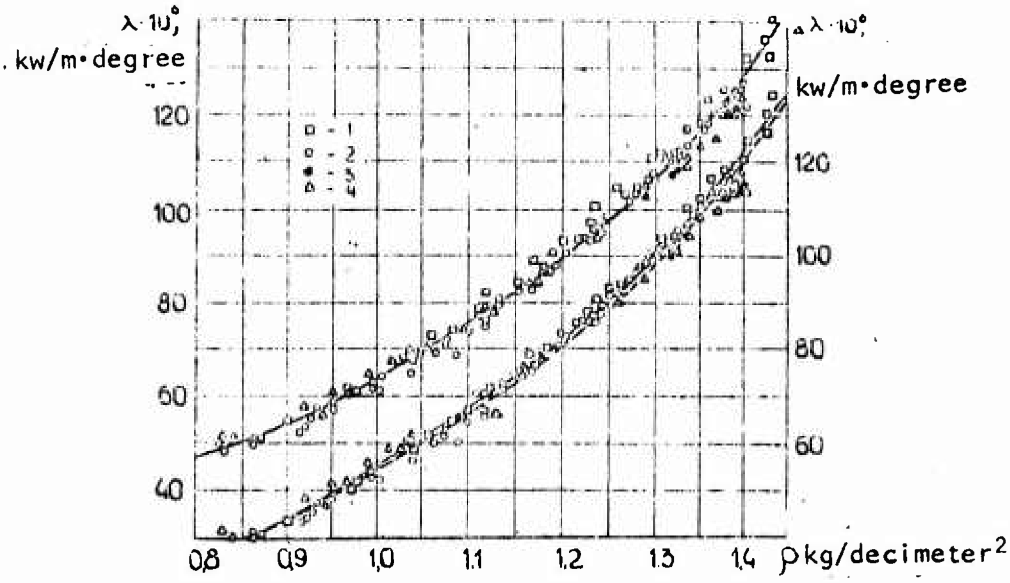

Figure 2. Generalization of experimental data with thermal conductivity of liquid argon: 1, Data of Ikenberry and Rice [35]; 2, Ziebland and Burton [29]; 3, Keyes [34]; 4, Uhlir [28].

References

1. Vasserman, A. A., Ya. Z. Kazavchinskiy and V. A. Rabinovich: *Teplofizicheskiye Svoystva Vozdukha i Yego Komponentov (Thermophysical Properties of Air and Its Components)*, Moscow, Nauka Press, 1966.

2. Forsch, C.: *Z. Phys.*, Vol. I, p. 177, 1900.

3. Verschaffelt, J. E. and C. Nicaise: *Comm. Leid.*, No. 159 b, 1917.

4. Rudenko, N. S. and L. W. Schubnikow: *Phys. Zeit der Sovjetunion*, Vol. 6, No. 5, p. 470, 1934.

5. Rudenko, N. S.: *ZhETF*, Vol. 9, No. 9, p. 1078, 1939.

6. Gerf, S. F. and G. I. Galkov: *ZhTF*, Vol. 10, No. 9, p. 725, 1940.

7. Gerf, S. F. and G. I. Galkov: *ZhTF*, Vol. 11, No. 7, p. 613, 1941.

8. Van Itterbeek, A. and O. van Paemel: *Physica*, Vol. 8, p. 133, 1941.

9. Van Itterbeek, A., H. Zink and O. van Paemel: *Cryogenics*, Vol. 2, No. 4, p. 210, 1962.

10. Forster, S.: *Cryogenics*, Vol. 3, No. 3, p. 176, 1963.

11. Boon, J. P. and G. Thomaes: *Physica*, Vol. 29, No. 3, p. 208, 1963.

12. Saji, J. and S. Kobayashi: *Cryogenics*, Vol. 4, No. 3, p. 136, 1964.

13. Verkin, B. R. and N. S. Rudenko: *ZhETF*, Vol. 20, No. 6, p. 523, 1950.

14. Zhdanova, N. F.: *ZhETF*, Vol. 31, No. 1 (7), p. 14, 1956.

15. Robinson, D. W.: *Bull SSR Annexe*, p. 329, 1955.

16. Filippova, G. P. and I. P. Iyukin: *IFZh*, Vol. 4, No. 3, p. 105, 1961.

17. Golubev, I. F., R. I. Shepeleva and L. V. Konovalova: *Trudy GIAP*, Vol. 13, p. 45, 1963.

18. Batschinski, A.: *Phys. Z.*, Vol. 13, p. 1157, 1912.

19. Predvoditelev, A. S.: *IFZh*, Vol. 4, No. 8, p. 3, 1961.

20. Vargaftik, N. B.: *Izvestiya VTI*, No. 1, p. 13, 1952.

21. Lin, S. H., K. Evring and W. J. Davis: *J. Phys. Chem.*, Vol. 68, No. 10, 1964.

22. Vasserman, A. A. and V. A. Rabinovich: *IFZh*, Vol. 12, No. 3, p. 342, 1967; Vol. 13, No. 2, p. 190, 1967.

23. Golubev, I. F.: *Vyazkost' Gazov i Gazovykh Smesey. (Viscosity of Gases and Gas Mixtures.)* Moscow, Fizmatgiz. Press, 1959.

24. Hamman, G.: *Ann. der Physik*, Vol. 32, No. 5, p. 594, 1938.

25. Borovik, Ye., A. Matveyev and Ye. Panina: *ZhTF*, Vol. 10, No. 12, p. 988, 1940.

26. Powers, R. W., R. W. Mattox and H. L. Johnston: *J. Amer. Chem. Soc.*, Vol. 76, p. 5968, 1954.

27. Borovik, Ye.: *ZhETF*, Vol. 17, No. 4, p. 328, 1947.

28. Uhlir, A.: *J. Chem. Phys.*, Vol. 20, No. 3, p. 463, 1952.

29. Ziebland, H. and J. Burton: *Brit. J. Appl. Phys.*, Vol. 9, p. 52, 1958.

30. Golubev, I. F. and M. B. Kal'sina: *Gazovaya Promyshlennost'*, No. 8, p. 41, 1964.

31. Ziebland, H. and J. Burton: *Brit. J. Appl. Phys.*, Vol. 6, p. 416, 1955.

32. Tsederberg, N. V. and D. L. Timrot: *ZhTF*, Vol. 26, No. 8, p. 1849, 1956.

33. Prosad, S.: *Brit. J. Appl. Phys.*, Vol. 3, p. 58, 1952.

34. Keyes, F. G.: *Trans. ASME*, Vol. 77, p. 1395, 1955.

35. Ikenberry, L. D. and S. A. Rice: *Journal Chem. Phys.*, Vol. 39, No. 6, p. 1561, 1963.

36. Golubev, I. F.: *Teploenergetika*, No. 12, p. 78, 1963.

37. Predvoditelev, A. S.: *Sbornik, Posvyashchennyy Pamyati Akad. P. P. Lazareva. (Collection Devoted to the Memory of Academician P. P. Lazarev.)* Moscow, p. 84, Academy of Sciences USSR, 1956.

38. Vargaftik, N. B.: *Izvestiya VTI*, No. 7, p. 13, 1951.

39. Abas-Zade, A. K.: *ZhTF*, Vol. 22, No. 1, p. 7, 1952.

40. Filippov, L. P.: *Vestnik MGU*, No. 12, 1954.

41. Reid, R. and T. Sherwood: *Svoystva Gazov i Zhidkostey. (Properties of Gases and Liquids.)* Moscow, Gostoptekhizdat. Press, 1964.

42. Bretschneider, S.: *Svoystva Gazov i Zhidkostey. (Properties of Gases and Liquids.)* Moscow, Khimiya Press, 1966.

STUDY OF MASS TRANSFER IN A BINARY MIXTURE OF RAREFIED GASES

P. V. Volobuyev, G. V. Lozhkin and P. Ye. Suyetin

Formulating the Problem

In recent years several studies have appeared on investigation of the relationship of diffuse and viscous mass transport in gases. Such a relationship in closed systems leads to the baro-effect phenomenon [1]. In multi-component mixtures, as a result of mutual causation of diffuse and viscous transport, irregular fluctuations in density develop [2]. The interaction of gas molecules with walls when there is a concentration gradient produces "diffuse slipping" of a mixture [3, 4].

An analysis of the phenomena named from the point of view of possible refinement of transport coefficients was of interest. We knew of attempts to explain the relatively large deviation of measured values of the coefficients of mutual diffusion D_{12} from calculated values as stemming from the emergence of a mean-mass flow caused by diffusion [5]. Below it will be shown that similar possibilities occur also in the analysis of coefficients of barodiffusion.

However, thus far the effect of the incipient mean-mass movement of gas on diffusion has not been clearly enough taken into account. In particular, the role of diffuse slipping when there is a constancy of pressures in the system remains unclear. Hence, it was natural to attempt to investigate "pure" diffusion [6] when the pressure gradient is compensated by special measures.

Graphically, the formulation of the task can be clarified with the aid of a simplified diagram (Figure 1). Two volumes v_I and v_{II} were adjusted in advance to the same pressure p for different gases, the molecular weights of which were m_1 and m_2 respectively ($m_2 > m_1$). Upon mutual diffusion of gases through a capillary with a cross-section area S_k, a pressure gradient was induced which was compensated by the symmetrical variation in volumes by means of shifting a calibrated rod with a cross-section area S_{rod}. The equality of pressures at the capillary ends was recorded by a differential micromanometer [7], serving as a null instrument. The sensitivity of the micromanometer was ~ 10^{-2} newtons/m^2. Since the magnitude of the coefficient for the conditions under study is ~ 1 newton/m^2, this sensitivity allows us to insure equality of pressures at capillary ends with adequate precision.

It is not difficult to show that the rate of change of volumes of the system for isobaric diffusion is determined by the density of the numerical flux of molecules of the mixture $\bar{J}$ through the capillary. Actually, variation in the total number of molecules N in each of the volumes can be represented as

$$\frac{\partial N_I}{\partial t} = J S_{\text{к}} ; \quad \frac{\partial N_{II}}{\partial t} = -J S_{\text{к}} . \tag{1}$$

But since the pressure is kept constant, the original equations become

$$n_I \frac{\partial V_I}{\partial t} = J S_{\text{к}} ; \quad n_{II} \frac{\partial V_{II}}{\partial t} = -J S_{\text{к}} \tag{2}$$

Under the conditions investigated

$$n_I = n_{II} = n$$

and

$$\frac{\partial V_I}{\partial t} = -\frac{\partial V_{II}}{\partial t} = \frac{\Delta V}{t} . \tag{3}$$

But ΔV = change in volume can be expressed by the extent of shifting of the compensating rod Δl.

$$\Delta V = S_{wT} \cdot \Delta \ell , \tag{4}$$

hence

$$J = \frac{p}{kT} \frac{S_{wT}}{S_k} \cdot \frac{\Delta \ell}{t} . \tag{5}$$

Thus, recording the rate of shifting of the compensating rod, we can experimentally determine the value of the density of the complete flux of molecules of the mixture in isobaric diffusion.

Thermodynamic Solution

The value of the density of the total molecular flux can be found by methods of irreversible thermodynamics, based on determination of the rate of increase of entropy S for the system under study [8].

$$\frac{\partial}{\partial t} \int_V \rho s \, dV = \int_V \frac{1}{T} \sigma'_{ik} \frac{\partial v_i}{\partial x_k} dV - \int_V \sum_{j=1}^{2} \vec{i}_j \frac{\nabla M_j}{T} \, dV \tag{6}$$

The mean-mass velocity V is conveniently represented in the form of two components

$$\vec{V} = \vec{V}(r) + \vec{V}(R). \tag{7}$$

The value of $\vec{V}(R)$ in macroscopic approximation is constant throughout the cross section.

It can be shown that the presence of slipping does not lead to additional change of entropy in the system. Moreover, taking into account that in [9]

$$\frac{\partial \sigma'_{ik}}{\partial x_k} = \nabla_i p \tag{8}$$

the first integral in the lefthand member of equation (6) is conveniently represented as

$$\int_V \frac{1}{T} \sigma'_{ik} \frac{\partial v_i}{\partial x_k} dV = - \int_V n \vec{V}(r) \frac{\nabla p}{nT} \, dV . \tag{9}$$

where $\vec{V}$ is the value of the mean-mass velocity, averaged over the capillary cross section, without taking slipping into account.

The expression for rise in entropy is simplified if we take into account the relationship between diffusion fluxes of components and the Gibbs-Duhem ratio. Further, it is convenient to pass on to the chemical potential, referred to a single molecule M_{j11} [10]

$$M_{j11}' = kT[\ln C_j + \ln p + f(T)]. \tag{10}$$

Then

$$\frac{\partial}{\partial t}\int_V \rho s\,dV = -\int_V \left(n\vec{V}(r) - \frac{\vec{i}_1 n}{\rho_2}\right)\frac{\nabla p}{nT}dV - \int_V \vec{i}_1\left(\frac{1}{m_1} + \frac{\rho_1}{\rho_2 m_1}\right)\frac{\nabla M_{1n}}{T}dV \tag{11}$$

The rate of entropy rise is determined as the sum of products of generalized fluxes $\vec{J}_e$ for the corresponding generalized forces $\vec{x}_e$. From (11) it follows that in this case

$$\vec{J}_1 = n\vec{V}(r) - \frac{\vec{i}_1 n}{\rho_2}, \qquad \vec{J}_2 = \vec{i}_1\left(\frac{1}{m_1} + \frac{\rho_1}{\rho_2 m_1}\right)$$
$$\vec{X}_1 = \frac{\nabla p}{nT} \qquad \vec{X}_2 = \frac{\nabla M_{1n}}{T} \tag{12}$$

The total flux of gas molecules through the capillary without cognizance taken of slipping is defined as

$$\vec{J}_1' = \vec{J}_1 + \vec{J}_2 \tag{13}$$

Hence, the rise in entropy can be represented as

$$\dot{S} = -(\vec{J}_1 + \vec{J}_2)\vec{X}_1' + \vec{J}_2'\vec{X}_2, \tag{14}$$

where

$$\vec{X}_1' = \vec{X}_1, \quad \vec{X}_2' = \vec{X}_2 - \vec{X}_1, \quad \vec{J}_2' = \vec{J}_2. \tag{15}$$

The generalized fluxes and forces are related by linear relationships

$$\begin{aligned} \vec{J}_1' &= L_{11}'\vec{X}_1' + L_{12}'\vec{X}_2' \\ \vec{J}_2' &= L_{21}'\vec{X}_1' + L_{22}'\vec{X}_2' \end{aligned} \tag{16}$$

Taking slipping into account allows us to refine the density of the total flux of molecules through the capillary

$$\vec{J} = \vec{J}_1' + n\vec{v}(R). \tag{17}$$

Its values when ∇p = zero in accordance with (12) and (14) are determined in the form

$$\vec{J}|_{X_1'=0} = L_{12}'\vec{X}_2' + n\vec{v}(R) \tag{18}$$

Using the Onsager relationship for coefficients $L_{\ k}$ [First subscript in symbol just given is illegible -- Tr.], we can write

$$\vec{J}|_{x_1'=0} = \vec{J}_2'|_{x_2'=0} \cdot \frac{\vec{X}_2'}{\vec{X}_1'} + n\vec{v}(R) \tag{19}$$

The condition $\vec{x}_2' = 0$, as follows from (10) and (15), under isothermal conditions is equivalent to $\nabla C = 0$. Hence, returning to the former symbols,

$$\vec{J}|_{\nabla p=0} = \left(\frac{1}{m_1} + \frac{\rho_1}{\rho_2 m_1}\right)\vec{i}_1|_{\nabla C=0} \cdot \frac{\nabla M_{1n}/T - \nabla p/nT}{\nabla p/nT} + n\vec{v}(R) \tag{20}$$

In accordance with [11].

$$\vec{i}_{1|\nabla C=0} = -\frac{n^2}{\rho} m_1 m_2 \mathcal{D}_{12} \alpha_\rho C(1-C)\frac{\nabla p}{p} . \qquad (21)$$

The rate of diffusive slipping is determined to the first approximation in [4]

$$\vec{V}(R) = \sigma_{12} \mathcal{D}_{12} \nabla C \qquad (22)$$

Taking (21) and (22) into account, we can write

$$\vec{J}_{|\nabla p=0} = -n \mathcal{D}_{12} (\alpha_p - \sigma_{12}) \nabla C . \qquad (23)$$

The value of the density of molecular flux averaged over the capillary length can conveniently be represented as

$$\vec{J}_{|\nabla p=0} = -\frac{p}{kT} \mathcal{D}_{12} \int_0^1 (\alpha_p - \sigma_{12}) dC \cdot \frac{1}{L_k} \qquad (24)$$

Thus, when there is isobaric diffusion the total molecular flux is determined by three kinetic coefficients, and not only by the coefficient of mutual diffusion D_{12}, as asserted in [5, 6]. The presence of the coefficient σ_{12} in equation (23) shows that even when $\nabla p = 0$, we must take into account the movement of the gas as a whole under the effect of the concentration gradient.

The expression we obtained for the density of the total molecular flux is of interest from the viewpoint of possible experimental analysis of the coefficient of barodiffusion. We know that, in contrast to the concepts adopted, in the thirteenth-moment approximation α_p proves to be substantially dependent on potential parameters. This function is determining for mixtures, the molecular masses of whose components are similar in value [12].

Direct measurement of the total molecular flux through the capillary in isobaric diffusion allows us to verify the conclusions of the thermodynamic solution set forth.

Comparison of Experimental and Calculated Results

Measurement of the total molecular flux in isobaric diffusion was made on an experimental apparatus prepared in accordance with the above-described basic layout. The design of the equipment is given in [1]. It was supplemented by a compensation device.

Shifting of the compensating rod made it possible to symmetrically vary the volumes v_I and v_{II}; the initial value of each of these was 704 cubic centimeters. A 0.8-cm-diameter rod was shifted through a teflon gasket. The position of the rod was established with a precision of 0.01 mm. The measurements were made at a temperature of 293°K in the pressure range $5 \cdot 10^3$ to $5 \cdot 10^4$ newtons/m^2.

Isobaric diffusion of four pairs of gases was investigated: He-Ar, He-N_2, H_2-N_2, and H_2-He. The values of the density of the total molecular flux measured in accordance with (5) in isobaric diffusion of the gases He-N_2 are given in Table 1. The results of the measurements show that the density of the total molecular flux under the conditions presented does not depend on absolute pressure. This is to be expected, starting from the expression of the density of the flux determined by the relationship (24).

In analyzing experimental data it was assumed that the gas concentration at the capillary ends did not vary during the measurement period. Its value was kept equal to the initial concentration in the volume [8]. This assumption was experimentally confirmed by measurements of the density of molecular flux of the He-Ar mixture for capillaries of different lengths. The corresponding results of measurements are given in Table 2. From the table it is clear that the products of flux density by capillary length, and consequently, the values of the difference in concentrations remain unchanged.

The scatter of experimental results when we investigated isobaric diffusion of the gases He-Ar through capillaries of different diameters proved to be somewhat greater. Upon changing the cross-sectional area of the capillary S_k from $6.90 \cdot 10^{-4}$ to $13.09 \cdot 10^{-4}$ cm^2, the measured value of flux density changed from $5.13 \cdot 10^{18}$ to $4.14 \cdot 10^{18}$ $cm^2 \cdot second^{-1}$. Capillary length in these measurements was 4.66 cm. The corresponding value of flux density found from formula (24) does not depend on capillary diameter and is $4.72 \cdot 10^{18}$ $cm^{-2} \cdot second^{-1}$.

Table 1. Measured Density of Total Molecular Flux As a Function of Pressure in Isobaric Diffusion of the Gases He-N_2 Through the Capillary $L_k = 4.57$ cm and $S_k = 6.90 \cdot 10^{-4}$ cm^2

№	P $n/m^{2} \cdot 10^{-3}$	$T, {}^0K$	t, sec.	Δl, мм	$J, \frac{1}{cm^2 \cdot sec.} \cdot 10^{-18}$
I	6,93	296	70,6	2,00	3,50
2	I4,7	290	75,0	I,00	3,56
3	26,8	297	I39	I,00	3,42
4	40,9	295	I09	0,50	3,35
5	55,5	296	I4I	0,50	3,5I

Table 2. Measured Density of Molecular Flux As a Function of Capillary Length in Isobaric Diffusion of the Gases Ar-He. $S_k = 13.09 \cdot 10^{-4}$ cm^2

№	$L_к$, см	$P, n/m^2 \cdot 10^{-3}$	$T, {}^0K$	t, sec.	Δl, мм	$J, \frac{1}{см^2 \cdot sec.} \cdot 10^{-18}$	$JL_к, \frac{1}{cm^2 \cdot sec.} \cdot 10^{-17}$
I	7,80	27,5	29I	I05	I,00	2,50	I,95
2	4,66	27,3	29I	95,4	I,50	4,I4	I,93
3	2,86	27,5	292	29,9	2,00	6,55	I,87

Table 3 presents a comparison of measured and calculated values of the density of total molecular flux for all gas pairs we investigated. Calculation of transport coefficients entering into expression (24) was made to the first approximation according to the Chapman-Enskog method for the Lennard-Jones potential. Integration with respect to concentrations was made in approximate terms using the trapezoidal formula. The table presents values of α_p and σ_{12} averaged over concentrations. The values of D_{12} presented correspond to atmospheric pressure and the temperature 293°K. The density of the total molecular flux of the mixture for the conditions under study did not depend on pressure for the gas pairs investigated. Only for the N_2-H_2 pair was a weak variation of flux density from $5.15 \cdot 10^{18}$ to $5.72 \cdot 10^{18}$ $cm^{-2} \cdot second^{-1}$ was observed for a pressure change in the system from $0.66 \cdot 10^4$ to $1.33 \cdot 10^4$ newtons/m^2.

It follows from Table 3 that the conclusions of theromdynamic theory satisfactorily agree with the experimental results. The main difference between measured molecular flux densities and those calculated from formula (24) did not exceed 8 percent for the three gas pairs H_2-N_2, He-N_2 and He-Ar. Only for H_2-He did this difference prove to be more substantial.

Additional comparison of the total molecular flux values obtained was made with experimental data in [5], which were recalculated for the values we measured. The results of the comparison are set forth in Table 3.

Table 3. Comparison of Calculated and Measured Values of Total Molecular Flux in Isobaric Diffusion of Gases Through a Capillary. $S_k = 6.90 \cdot 10^4$ cm^2, $L_k = 4.57$ cm

№	Gases	$\mathcal{D}_{12}$, $cm^2/sec.$	T, °K	$\bar{\sigma}_{12}$	$\bar{\alpha}_p$	$J, \frac{1}{cm^2\,sec} \cdot 10^{-18}$ Calculated	$J, \frac{1}{cm^2\,sec} \cdot 10^{-18}$ Experiment	$J, \frac{1}{cm^2\,sec} \cdot 10^{-18}$ From data in [5]
I	H_2-N_2	0,800	297	I,706	3,045	5,79	5,I5 ÷ 5,72	6,67
2	He-N_2	0,705	295	I,I29	2,II0	3,76	3,47	4,65
3	He-Ar	0,734	29I	I,358	2,522	4,72	5,I3	5,05
4	H_2-He	I,390	298	0,349	0,688	2,54	3,42	6,48

Symbols

C = numerical concentration of light component molecules; $\vec{v}(r)$ = usual Poiseuille velocity, the value of which is zero at the wall; $\vec{v}(R)$ = slipping rate of gas caused by longitudinal concentration gradient; σ_{12} = coefficient of diffusive slipping.

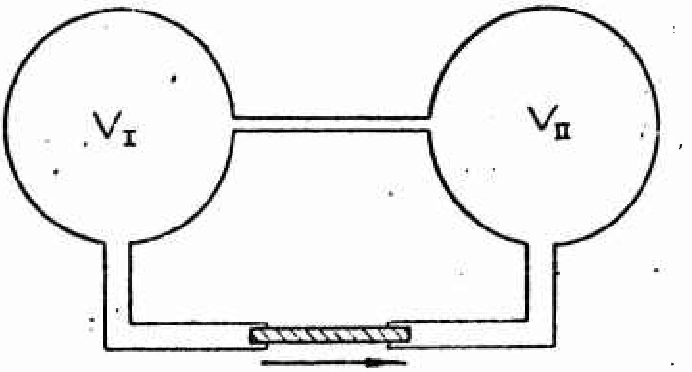

Figure 1. Simplified diagram of device for investigating diffusion of binary gas mixture

References

1. Suyetin, P. Ye. and P. V. Volobuyev: *ZhTF*, Vol. 34, No. 6, p. 1107, 1964.

2. Miller, L. and E. A. Mason: *Phys. Fluids*, N4, p. 711, 1966.

3. Kramers, H. A. and J. Kistemaker: *Physica*, Vol. 10, p. 699, 1943.

4. Volobuyev, P. V. and P. Ye. Suyetin: *ZhTF*, Vol. 37, No. 7, p. 1292, 1966.

5. Kosov, N. V. and L. I. Kurlapov: *Nekotoryye Voprosy Obshchey i Prikladnoy Fiziki. (Several Problems of General and Applied Physics.)* Nauka Press, Alma-Ata, 1966.

6. McCarty, K. P. and E. A. Mason: *Phys. Fluids*, N3, p. 908, 1960.

7. Suyetin, P. Ye. and P. V. Volobuyev: *Zavodskaya Laboratoriya*, No. 3, p. 374, 1964.

8. Suyetin, P. Ye. and P. V. Volobuyev: *ZhTF*, Vol. 35, No. 9, p. 1689, 1965.

9. Landau, L. V. and Ye. M. Lifshits: *Mekhanika Sploshnykh Sred. (Mechanics of Continuous Media.)* GITTL Press, Moscow, 1953.

10. de Groot, S. and P. Mazur: *Neravnovesnaya Termodinamika. (Irreversible Thermodynamics.)* IL Press, Moscow, 1964.

11. Hirschfelder, J., C. Curtis, and R. Byrd : *Molekulyarnaya Teoriya Gazov i Zhidkostey. (Molecular Theory of Gases and Liquids.)* IL Press, Moscow, 1961.

12. Zhdanov, V., Yu. Kagan and A. Sazykin: *ZhETF*, Vol. 42, No. 3, p. 857, 1963.

TRANSPORT COEFFICIENTS OF MULTI-COMPONENT MIXTURES

G. N. Dul'nev

Many of the artificial materials encountered in nature are multi-component mixtures, which can be divided into two classes by structural type. The first class includes mixtures with isolated closed inclusions: in the binding component (first component) inclusions of another material (second component) not in contact with each other are disseminated. The second class includes mixtures with components in contact or mutually penetrating each other. In analyzing transport processes (of heat, electricity, etc.) through multi-component mixtures, in some cases it is possible to adopt a macroscopic point of view, that is, to ignore the fact that materials consist of atoms and molecules, and to consider them as continuums. Then, based on phenomenological analysis of the transport process, it is possible to establish the effect of transport coefficients of the mixture as a function of its structure, and to establish the transport coefficients of the mixture components as a function of their concentrations. For example, the effective transport coefficient of a binary mixture Λ is associated with transport coefficients Λ_1, Λ_2 of the components and their concentrations m_1 and m_2 by the function

$$\Lambda = f(\Lambda_1, \Lambda_2, m_1, m_2) \tag{1}$$

With this approach to the analysis of transport processes, the following assumption is adopted: transport coefficients of pure components and also components in a mixture are identical.

Mixtures satisfying this assumption will be called mechanical mixtures in what follows.

Mechanical mixtures include a large number of systems consisting of solid components, and also porous bodies with gaseous or liquid inclusions and granular materials.

If when mixing various materials processes leading to change in the coefficients of the original components are induced, the effective transport coefficient will depend not only on the concentration of the original components and their transport coefficients, and functions of the type (1) cannot be used in calculating the effective transport coefficients.

Mechanical mixtures with closed isolated inclusions have been examined in detail in the literature, and several formulas have been proposed for calculating their effective transport coefficients. Among various authors, functional relationships of the type (1) do not agree, due mainly to the diversity of forms of the inclusions they considered. For example, in 1873 Maxwell calculated the effective electrical field of a system consisting of a continuous isotropic mass in which extraneous particles spherical in form were disseminated [1]; later, the problem was generalized by several authors who considered particles of more complex form. We note that in the initial studies the main consideration was given to dielectric permeability of a mixture consisting of an isotropic medium containing within it particles of elliptical, spherical, cylindrical, and other forms. Later, similar investigations were made by Rayleigh who considered the electroconductivity of a system consisting of a media with particles disseminated in it [2]. The results obtained were later applied for thermal conductivity phenomena, and the methods of generalized conductivity found further development in this field. A review of numerous studies on generalized conductivity of systems of the first class is given in [3].

The results of calculations using formulas proposed by various authors afford the following conclusion: the form of inclusions has a little effect on the value of the effective transport coefficient, it here being assumed that the inclusions are isometric, that is, in all directions the inclusion dimensions differ little from each other.

In our view, for mixtures of the first class with isometric inclusions, investigation of generalized conductivity was most correctly carried out by V. I. Odelevskiy, who proposed the following formula for calculating generalized conductivity of a binary system [5]

$$\frac{\Lambda}{\Lambda_1} = 1 - \frac{m_2}{\frac{1}{1-\nu} + \frac{1-m_2}{3}}; \qquad \nu = \frac{\Lambda_2}{\Lambda_1} \tag{2}$$

Considerably fewer studies are found dealing with the analysis of effective transport coefficients of mechanical mixtures of the second class, that is, mixtures with mutually penetrating components. The qualitative distinction of a structure of this class is the absence of continuous gaps in the substance of the first component and the presence of alternating sections filled with the substance of diverse components oriented perpendicularly to the thermal flux and also parallel to it. Moreover, components of mixtures in the second class are index-equivalent, that is, when the indexes of the parameters Λ_i and m_i are changed, the result remains the same. Mixtures with closed enclosures do not satisfy this condition. The distinction noted for structures of the second class is already reflected in the first and earliest simplified model proposed by Shuhmeister [6]. His model consisted of a combination of two pairs of flat walls, one pair aligned parallel to the flux, and the other perpendicular to it. The Shuhmeister model did not fully enough reflect the actual structure of mixtures of the second class, which compelled him to resort to introduction of empirical coefficients for better agreement of experimental and calculated data.

A different approach to the analysis of effective thermal conductivity of structures with mutually penetrating inclusions was put forth by Meisenard: the transport coefficient was determined twice from formulas of the type (2) for structures of the first class. The first calculation was made upon an arbitrary choice of one of the components such as the binding component, the second calculation was made using the same formula, but the other component was taken as the binding component; the effective transport coefficient was determined as the arithmetic mean of these two calculations [7]. With the aid of these operations the requirement of index-equivalents of components for structures of the second class was evidently satisfied. However, the effects of thermal conductivity of second-class mixtures calculated by this method often deviated appreciably from experimental data, which ultimately compelled Meisenard to recommend various empirical formulas for practical use.

In 1965 the present author proposed a model of a mixture with mutually penetrating components and analytically substantiated the form of the functional relationship (1) for this class of mixtures[1] [4]

$$\lambda = \lambda_1 \left[c^2 + \nu (1-c)^2 + \frac{2\nu c(1-c)}{\nu c + (1-c)} \right], \qquad (3)$$

where c = parameter associated with the bulk concentration m_2 of the second component by the equation

$$m_2 = 2c^3 - 3c^2 + 1$$

The solution of the latter equation is of the form

$$c = 0.5 + a\cos\frac{\varphi}{3}$$

$$0 \leq m_2 \leq 0.5 \qquad a = -1 \qquad \varphi = \arccos(1-2m_2)$$

$$0.5 \leq m_2 \leq 1.0 \qquad a = 1 \qquad \varphi = \arccos(2m_2-1)$$

Later, the model with mutually penetrating components was generalized for multi-component mixtures, and also for mixtures that are a combination of structures of the first and second classes [8].

We note that a considerable number of natural and artificial materials are classified as mixtures with mutually penetrating inclusions, therefore it was of interest to use the functions obtained in calculating effective transport coefficients of various mechanical mixtures.

Solid porous systems. A comparison is made in [9] of values of effective thermal conductivity calculated from formula (3) and experimentally obtained for a group of construction and industrially dispersed materials. The main difficulty in plotting the empirical function (1) from experimental data

---

[1] See p. 82

was that the authors of the experiments, as a rule, did not indicate all parameters entering into the formula (1). Usually, for construction and industrial materials the effective thermal conductivity, kind of material (sometimes extremely complex), porosity, or bulk weight was indicated. Therefore, the authors of study [3] had to determine the parameters that enter into the function (1) by an indirect approach, sometimes, approximately. Here the following materials were examined: various kinds of brick (pumice-concrete, trapel, slag, silicate, etc.); concrete (air-entrained concrete, slag-concrete, rubblestone concrete, etc.), and also several other construction and industrial materials.

In spite of incomplete information on properties of components and the highly complex structure of the mechanical mixtures indicated above, theoretic functions of the type (3) lead to results satisfactorily agreeing with experimental data of the various authors. Additionally, the qualitative nature of the function (1) agrees fully, and quantitative deviations of calculated and experimental data rarely exceed the region caused by experimental error or scatter of the characteristics of the original components.

A comparison of calculated and experimental thermal conductivity values of chamotte ceramics in the temperature range 80-1200°K is given in [10]. These ceramics can be considered as a mechanical multi-component mixture in which both closed and mutually penetrating inclusions are present. The skeleton of the ceramics consists mainly of two components: SiO_2 in the amorphous phase and Al_2O_3 in the crystalline phase. Here particles of aluminum oxide are dispersed in a continuous medium of silicon dioxide, that is, the particles constitute a two-component mechanical mixture of the first class. The ceramics are permeated by mutually penetrating pores which in the experiments were filled with the following gases: helium, freon-12 and air at pressures of $0.993 \cdot 10^5$ newton/m^2 and 0.133 newton/m^2. Calculation of effective thermal conductivity led to good agreement with experimental data -- deviations do not exceed the limits of measurement error.

Experimental data on the effective thermal conductivity of sintered porous bronzes as a function of bulk concentration of air pores, varied within the range 5-40 percent, are presented in [7]. Comparison of experimental data with results of calculations from formula (3) also leads to good agreement.

Mechanical solid mixtures also include alloys with practically insoluble components. Experimental data on thermal conductivity and electroconductivity of such alloys have been borrowed from [11-13], in which a study is made of thermal conductivity and electroconductivity of the following binary alloys: Bi-Cd, Bi-Ag, Pb-Sb, Pb-Sn, and Pb-Mn.

Comparison of experimental data with results of calculations made from formula (3) shows that the deviations do not exceed the limits of measurement error.

Mixture of a solid porous material with liquid. Such mixtures are found both in the natural state (petroleum- and water-bearing soil) and are also prepared artificially.

Results of experimental investigation of thermal conductivity of petroleum- and water-bearing soil as a function of bulk concentration of liquid are given in [14]. Experiments on measurement of thermal conductivity were conducted on specimens of porous quartzite sandstones and sands filled with water, petroleum, air and other gases. Deviations of experimental data from results of calculations made using formula (3) did not exceed 10-15 percent.

Experimental data on thermophysical properties of an artificial system of silicate spheres (solid skeleton) filled with various liquids (benzene, ethyl alcohol, distilled water, and acetone) are set forth in [15]. The results of calculation of effective thermal conductivity from formula (3) differ by no more than ±6.5 percent from experimental data.

Fibrous materials. The structure of fibrous material (cotton, wool, felting, fibrous insulation, etc.) with chaotically distributed fibers is such that it can be regarded as a two-component (fiber and gas-filler) mixture with mutually penetrating inclusions. This makes it possible in calculating effective thermal conductivity of such systems to use formula (3). The main difficulties here are associated with determination of thermal conductivity λ_2 of the gas-filler. It is not hard to show that λ_2 equals the total of molecular λ_{2M} and radiant $\lambda_{2\Lambda}$ components of thermal conductivity

$$\lambda_2 = \lambda_{2M} + \lambda_{2\Lambda} \tag{4}$$

The molecular component of the thermal conductivity coefficient can be determined from the formula in [16]

$$\lambda_{2M} = \frac{\lambda_0}{1 + \frac{B}{H\delta}}, \quad B = \frac{4k}{k+1}(P_r)^{-1}\frac{2-a}{a}\ell_0 H_0 \tag{5}$$

The radiant component of the coefficient of thermal conductivity for most fibrous systems equals, to the first approximation, [17]

$$\lambda_{2\Lambda} = \frac{16}{3}\frac{\sigma_0 T^3 y}{\alpha} \tag{6}$$

where y = parameter dependent on thickness of material, blackness of enclosing surfaces, and coefficient of attenuation α.

Analysis of experimental data and their comparison with the results of calculations made using formulas (3)--(6) have shown that the effective thermal conductivity of fibrous materials can be calculated from these formulas with satisfactory precision.

Dendritic systems. The systems considered above with mutually penetrating inclusions are based on a model whose components are formed by cross-links of constant cross sectioning [4]. This model narrows the range of applicability of formula (3) and does not allow it to be extended for certain kinds of structures, for example, structures obtained by sintering of grains under compressive loads. A characteristic feature of these structures is the sharp decrease in cross-sectional area of the solid component at sites of grain contact and the formation of "necks."[2] This structural feature leads to the need to take into account the nonuniformity of cross-sectional area in the direction of thermal flux. It can be shown that taking this effect

---

[2] See p. 82

into account leads to changing the value of the first member in the formula (3), and the rest of the formula remains as before. Such a modification of formula (3) is given in [18, 19].

Calculation of temperature fields using a model with variable cross-sectional area of the solid component and comparison of results obtained with experimental data of precision radiophysical measurements of the moon's temperature at different depths afforded a prediction of the nature of the structure of the moon's surface layer [18]. We note that in this case the reverse problem was solved: from a known value of effective thermal conductivity the structure of a material was decided. The possibility of using the modified formula (3) in calculating effective thermal conductivity of granular systems is shown in [19]. Satisfactory agreement of calculation with experimental data has been obtained for several granular materials, however, this study calls for further development and refinement of certain assumptions.

Thermal conductivity of liquid mixtures. It was of interest to use the phenomenological theory of generalized conductivity for the analytical determination of thermal conductivity of liquid mixtures or solutions. As we know, solutions denote mixtures of two or more liquids that are molecularly intermingled. Usually, transport processes in liquid mixtures are viewed from the vantage point of the molecular-kinetic theory. However, heat transport processes have still not been adequately studied even for homogeneous liquids, which leads to defects of theoretical formulas used in calculating transport coefficients. The problem is still further complicated in analysis of transport processes through liquid mixtures. The lack of a sufficiently reliable analytical method of calculating effective thermal conductivity of liquid mixtures leads to the use of various empirical functions.

Let us examine the possibility of using a model with mutually penetrating components in calculating the thermal conductivity of liquid mixtures. Here we must substantiate the validity of the assumption adopted in deriving formula (3), to the effect that thermal conductivities of the original components in the solution are constant. To some extent this assumption is indirectly confirmed by certain studies on solution structure. The microcrystalline hypothesis of the liquid state was adopted in explaining X-ray scattering in liquids and solutions; according to this hypothesis, the structure of the liquid is represented as small "crystallites" formed by aggregates of several thousands of molecules that are dimensionally close to finely pulverized powder. These components are unstable, change continuously, break down, and form new components [20, 21]. If particular specified positions of the atoms of the liquid are observed, it is always possible to find one of the ordered states which can be represented, starting with any space lattice [22]. The possibility of the existence of structural formations in solutions of associated liquids is even more probable. At high temperatures a breakdown of ordered regions occurs and the hypothesis of microcrystalline structure becomes less plausible. For temperatures higher than the melting point, the structure of the liquid is described based on the quasi-crystalline hypothesis: the liquid is considered as a state of matter that is quasi-crystalline in structure. This hypothesis derives from the group movement of molecules of the liquid; the transition of the latter into the gaseous state denotes the absence of group movement, that is, the presence of individual movement of molecules of the compound [23]. Thus, various hypotheses on the structure of a liquid derive from the existence of large molecular complexes. This allows us to adopt the assumption that in the mixture the complexes themselves retain their thermal conductivity value unchanged. Further, in describing transport of all possible kinds of space lattices, it is natural to dwell on the structure of the mutually penetrating components and to use formula (3) when we calculate the thermal conductivity of the mixture.

The suitability of the proposed model of liquid solutions was found by comparing theoretical and experimental values of effective thermal conductivity of more than forty different mixtures of normal and associated liquids; the main deviation of the calculated data from the experimental did not exceed 7 percent [24].

Thermal conductivity of gas mixtures. Most gas mixtures cannot be classified as purely mechanical, since thermal conductivity of components in the mixture can differ from thermal conductivity of the pure gas, which is due to change in mean free path upon mixing the gases.

However, in this case as well it is possible to use the effective thermal conductivity of formula (3) obtained for mechanical mixtures in calculating. It is only necessary to substitute into formula (3) the values of the coefficients of thermal conductivity of the components found for the mixture. We know that the coefficients of thermal conductivity λ_1' and λ_2' of the components of a binary mixture are associated as follows with thermal conductivities λ_1 and λ_2 of the pure components [25]

$$\lambda_i' = \frac{\lambda_i}{m_i + m_j A_{ij}}, \quad A_{ij} = \left(\frac{S_i + S_j}{2S_i}\right)^2 \sqrt{\frac{M_i + M_j}{2M_i}} \, \frac{\gamma_{ij}}{\gamma_i}$$

$$\gamma_i = 1 + \frac{c_i}{T}; \quad \gamma_j = 1 + \frac{c_j}{T}, \quad \gamma_{ij} = 1 + \frac{c_{ij}}{T} \tag{7}$$

Here we let i and j denote the first and second components of the binary mixture. Intermolecular forces of interaction are taken into account by the Sutherland constants c_i and c_j. Further, the values of c_{ij} for a mixture of nonpolar gases are determined from the formula in [26], $c_{ij} = \sqrt{c_i c_j}$, but for mixtures of gases containing polar components -- from the formula in [25], $c_{ij} = 0.733\sqrt{c_i c_j}$.

Results of calculations of effective thermal conductivity of gas mixtures from formulas (3) and (7) agree well with experimental data.

We note that the method of calculating effective thermal conductivity of gas mixtures advanced above is not unexpected. Introduction of a definite structure for the gas mixture must be viewed as a procedure that found its initiation as far back as studies by A. Wasiljewa [27], who proceeded on the basis of an additive relationship among the parameters λ, λ_1, and λ_2. The additive formula presupposes a complex structure for the mixture, and layers must lie parallel to the flux. In later studies, this procedure was refined both by the introduction of various empirical coefficients, as well as by the use of other structures. In the main, structures of mixtures with closed inclusions of components have been used [7]. A structure with mutually penetrating inclusions better corresponds, in our view, to the chaotic arrangement of gas molecules in a mixture. Evidently, this can account for the better agreement of experimental data with calculated data obtained from formulas (3) and (7) in which there are no empirical coefficients at all.

Symbols

Λ = generalized transport coefficient (thermal conductivity, electroconductivity, and dielectric constant); m_i = bulk concentration of component i; λ_i = coefficient of thermal conductivity of component i; λ_{iM} and $\lambda_{i\Lambda}$ = molecular and radiant constituents of component i; λ_o = coefficient of thermal conductivity of gas under normal conditions; λ'_i = coefficient of thermal conductivity of component i in the gas mixture; $k = c_p/c_v$, ratio of heat capacities of gas at constant pressure and heat capacity of gas at constant volume; Q = coefficient of accommodation; Pr_o = Prandtl criterion for normal pressure; l_o = mean free path of molecule at normal pressure H_o; H = pressure of filler gas; σ_s = Stefan-Boltzmann constant; α = coefficient of attenuation of radiation of material; T = mean value of absolute temperature of material; S_i and S_j = molecular diameters of components i and j; M_i and M_j = molecular masses of components i and j; c_i and c_j = Sutherland constants for gas components i and j.

Footnotes

1. To p. 74 Formula (3) was derived for the thermal conductivity of a mixture, however, its form is retained when we examine electroconductivity, and dielectric and magnetic permeability of a mixture.
2. To p. 77 We called such structures dendritic.

References

1. Maxwell, C.: *Treatise on Electricity and Magnetism,* Oxford, 1873.

2. Rayleigh, W. R.: *Phil. Mag.,* Vol. 34, p. 48, 1892.

3. Chudnovskiy, A. F.: *Teplofizicheskiye Kharakteristiki Dispersnykh Materialov. (Thermophysical Characteristics of Disperse Materials).* Fizmatgiz. Press, Moscow, 1962.

4. Dul'nev, G. N.: *IFZh,* Vol. 9, No. 3, p. 399, 1965.

5. Odelevskiy, V. N.: *ZhTF,* Vol. 21, No. 6, 1951.

6. Shuhmeister, J: *Ber. Kaiser. Akad. Wien. Math. - Nature,* No. 76. p. 283, 1877.

7. *Moesenard A.* Le *conductivite thermique des solides, liquides, gas et leurs melanges,* Paris, 1965,

8. Dul'nev, G. N. and Yu. P. Zarichnyak: *IFZh,* Vol. 12, No. 4, p. 419.

9. Dul'nev, G. N. and L. A. Komkova: *IFZh,* Vol. 9, No. 4, 1965.

10. Vasil'yev, L. L. and Yu. Ye. Frayman: *IFZh,* Vol. 9, No. 6, p. 762, 1966.

11. Mikryukov, V. Ye.: *Teploprovodnost' i Elektroprovodnost' Metallov i Splavov. (Thermoconductivity and Electroconductivity of Metals and Alloys.)* Metallurgizdat. Press, Moscow, 1959.

12. Chirkin, V. S.: *Teploprovodnost' Promyshlennykh Materialov. (Thermoconductivity of Industrial Materials.)* Moscow, 1959.

13. Mekhrabov, A. O.: *Issledovaniye Fizicheskikh Svoystv Binarnoy Sistemy Pb-Mn v Oblasti, Bogatoy Svintsom. (Study of Physical Properties of the Binary System Pb-Mn in the Lead-Rich Region.)* Author's Abstract of Dissertation, Azerbaydzhan State University Press, Baku, 1967.

14. Woodside, W. and J. Messmer: *Journ. Appl. Phys.,* Vol. 32, N9, p. 1688, 1961.

15. Verzhinskaya, A. B. and R. Sh. Vaynberg: *IFZh,* Vol. 12, No. 1, 1967.

16. Prasolov, R. S.: *Masso- i Teploperenos v Topochnykh Ustroystvakh. (Mass and Heat Transfer in Furnace Installations.)* Energiya Press, Moscow-Leningrad, 1964.

17. Poltz, H. Mitteiluny Phys. *Tech. Bundesanstalt Eigegangen,* No. 24, p. 515, 1964.

18. Dul'nev, G. N., Yu. P. Zarichnyak and B. L. Muratova: *Izv. VUZov, Radiofizika*, Vol. 9, 1966.

19. Vasil'yev, L. L.: *Sb. Issledovaniya po Teploprovodnosti. (Collection of Studies on Thermal Conductivity.)* Edited by Academician A. V. Lykov, Minsk, 1967.

20. Volyak, L. D.: *DAN SSSR*, Vol. 74, p. 307, 1950.

21. Benewitz, K. and E. Spittgerlere:*Z.S.* Phys. *Chem.*, Vol. III, p. 125, 1927.

22. Kratky: Phys. *Zeit.*, No. 34, p. 482, 1933.

23. Abas-Zade, A. and S. Bagdasaryan: *Vvedeniye v Fiziku Zhidkostey. (Introduction to the Physics of Liquids.)* Azeruchpedgiz. Press, 1961.

24. Dul'nev, G. N. and Yu. P. Zarichnyak: *IFZh*, Vol.11, No. 6, 1966.

25. Grus, H. and H. Schmick: *Wiss. Veroffentl. Siemens-Konzern*, Vol. I, p. 202, 1928.

26. Sutherland, W.: *Phil. Mag.*, Vol. 36, No. 5, p. 507, 1893.

27. Wasiljewa, A.: Phys. *Zeitschr.*, N 22, p. 737, 1904.

THERMAL CONDUCTIVITY OF ORDERED FIBROUS SYSTEMS

G. N. Dul'nev, Yu. P. Zarichnyak and B. L. Muratova

We designate as a fibrous system with ordered structure a material whose fibers are oriented even in just one direction, that is, lying in a plane perpendicular to the heat flux. Fibrous systems with ordered structure are used as construction and heat-insulation materials (cloth, mats). Theoretical study of the heat transfer process in fibrous materials with ordered structure has been presented in several works [1-4], however functional relationships put forth for calculation of effective thermal conductivity are as a rule semi-empirical, and therefore have a limited range of applicability.

Let us examine the transfer of heat in fibrous systems with ordered structure. Before we select the model of the fibrous system, let us adopt the following assumptions to simplify the model: 1) all fibers lie in a plane perpendicular to the heat flux and intersect each other at right angles; 2) the cross section of fibers is square; 3) the entire fibrous system has a homogeneous structure, that is, there are no subdivisions into strands, web, and surface layer of nap.

With the assumptions listed taken into account, the model of a fibrous system with ordered structure can be represented in the form of a lattice of intersecting crossbars, arranged in chessboard fashion (Figure 1, a). Using the methods in [4-6], we conduct an investigation of the transport process in the volume of an "elementary cell" (Figure 1, b) of the smallest volume, whose repetition in a specified manner can constitute the entire original model of the fibrous structure. As follows from determination of the bulk concentration in Figure 1, the relationship between geometric parameters of the elementary cell Δ and L and the bulk concentration of dry fibers m_1 and the gaseous component m_2 is expressed by

$$m_1 = \frac{\Delta}{L} \cdot \quad m_1 + m_2 = 1 \tag{1}$$

Let us consider the thermal resistance of the elementary cell in the direction of the thermal flux.

We broke down the system of horizontal isothermal and vertical adiabatic planes, using the elementary cell, into individual sections whose thermal resistances we determined from the formula for a flat wall (Figure 1, b)

$$\begin{gathered} R_1 = \frac{\Delta}{\Delta^2 \lambda_1}; \quad R_2 = R_1; \quad R_3 = \frac{\Delta}{\Delta(L-\Delta)\lambda_1}; \quad R_5 = R_3; \\ R_4 = \frac{\Delta}{\Delta(L-\Delta)\lambda_2}; \quad R_6 = R_4; \quad R_7 = \frac{2\Delta}{(L-\Delta)^2 \lambda_2}. \end{gathered} \tag{2}$$

A diagram of the combination of thermal resistances of the sections constituting an elementary cell is given in Figure 1, c. The total (effective) resistance R of the elementary cell is determined from the expression

$$\frac{1}{R} = \frac{1}{R_1 + R_2} + \frac{1}{R_3 + R_4} + \frac{1}{R_5 + R_6} + \frac{1}{R_7} \tag{3}$$

The effective coefficient of thermal conductivity λ of the elementary cell and its thermal resistance R by definition are related by the function

$$R = \frac{2\Delta}{L^2 \lambda} \tag{4}$$

Equating equations (3) and (4) and expressing resistances by formula (2), we get an expression for the effective thermal conductivity of the ordered fibrous system

$$\lambda = \lambda_1 \left[(1-m_2)^2 + m_2^2 \nu + \frac{4 m_2 (1-m_2)}{1 + \frac{1}{\nu}} \right], \quad \nu = \frac{\lambda_2}{\lambda_1} (5) \tag{5}$$

Thus, the effective thermal conductivity of the fibrous system with ordered structure λ depends on thermal conductivity of the fibers, λ_1, and the gas-filler, λ_2, and on their bulk concentrations.

The limiting transitions confirm the suitability of function (5) throughout the entire range of change in bulk concentration of components. Actually, when $m_2 = 0$, $\lambda = \lambda_1$, and when $m_2 = 1$, $\lambda = \lambda_2$.

Further analysis involves selection of numerical values of coefficients of thermal conductivity λ_1 and λ_2. The coefficient of thermal conductivity of the solid component (fiber) λ_1 is chosen from handbook data or from the results of the investigators' own measurements of the thermal conductivity of the material of which the synthetic fibers are made. Further, it is assumed that the thermal conductivity of the original material remains unchanged in the manufacturing of the fibers.

The coefficient of thermal conductivity of the gaseous component λ_2 depends on a number of parameters

$$\lambda_2 = f(\lambda_{2M}, K, \lambda_{2\Lambda}). \tag{6}$$

Thermal fluxes induced by molecular transport q_{2M}, radiative transport $q_{2\Lambda}$, and convective transport q_{2k} act independently. Therefore, the total thermal flux q equals their sum

$$q = q_{2M} + q_{2\Lambda} + q_{2K} \tag{7}$$

Thermal flux q_i, effective thermal conductivity σ_i, and temperature difference $(t_1 - t_2)$ at the bounding surfaces of the elementary cell are associated by the relationship

$$q_i = \sigma_i (t_1 - t_2), \quad i = 2M, 2K, 2\Lambda. \tag{8}$$

Thermal conductivity σ_1 is equal to

$$\sigma_i = -\frac{\lambda_i S}{2\Delta}, \qquad (9)$$

where S and 2Δ = cross-sectional area and thickness of elementary cell, respectively.

From (7)-(9) it follows that

$$\lambda_2 = \lambda_{2M} + \lambda_{2K} + \lambda_{2\Lambda} \qquad (10)$$

Let us represent the sum of molecular and convective components of the coefficient of thermal conductivity of the gaseous component in the following form

$$\lambda_{2M} + \lambda_{2K} = \lambda_{2M}(1+K), \quad K = \frac{\lambda_{2K}}{\lambda_{2M}}. \qquad (11)$$

Then expression (10) can be written as

$$\lambda_2 = \lambda_{2M}(1+K) + \lambda_{2\Lambda}. \qquad (12)$$

The calculations made show that thermal conductivity of the gas-filler in fibrous systems at normal pressure is practically the same as thermal conductivity of the pure gas-filler λ_0 throughout the entire possible range of change in concentrations of components, fiber dimensions, and temperature drop, that is,

$$K \approx 0 \text{ and } \lambda_{2M}(1+K)\big|_t \approx \lambda_0\big|_t. \qquad (13)$$

Evaluation of the radiated component of the coefficient of thermal conductivity is made by a more complex approach, namely: radiated heat transport is considered not in an elementary cell, but throughout the entire fibrous system as a whole, with the characteristics of the bounding surfaces taken into account, especially important for thin-layer materials. The fibrous system with ordered structure is represented in this case in the form of a continuous isotropic medium attenuating thermal radiation. Further, the following assumptions are made: 1) surfaces of the isotropic attenuating medium are parallel isothermal planes; 2) scattering of radiation at fibers is absent (that is, the integral coefficient of medium attenuation equals the integral coefficient of absorption $\varkappa$); 3) the index of refraction of the medium equals unity; 4) linear distribution of temperatures is assumed in the isotropic attenuating medium. In this case it is possible to relate the value of the radiated component with integral characteristics of the attenuating medium by a function of the form [7]

$$\lambda_{\Lambda} = \frac{16}{3}\frac{\sigma_0 T^3 \gamma}{\alpha} \approx 0{,}302\frac{\gamma}{\alpha}\left(\frac{T}{100}\right)^3 \qquad (14)$$

The expression we obtained for the radiated component $\lambda_{2\Lambda}$ is substituted into formula (12) and is used in determination of thermal conductivity of the gas-filler in the elementary cell. In this way we make one more assumption to the effect that the radiated component of the gas-filler calculated for the entire system as a whole equals the radiated component of the coefficient of thermal conductivity in the elementary cell.

In determining the coefficient of attenuation α, we use a method applied for a system consisting of opaque spherical particles uniformly distributed in a transparent medium [8].

We will hold that individual fibers act in the role of particles attenuating radiation in a fibrous system with ordered structure. Then, from the definition

$$\alpha = \frac{S_{осл}}{S \cdot b}, \qquad (15)$$

where it is convenient to take the surface of the elementary cell equal to $S = L^2$ as the surface on which radiation S impinges; and for the thickness of the layer b in which attenuation of radiation takes place, the thickness of the elementary cell, that is, $b = 2\Delta$. In this case, S_{atten} = surface attenuating radiation and equal to the projection of fibers onto a plane perpendicular to the thermal flux.

$$S_{\text{осл}} = (2L - \Delta)\Delta .$$

Substituting into formula (15) values of parameters and taking cognizance of expression (1), we get an expression for the coefficient of attenuation

$$\alpha = \frac{1 - m_2^2}{2\Delta} \approx \frac{1 - m_2^2}{D} \qquad (16)$$

Thus, by knowing λ_1, λ_o, m_2, D, 7, and T, and using the functions (5), (12-14), and (16), we can calculate the effective thermal conductivity of the fibrous system with ordered structure in a dry state.

However, the majority of fibrous materials are used under conditions of some moisture content. Moisture in the form of water vapor or accumulations of water droplets on fibers can lead to a considerable change in effective thermal conductivity of fibrous materials. Empirical functions allowing us to take account of change in effective thermal conductivity in the presence of moisture are to be found in the literature [4, 9]. We will establish the effective thermal conductivity as an analytical function of the moisture content of a fibrous system. Experimental measurements show that the normal moisture content of so-called air-dry material lies within the limits 0-15 percent [9].

It is customary to take as the normal moisture content in standard tests of textile materials the moisture content by weight (that is, the ratio of weight of moisture to weight of absolutely dry material) of the material kept for 24 hr under conditions of relative humidity ϕ = 65 percent and at an air temperature of 20°C. It is assumed that within the limits of normal moisture content, voids within fibers are filled with water, and at higher moisture content the water lies around each fiber [9]. This conclusion allows us to assume that within the limits of the air-dried state (bulk concentration of moisture in material is less than 6 percent) the moisture is uniformly distributed within the fiber, that is, to assume that it forms a three-dimensional mutually penetrating structure with the solid fiber.

The effective thermal conductivity λ^* of such a system is associated with the thermal conductivity of water λ_{2f} and with its bulk concentration m_{2f} by the function [5]

$$\lambda^* = \lambda_1\left[C_f^2 + \nu_f(1-C_f)^2 + \frac{2\nu_f C_f(1-C_f)}{\nu_f C_f + (1-C_f)}\right], \qquad (17)$$
$$\nu_f = \frac{\lambda_{2f}}{\lambda_1}, \quad m_{2f} = 2C_f^3 - 3C_f^2 + 1.$$

The effective thermal conductivity λ of a moist (air-dried) fibrous system is calculated from the value found for the thermal conductivity of the moist fiber λ^*. For unordered systems[1] the calculation proceeds according to formula (17), and for ordered systems according to formula (5).

A comparison of the results of calculating the effective thermal conductivity with experimental data [1-4, 9-14] was made to test the suitability of the proposed method and to determine the range of its applicability. The results of the comparison are shown in Figures 2 and 3. The theoretical curve calculated from formulas (17) and (5) is plotted by a solid line on the graphs.

The satisfactory agreement of calculation results with experimental results evidences the suitability of the method set forth above in calculation of the fibrous systems.

A graph of the effective thermal conductivity of fibers as a function of density $\lambda = \lambda(\rho)$ is often given in the literature. A clearly pronounced minimum of effective thermal conductivity in the low-density region exists in such a graph (Figure 4, a). The existence of a minimum can be explained by increase in the fractional representation of the radiative component for low-bulk densities and by a rise in the conductive fractional representation when there is an increase in the density of the fibrous system. If the

---

[1] See p. 95

function $\lambda = \lambda(\rho)$ is transformed to $\lambda = \lambda(m_2)$, and we also graphically represent the function $\lambda_\Lambda = \lambda_\Lambda(m_2)$ for the established values of l, ε and D, it is easy to see (Figure 4, b) that an increase in λ_Λ corresponds to an increase in λ for the same concentrations. Therefore, when we represent the graph in the form $\lambda/\lambda_2 = f(m_2)$ the minimum on the curve disappears.

Symbols

Δ = thickness of crossbar in elementary cell; L = width of elementary cell; m_1 = bulk concentration of solid component; m_2 = bulk concentration of gaseous component; λ_1 = thermal conductivity of solid component; λ_2 = thermal conductivity of gaseous component; λ_{2M} and $\lambda_{2\Lambda}$ = molecular and radiated components of coefficient of thermal conductivity of the gaseous component in the fibrous system; k = coefficient that takes into account the convective component of the coefficient of thermal conductivity; T = mean arithmetic temperature of the bounding surfaces of the fibrous material; σ_S = Stefan-Boltzmann constant; α = absorption coefficient of fibrous medium; Y = parameter dependent on the coefficient of absorption, degree of blackness of surfaces bounding the fibrous system, and the thickness of the fibrous system (values of the function $Y = Y(\alpha, \varepsilon, l)$ are tabulated in [8]); D = fiber diameter; λ_o = thermal conductivity of gas-filler at temperature T; λ_{2f} = thermal conductivity of water; m_f = bulk concentration of water; ε = degree of blackness of bounding surfaces of fibrous system.

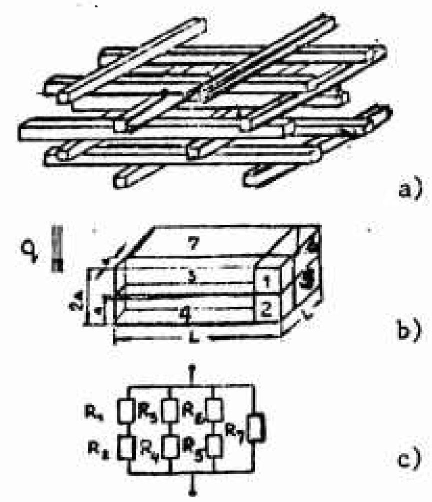

Figure 1. Model of ordered fibrous structure: a) Overall appearance; b) Elementary cell; c) Diagram of thermal resistances of elementary cell

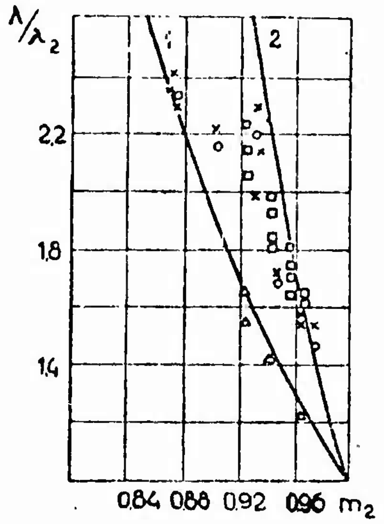

Figure 2. Thermal conductivity of glass wool: 1, Calculated from formula (17) for $\nu = \lambda_{2\,\min}/\lambda_1$; 2, Calculated from formula (17) for $\nu = \lambda_{2\,\max}/\lambda_2$; ○, Experimental data from [11]; □, Experimental data from [12]; x, Experimental data from [13]; Δ, Experimental data from [14].

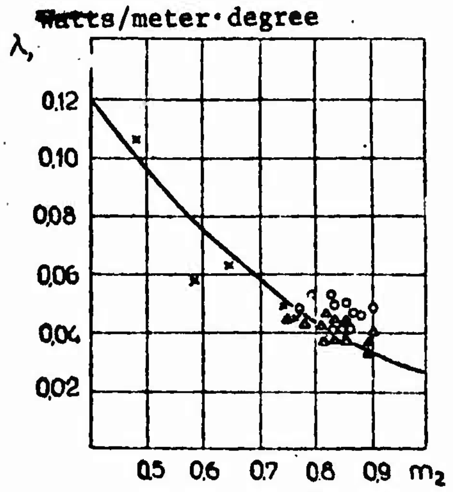

Figure 3. Thermal conductivity of wool and capron fabric (air-dried materials): $\lambda_1 = 0.21$, $\lambda_2^* = 0.25$, $\nu = 0.108$, x, Experimental data of the Leningrad Institute of Precision Mechanics and Optics; ○, Experimental data of the Central Scientific Research Institute of the Garment Industry [10]; Δ, Experimental data of the Central Scientific Research Institute of the Wool Industry [4]; —, Calculated from formula (5)

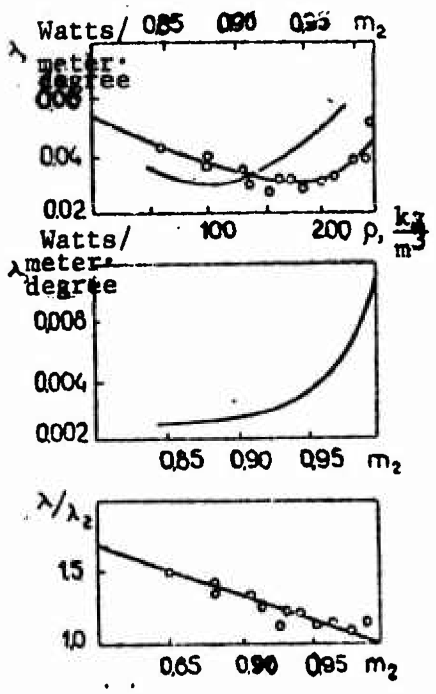

Figure 4. Thermal conductivity as a function of density for fibrous materials: ○, Experiment; —, Calculated from formula (17).

Footnotes

1. To p. 91 We take nonordered structures to be fibrous systems with chaotic arrangement of fibers in all directions.

References

1. Verschoor, J. D. and P. Greebler: *Transactions ASME,* Vol.74, No. 6, p. 961-969, 1952.

2. *Sb. Voprosy Glubokogo Okhlazhdeniya (Collection: Problems of Deep Cooling),* Edited by Professor M. P. Malkov, p. 362, IL Press, Moscow, 1961.

3. Kaganer, M. G.: *Teplovaya Izolyatsiya v* Tekhnika *Nizkikh Temperatur (Thermal Insulation in Low-Temperature Equipment),* Mashinostroyeniye Press, Moscow, 1966.

4. Zyrin, S. G.: *Nauchno-issledovatel'skiye Trudy TsNIISherti,* No. 8, 1953.

5. Dul'nev, G. N., *IFZh,* Vol. 9, No. 3, p. 399, 1965.

6. Odelevskiy, V. I.: *ZhTF,* Vol. 21, No. 6, 1951.

7. Poltz, H.: *Mitteilung aus der Physikalisch Technischen Eingingegangen,* No. 24, p. 515-527, 1964.

8. Shorin, S. N.: *Teploperedacha. Izvestiya V. Sh. (Heat Transfer. News of the Higher Schools),* 1964.

9. Kolesnikov, P. A.: *Teplozaschitnyye Svoystva Odezhdy (Heat-Protective Properties of Clothing),* IL Press, Moscow, 1965.

10. Knorov, A. V. and A. V. Chuyko: *Sovremennyye Izolyatsionnyye Materialy v Stroitel'stve i Tekhnike (Modern Insulation Materials in Construction and Technology),* Trudrezervizdat Press, 1958.

11. Barbarina, T. M. et al: *Trudy Vses. NII Stekla,* No. 34, 1954.

12. Chirkin, V. S.: *Teploprovodnost' Promyshlennykh Materialov (Thermal Conductivity of Industrial Materials),* GNTI Mash. Press, 1957.

13. Chernaya, R.: *Kholodil'naya Teknika,* No. 4, 1948.

14. Shevel'kov, V. L.: *Teplofizicheskiye Kharakteristiki Teploizolyatsionnykh Materialov (Thermophysical Characteristics of Heat-Insulation Materials)*, Gosenergoizdat Press, Moscow, 1958,

ANALYSIS OF TRANSPORT COEFFICIENTS OF MULTI-COMPONENT SYSTEMS

Yu. P. Zarichnyak

It was shown in [1-4] that use of methods of the generalized conductivity theory affords prediction of effective transport coefficients of mechanical mixtures if the nature of the structure of the mixture, characteristics of the components, and their concentrations are known.

However, calculation of effective transport coefficients has been made mainly for structures with isolated inclusions of components, since functional relationships for calculating effective transport coefficients of structures with mutually penetrating components are semi-empirical in nature. A model for a structure with mutually penetrating components was proposed for the first time in [4] and a functional relationship for calculating effective transport coefficients was obtained free of empirical coefficients. Further development of the model was made in [5] and the method of calculation [4] for the case with any number of components was put forth in [4] along with the method of calculating the effective transport coefficients for structures that are combinations of the foregoing (with isolated inclusions of components, and with mutually penetrating components).

Below we examine how suitable the proposed methods are for calculating the effective transport coefficients of various mechanical mixtures.

Mixtures Containing Solid, Liquid and Gaseous Components

Choice of functional relationships for calculating effective transport coefficients is governed by the structure of the mixture. The structure of natural petroleum- and water-bearing soil is as a rule disordered. Investigation of the permeability of water- and gas-bearing structures (sands and sandstones) shows that the lubricating liquid or gas uniformly fills all porous space in the structure [6]. We use the model with mutually penetrating components in calculating the effect of transport coefficient λ.

and the coefficient of thermal conductivity for such a structure is equal to [4]

$$\lambda = \lambda_1\left[c^2 + \nu(1 - c^2) + \frac{2\nu c(1-c)}{\nu c + (1-c)}\right], \quad \nu = \frac{\lambda_2}{\lambda_1} \qquad (1)$$

Here, C = geometric parameter associated with bulk concentration of the second component m_2 by the relationship

$$m_2 = 2c^3 - 3c^2 + 1 \qquad (2)$$

Since structure components are geometrically interchangeable, the order in which indexes are written is of no importance. For determinateness, we assign the index 1 to the solid component, index 2 to the liquid or gaseous component. Experimental values of effective thermal conductivity of water- and gas-bearing quartzite sands and sandstones are given in [3]. The original parameters for calculating effective thermal conductivity are selected as follows. While the data on thermal conductivity of water λ_2 given in the handbook literature agree for practical purposes, the thermal conductivity of natural quartzite λ_1 is a value not as definite which varies within the limits 6-8.5 watt/m·degree [7-9]. Indeterminancy in the values of the original parameters allows us to predict only the probable zone of values of the effective thermal conductivity coefficients. Calculated values of effective thermal conductivity of water-bearing soil have been compared with experimental data [3], shown in the graph in the form of rectangles, the length of whose sides is determined by the error of measurements. Further, the scatter of experimental values along the vertical is caused by the error of thermal physical measurements, and along the horizontal -- by the error of measurement of bulk concentration of the components.

Comparison of experimental and calculated data affords satisfactory agreement.

However, use of the function (1) in calculating thermal conductivity of gas-bearing soil leads to considerable deviation from experimental data (Figure 1).

It can be assumed that the cause of the deviation is the incomplete agreement of the selective model with the real structure of gas-bearing sandstone. Actually, it is assumed in the model that we adopted in deriving the functional relationship (1) that the cross-sectional area of crossbars of the cubic three-dimensional lattice of any of the components can vary only within small limits, that is, that any abrupt narrowing of the cross-sectional area is absent. When there is a small difference in transport coefficients of components, the existence of abrupt narrowing of cross-sectional area of the solid phase does not have any substantial effect on the value of the effective transport coefficient (curves 1 and 2 in Figure 1). The transport coefficient of the gaseous component λ_2 can be two orders or more of magnitude different from the transport coefficient of the solid component. In this case we must take cognizance of the effect of narrowing in cross-sectional area of components. The model that takes into account the existence of narrowing when there is a considerable difference in transport coefficients of components ($\nu \simeq 0$) was examined in [10]. The functional relationship in calculating effective transport coefficients is of the form

$$\lambda = \lambda_1 \frac{2c^2}{3-c} \cdot \frac{y^2}{\Phi(y,z)}, \quad z = \frac{c}{3-c} \cdot \tag{3}$$

$$y = \sqrt{\frac{\bar{S}_{\text{к}}}{\bar{S}_{\text{т}}}} \cdot \tag{4}$$

The analytical and graphic representation of the function $\Phi(y, z)$ taking into account the additional resistance of narrowing, is given in [10].

The chief complexity in calculation based on the formulas (3, 4) given above stems from assigning the value y. As a rule, the value of the parameter characterizing the narrowing dimensions is determined experimentally [3, 11]. This appreciably narrows the possibility of using calculation methods and does not avoid the necessity of conducting laborious experiments. Qualitative investigation of the structure of granular porous and sintered materials affords the assumption that the parameter y depends on porosity (bulk concentration of the liquid or gaseous phase) and on the nature of the structure of the material, and also allows us to propose a method of determining its value. Let us look at the behavior of parameter y when we vary the porosity of different structures.

It is natural to assume that there are no narrowings of any kind in a continuous solid body, that is, $y = 1$. We will arbitrarily produce in a continuous body voids that are not elongated in form, gradually increasing their bulk concentration. For small values of bulk concentration of the voids, $m_2 < 0.2$, and they are isolated or partially interconnecting inclusions.

The emergence of abrupt narrowing is of low-probability and the value of y is close to unity (cf. curve 1, Figure 2). When the bulk concentration of voids is further increased, the emergence of abrupt narrowing of cross-sectional area of the solid component becomes more probable, which at high porosity $m_2 > 0.8$ lead to the appearance of local breaks in the solid skeleton. Further, the effective transport coefficient decreases both owing to the reduction in the bulk fraction of the conducting component, as well as owing to the emergence of narrowing -- necks and breaks.

When m_2 approaches unity, y approaches zero. Let us examine variations of parameter y in a granular structure. The areas of contact of particles are very small in actual granular materials ($0 < y < 5 \cdot 10^{-2}$) and the value of y varies slightly with rise in bulk concentration of the solid phase all the way to $m_2 < 0.3$ (cf. curve 2, Figure 2). Under the effect of external influences (compression, heating, and precipitation of solid phase at contact points), the bulk concentration of voids continues to fall. An abrupt rise in the value of y must occur, and when $m_2 < 0.1$, $y \simeq 1$. Variation of the function $y = f(m_2)$ can become evident for specific materials, by investigating their geometry for a wide range of variations in bulk concentration of components or by back calculation from experimental values of effective transport coefficients. Since actual structures of sandstones and sintered materials occupy intermediate values between granular structure and structure with mutually penetrating components with crossbars of constant cross-sectional area, it is logical to assign linearity to y as a function of

m_2 (cf. Figure 2), that is

$$y = 1 - m_2 . \qquad (5)$$

The linear approximation of the function $y = f(m_2)$ does not contradict the physical sense and satisfies clarification at limiting transitions.

Results of the calculation of effective transport coefficients by formulas (1) and (3) have been compared with experimental data [3, 12] for thermal and electroconductivity of gas-bearing sandstone and sintered porous specimens made of bronze, nickel and iron (Figures 1, 3 and 4). The zone of scatter of experimental values of transport coefficients are probably caused by a certain difference in technological sintering conditions for the specimens (temperature, specific load) for individual researchers. Investigation of the relationship of size of original powder particles with effective transport coefficient has shown that particle size has practically no effect on the value of the transport coefficient of a sintered specimen [12].

Analysis of results affords the finding that at low bulk concentration of the gaseous phase $m_2 < 0.2$, experimental data is best described by the function (1) (model with crossbars of constant cross-sectional area). When the bulk concentration of the gaseous phase is increased, especially in the case of a sharp difference in transport coefficients of the components, taking the existence of narrowing (3) into account leads to better agreement of calculation results with experimental data.

Mixtures of Liquid Components (Solutions)

The possibility of using the functional relationship (1) for calculating effective thermal conductivity of solutions is indicated in [13]. In the present study, results of calculation of effective thermal conductivity of 15 different mixtures of organic liquids were compared with experimental data taken from [14] (cf. Table 1) and agree satisfactorily for mixtures of both normal as well as associated liquids. The mean deviation of calculation from experiment is only 3 percent; the maximum deviation does not exceed 8 percent for the entire range of change in component concentrations.

Table 1.

	Components of mixture (solution)	Bulk concentration of first component	Thermal conductivity				Deviation, in percent
			Component		Mixture (solution)		
					Exp.	Calc.	
			λ_1	λ_2	$\lambda_{\text{э}}$	$\lambda_{\text{р}}$	$\frac{\lambda_{\text{э}}-\lambda_{\text{р}}}{\lambda_{\text{э}}}$
I	2	3	4	5	6	7	8
1.	Cyclohexane-benzene	0,778	0,II5	0,0975	0,II	0,II0	-0,8
		0,470	0,II5	0,0975	0,I043	0,I05	-I,0
		0,220	0,II5	0,0975	0,I00	0,I0I	-I,I
2.	Bromobenzene-benzene	0,84I	0,II6	0,09	0,I060	0,III	-5,I
		0,648	0,II6	0,09	0,098	0,I06	-8,2
		0,430	0,II6	0,09	0,093	0,I00	-7,9
3.	n-heptane-n-hexadecane	0,7I2	0,I22	0,I00	0,II5	0,II5	-0,I6
		0,470	0,I22	0,I00	0,II0	0,II0	-0,I8
		0,220	0,I22	0,I00	0,I05	0,I04	0,5
4.	Cyclohexane-toluene	0,624	0,I075	0,0975	0,I027	0,I03	0,9
		0,466	0,I075	0,0975	0,I0I3	0,I02	-0,73
		0,350	0,I075	0,0975	0,I00	0,I00	0,4
5.	Bromobenzene-chlorobenzene	0,805	0,I05	0,09	0,I00	0,I0I	-I,8
		0,576	0,I05	0,09	0,0955	0,0983	-2,9
		0,3I5	0,I05	0,09	0,0925	0,0945	-2,I
6.	n-octane-n-heptadecane	0,725	0,I23	0,I025	0,I20	0,II7	2,5
		0,470	0,I23	0,I025	0,II55	0,II2	3,3
		0,226	0,I23	0,I025	0,II0	0,I07	2,9
7.	n-hexyl alcohol-methyl alcohol	0,7I2	0,I70	0,I290	0,I560	0,I57	-0,6
		0,522	0,I70	0,I290	0,I450	0,I49	-I,3
		0,268	0,I70	0,I290	0,I367	0,I39	-I,6
8.	n-nonyl alcohol-methyl alcohol	0,752	0,I70	0,I35	0,I562	0,I60	-2,7
		0,508	0,I70	0,I35	0,I475	0,I52	-2,9
		0,265	0,I70	0,I35	0,I400	0,I43	-2,5
9.	n-heptane-n-hexyl alcohol	0,700	0,I295	0,I00	0,I20	0,I20	0,I5
		0,450	0,I295	0,I00	0,II2	0,II2	-0,3
		0,205	0,I295	0,I00	0,I05	0,I05	-0,4I
10.	n-decane-n-butyl alcohol	0,466	0,I258	0,I06	0,II58	0,II5	0,65
		0,225	0,I258	0,I06	0,III6	0,II0	I,2
11.	Bromobenzene-n-nonyl alcohol	0,648	0,I35	0,09	0,II92	0,II6	3,3
12.	Isooctane-n-decyl alcohol	0,450	0,I37	0,082	0,I05I	0,I03	I,6
13.	Toluene-methyl alcohol	0,556	0,I70	0,I075	0,I48	0,I39	6,2
		0,527	0,I70	0,I075	0,I325	0,I36	-3,3
		0,270	0,I70	0,I075	0,I20	0,I2I	-I,4
14.	n-xenol-benzyl alcohol	0,708	0,I37	0,I07	0,I266	0,I27	-0,65
		0,450	0,I37	0,I07	0,I234	0,II9	3,0
15.	n-octane-decyl alcohol	0,720	0,I37	0,I025	0,I255	0,I26	-0,6I
		0,378	0,I37	0,I025	0,II75	0,II4	2,6
		0,2I2	0,I37	0,I025	0,II0	0,I09	0,9I

Symbols

λ = effective transport coefficient of mixture; λ_i = transport coefficient of i-th component; C = geometric parameter of model; y = parameter taking into account narrowing in structure, $y = \sqrt{S_k/S_T}$; $\overline{S}_k$ = averaged contact area; $\overline{S}_T$ = averaged area of maximum cross section.

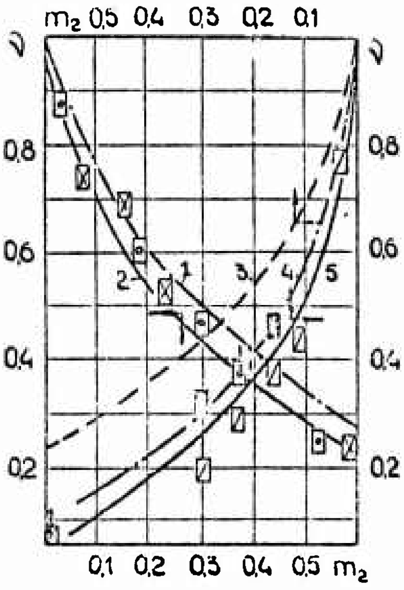

Figure 1. For calculation of thermal conductivity of water- and gas-bearing soil: ⧄, Sandstone-air; ☒, Sandstone-water; □, Sand-water; ■, Sandstone-heptane; 1, Calculated from formula (1), λ_{max}; 2, From formula (1), λ_{min}; 3, From formula (1), λ_{aver}; 4, From formula (3), λ_{max}; 5, From formula (3), λ_{min}.

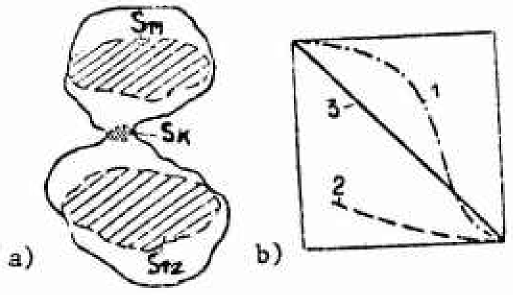

Figure 2. Recording narrowing of cross-sectional area: a, Schematic representation of narrowing; b, The function $y = f(m_2)$; T, Solid porous and sintered materials; 2, Granular material; 3, Linear approximation of function.

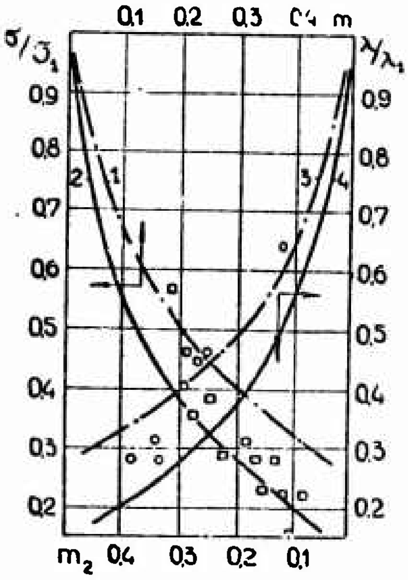

Figure 3. Transport coefficients of sintered porous bronze (Cu 89 percent, Sn 11 percent): 1, Calculation of effective electroconductivity from formula (1); 2, As above from formula (3); □, Experiment; 3, Calculation of effective thermal conductivity from formula (1); 4, As above from formula (3), 0, Experiment

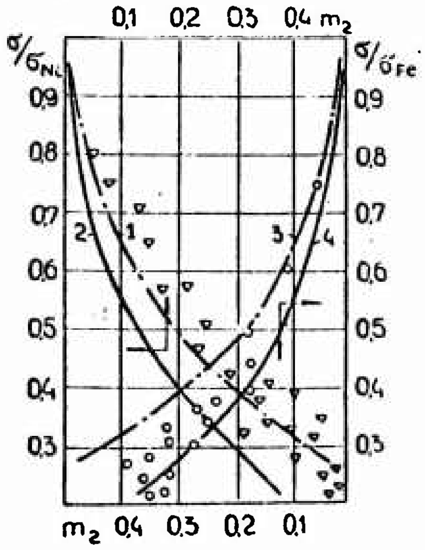

Figure 4. Electroconductivity of sintered specimens of nickel and iron: 1, Calculated from formula (1); 2, As above from formula (3); ∇, Experimental data for porous nickel; 3, Calculated from formula (1); 4, As above from formula (3); 0, Experimental data for porous iron.

References

1. Chudnovskiy, A. F.: *Teplofizicheskiye Kharakteristiki Dispersnykh Materialov (Thermophysical Characteristics of Disperse Materials)*, Fizmatgiz Press, Moscow, 1962.
2. Meisenard , A.: *La conductivite thermique des liquides, gas et leurs melanges*, Paris, 1965.
3. Woodside, W. and J. Messmer: *J. Journ. Appl. Phys.*, Vol. 32, N 9, p. 1688, 1961.
4. Dul'nev, G. N.: *IFZh*, Vol. 9, No. 3, p. 399, 1965.
5. Dul'nev, G. N. and Yu. P. Zarichnyak: *IFZh*, Vol. 12, No. 4, 1967.
6. Kallinz, R.: *Techeniye Zhidkosti Cherez Poristyye Materialy (Flow of Liquids Through Porous Materials)*, Mir Press, Moscow, 1964.
7. Berch, F., D. Sherer and G. Spayser: *Spravochnik dlya Geologov po Fizicheskim Konstantam (Handbook for Geologists on Physical Constants)*, IL Press, Moscow, 1949.
8. [illegible], B. N.: *Teploprovodnost' Stroitel'nykh Materialov (Thermal Conductivity of Construction Materials)*, Gosstroyizdat, Moscow, 1955.
9. *Handbook of Thermophysical Properties of Solid Materials* New York, 1961.
10. Dul'nev, G. N., Yu. P. Zarichnyak and B. A. Muratova: *Izv. Vuzov. Radiofizika*, Vol. 9, No. 5, p. 849, 1966.
11. Vasil'yev, L. L.: *Sb. issledovaniya po teploprovodnosti (Collection: Studies on Thermal Conductivity)*, Edited by Academician A. V. Lykov, Nauka i Tekhnika Press, Minsk, 1967.
12. Gzootenhuis P., R. Powell and P. Tye: *Proc. Phys. Soc.*, No. 65, p. 7, 1952.
13. Dul'nev, G. N. and Yu. P. Zarichnyak: *IFZh*, Vol. 11, No. 6, 1966.
14. Mukhammedzyanov, G. Kh., A. A. Garzimanov and A. G. Usmanov: *Izv. Vuzov. Neft' i Gaz*, No. 10, 1964.

COEFFICIENT OF VISCOSITY OF LITHIUM VAPOR IN THE TEMPERATURE RANGE T = 3000-6000°K AND THE PRESSURE RANGE P = 1-100 BAR

P. M. Kessel'man and S. F. Gorykin

Any kind of data on viscosity of dissociated lithium vapor are lacking at present in the literature. Still, such data can be of definite interest in solving a number of special problems.

Calculations show that in the region of parameters the following dissociation reaction takes place in lithium vapor:

$$Li \rightleftharpoons 2Li \tag{1}$$

An attempt is made in this present study (the first, as far as we know) to theoretically calculate the viscosity coefficient of dissociated lithium vapor in the temperature range 3000-6000°K and a pressure range 1-100 bar.

The molecular-kinetic theory gives us the following expression for the coefficient of viscosity of a two-component mixture [1]:

$$\eta_{cm} = \frac{\begin{vmatrix} H_{11} & H_{12} & x_1 \\ H_{12} & H_{22} & x_2 \\ x_1 & x_2 & 0 \end{vmatrix}}{\begin{vmatrix} H_{11} & H_{12} \\ H_{12} & H_{22} \end{vmatrix}}$$

where H_{11}, H_{12} and H_{22} have the following rigorous mathematical expressions:

$$H_{11} = \frac{x_i^2}{\eta_i} + \frac{2x_1x_2}{\eta_{12}} \frac{M_1M_2}{(M_1+M_2)^2}\left[\frac{5}{3A^*_{12}} - \frac{M_2}{M_1}\right] \tag{3}$$

$$H_{12} = -\frac{2x_1x_2}{\eta_{12}}\frac{M_1M_2}{(M_1+M_2)^2}\left[\frac{5}{3A_{12}^*} - 1\right] \tag{4}$$

$$H_{22} = \frac{x_2^2}{\eta_2} + \frac{2x_1x_2}{\eta_{12}}\frac{M_1M_2}{(M_1+M_2)^2}\left[\frac{5}{3A_{12}^*} - \frac{M_1}{M_2}\right] \tag{5}$$

$$\underset{(i=1,2)}{\eta_i \cdot 10^7} = 266{,}93\,\frac{\sqrt{TM_i}}{\sigma_i^2\,\Omega_i^{(2,2)*}(T_i^*)} \cdot f_\eta^{(3)} \tag{6}$$

$$\eta_{12} \cdot 10^7 = 266{,}93\,\frac{\sqrt{2TM_1M_2/(M_1+M_2)}}{\sigma_{12}^2\,\Omega_{12}^{(2,2)*}(T_{12}^*)} \cdot f_\eta^{(3)} \tag{7}$$

Since there is a complete lack of experimental data with which we could directly determine the potential parameters: ε_i, σ_i, ε_{12} and σ_{12}, for lithium vapor, in the present study the method of calculation is the determination of these parameters from the corresponding data for the second virial coefficient obtained by theoretical calculation.

In [2] a method is formulated for describing thermal physical properties of chemically nonreacting gases, based on the possibility of representing the interaction of particles by some averaged potential function with variable parameters ε and σ that are temperature-dependent,

$$U = 4\varepsilon(T)\left\{[\sigma(T)/r]^{12} - [\sigma(T)/r]^{6}\right\} \tag{8}$$

This method can be used for any compounds. It is important to note that by using this method, with just the potential parameters $\varepsilon(T)$ and $\sigma(T)$ we can reliably describe not only equilibrium properties, but also transport coefficients of gases for a wide range of temperatures, including also the high-temperature region.

To determine potential parameters by means of this method, we must have original data on virial coefficients.

Calculation of the second virial coefficient B_1 corresponding to interactions of free atoms was made in accord with the method in [3]. Lacking the opportunity to dwell in detail on the determination of the potential curves necessary in calculating B_1, we note that they were chosen from literature sources, or were calculated by the present authors [8, 12, 13].

Table 1. Values of Potential Parameters of Lithium

T^0K	$B_1 \frac{cm^3}{mole}$	$B_2 \frac{cm^3}{mole}$	$\frac{\varepsilon_2}{K}$	σ_2 Å
3000	- 51,0	- 134,9	2875	3,375
3500	- 43,8	- 96,0	2860	3,371
4000	- 38,2	- 68,2	2845	3,368
4500	- 33,0	- 50,0	2830	3,366
5000	- 28,2	- 38,2	2815	3,364
5500	- 23,8	- 29,7	2800	3,362
6000	- 19,6	- 23,3	2785	3,361
6500	-	- 17,9	2769	3,360
7000	-	- 13,2	2753	3,359
7500	-	- 9,2	2734	3,358
8000	-	- 5,9	2709	3,357
8500	-	- 3,2	2678	3,356
9000	-	- 0,9	2651	3,355
9500	-	+ 1,1	2655	3,354
10000	-	+ 2,8	2677	3,353

The corresponding data for B_1 are given in Table 1. We note that B_1 corresponds to those interactions among atoms that do not lead to the formation of stable two-atomic molecules. Therefore we can assume that some averaged potential function (in the case of interaction of particles with filled electron orbitals) corresponds to the second virial coefficient B_1 referred to the entire system of free atoms.

Since in the general case the potential function (8) can be used for any gas, it seems reasonable to select the corresponding parameters of this potential, using as the basis data for the second virial coefficient B_1. These parameters, as is to be expected, are constant and have the values $\varepsilon_1/k = 2723$°K; $\sigma_1 = 3.207$Å.

Based on these parameters, formula (6) was used to calculate the viscosity coefficient of atomic lithium, which was then employed in calculating η_{mix}. In evaluating the reliability of the results obtained for η_1, we made a comparison with the corresponding data found in the literature. As we know, the viscosity coefficient of an atomic gas can be determined theoretically by using collision integrals $\Omega^{(2.2)}$ calculated and averaged over all potential curves of interacting atoms. This has been done by a number of authors for atomic lithium [4-6].

Comparison of the viscosity coefficient calculated in the present study with the most reliable data by the author cited [4, 5] reveals good agreement of the values under comparison. Thus, the deviation of our data from the data in [4] does not exceed 7 percent for the entire temperature range T = 3000-6000°K under comparison.

As for the reliability of results given in [6], which differ appreciably (by 30-40 percent) from the data in [4, 5], we note that we subscribe to the criticism of this study which was given in [4]. The analysis made allows us to conclude that the parameters ε_1 and σ_1 obtained and that data on the viscosity coefficient of atomic lithium calculated by means of these parameters are sufficiently reliable and can be employed in calculating η_{mix}.

Passing along to molecular lithium, we must bear in mind that obtaining parameters of the potential function (8) by ordinary methods used for molecular gases, that is, based on experimental data for compressibility, is not possible owing to the absence of the latter.

Therefore, in determining the parameters $\varepsilon_2(T)$ and $\sigma_2(T)$ for the Li_2-Li_2 interaction, it seemed reasonable, on analogy with atomic lithium, to take as the basis data for the second virial coefficient of molecular lithium B_2, calculating them by a theoretical approach.

Statistical physics affords the possibility of calculating the values of the second virial coefficient from the formula

$$B = 2\pi N \int_0^\infty \left[1 - \exp u(r)/\kappa T\right] r^2 dr \,, \tag{9}$$

if we know the curve of the potential energy u(r) of the particles under study.

In the present study, the potential curve for interaction of the Li_2-Li_2 system was calculated by the full pairing method [7] with account taken of dispersion forces of attraction at large intermolecular distances.

The dispersional energy, as we know, is described with adequate precision by the formula

$$u = -\frac{C}{r^6} \tag{10}$$

The constant C was calculated from the Milliken formula [1]. Values of the characteristic energy and the polarizability of the molecule Li_2 necessary for the calculation were taken, respectively, from [8] and [9].

The potential curve obtained was used in calculating the second virial coefficient for molecular lithium B_2 in accordance with formula (9). The calculation was made on an electronic digital computer using the Simpson formula.

Data on B_2, by analogy with the foregoing, were taken as the basis in determining parameters of the potential function (8). These parameters were obtained as unique quantities, if both branches of the curve B(T) were present -- negative and positive. For this purpose, data on B_2 were calculated up to T = 10,000°K.

The parameters described and the values of B_2 are also presented in Table 1.

It is clear from the table that potential parameters of Li_2, like those for other homonucleus diatomic molecules, are weakly dependent on temperature. These potential parameters were used in calculating the viscosity coefficient of molecular lithium according to formula (6).

In calculating viscosity coefficient η_{12}, we must know the parameters ε_{12} and σ_{12} characterizing the energy of interaction of unlike particles.

We note that corresponding to potential function (8) is some generalized model, according to which any compound can provisionally be considered as a pseudospherical gas with centrally symmetrical operation of forces. This circumstance affords the possibility of using the potential function (8) in describing also dissimilar interactions by using the corresponding parameters ε_{12} and σ_{12}.

To determine these parameters, we can use well known empirical combining rules

$$\sigma_{12} = \frac{1}{2}(\sigma_1 + \sigma_2); \qquad \varepsilon_{12} = \sqrt{\varepsilon_1 \varepsilon_2}\ , \tag{11}$$

which, as we know, are effective for the spherical model of a gas. In this way we obtained the parameters ε_{12} and σ_{12} for the interaction Li-Li_2 and we calculated the values of η_{12} in accordance with formula (7).

Calculation of compositions in this present study was made with cognizance of the nonideality of the mixture components. For reactions of the type (1), the law of reacting masses gives the following function:

$$\frac{(1 - X_2)^2}{X_2} = \frac{K_p}{P} \tag{12}$$

The nonideality of the components was taken into account by introducing the appropriate correction K_j into the equilibrium constant

$$K_p = \frac{K_{p_0}}{K_j} \tag{13}$$

The quantity k_j is expressed by the activity of the components j and i

$$K_j = \frac{\gamma_1^2}{\gamma_2} \tag{14}$$

Table 2. Viscosity Coefficient of Dissociated Lithium Vapors, $\eta \cdot 10^6$ [n·sec/m^2]

T^0K P, bar	3000	3500	4000	4500	5000	5500	6000
1	2497	2879	3262	3633	3987	4328	4647
5	2591	2933	3296	3657	4004	4340	4667
10	2703	2997	3338	3686	4026	4357	4681
15	2808	3059	3379	3715	4055	4374	4693
20	2907	3120	3419	3744	4070	4392	4707
25	2997	3179	3459	3773	4091	4408	4721
30	3086	3236	3497	3800	4112	4424	4734
35	3172	3291	3539	3826	4133	4440	4747
40	3252	3346	3573	3856	4154	4457	4760
45	3329	3398	3610	3883	4175	4473	4772
50	3402	3450	3646	3910	4196	4489	4785
60	3539	3549	3717	3961	4236	4521	4811
70	3665	3643	3786	4014	4276	4553	4837
80	3782	3730	3852	4065	4316	4585	4862
90	3890	3819	3917	4115	4355	4616	4887
100	3992	3902	3979	4162	4393	4647	4911

For the range of parameters described only by the second virial coefficient, the expression for the activity can be represented as:

$$\ln j_1 = \frac{B_1 P}{RT} . \tag{15}$$

The values of the equilibrium constant K_{eq_0} were taken from [11]. In this way, we have available all the necessary data for calculating η_{mix}. Since formulas (2-7), given by rigorous kinetic theory, take into account only pairwise interactions, we are limited to the range of pressures 1-100 bar.

The effect of ionization was not taken into account, since the fraction of ions at temperatures not exceeding 6000°K is negligibly small [6]. The results of the calculation are shown in Table 2.

Variation in η_{mix} with pressure must be related to change in mixture composition.

In conclusion we note that unfortunately we do not have the opportunity to evaluate the precision of the results obtained with the corresponding experimental data, in view of the absence of the latter. However, taking into account the reliability of the method of calculation used, justifying itself in calculations for many mixtures [3], the authors believe that errors in the viscosity coefficient η_{mix} must not exceed 15 percent.

Symbols

x_i = mole fraction of i-th component; M_i = molecular weight of i-th component; T = absolute temperature; P = pressure; η = coefficient of dynamic viscosity; K = Boltzmann constant; $A^*_{12} = \Omega^{(2.2)*}/\Omega^{(1.1)*}$; $\Omega^{(1.1)*}$ and $\Omega^{(2.2)*}$ = corresponding collision integrals tabulated in [1]; ε and σ = parameters of potential function; $f_\eta^{(3)}$ = correctional coefficient tabulated in [1]; $T^* = kT/\varepsilon$, reduced temperature; N = Avogadro's number; B_2 = second virial coefficient; r = distance between interacting particles; K_{eq_0} = equilibrium constant for the ideal-gas approximation; K_{eq} = equilibrium constant with nonideality of components taken into account; j_i = activity of component; R = universal gas constant.
Indexes: 1, Atomic component; 2, Molecular component.

References

1. Hirschfelder, J., C. Curtis, and R. Byrd : *Molekulyarnaya Teoriya Gazov i Zhidkostey (Molecular Theory of Gases and Liquids)* IL Press, Moscow, 1961.

2. Kessel'man, P. M.: *Teplofizika Vysokikh Temperatur.*, Vol. 2, p. 879, 1964.

3. Kessel'man, P. M.: *Toktorskaya Dissertatsiya (Doctoral Dissertation)*, Odessa, 1966.

4. Belov, V. A. and N. I. Klyuchnikov: *Teplofizika Vysokikh Temperatur*, Vol. 3, p. 645, 1965.

5. Davies, R. H., E. A. Mason and R. J. Munn: *Phys. Fluids*, Vol. 8, 1965.

6. Krupenie, P. A., E. A. Mason and I. T. Vanderslice: *J. Chem. Phys.*, Vol. 39, p. 2399, 1963.

7. Vanderslice, I. T., E. A. Mason and I. T. Lippincott: *J. Ch. Ph.*, Vol. 30, 1959.

8. Shpil'rayn, E. E.: *Avtoreferat Doktorskoy Dissertatsii (Author's Abstract of Doctoral Dissertation)*, NIIVT Press, Moscow, 1964.

9. Kolker, H. I. and M. P. Karplus: *J. Chem. Phys.*, Vol. 39, p. 2011, 1963.

10. Karapet'yan, A. Kh.: *Khimicheskaya Termodinamika (Chemical Thermodynamics)*, Moscow, 1959.

11. Gurvich. L. V., G. A. Khachkaruzov, V. A. Medvedev, et al.: *Teplofizicheskiye Svoystva Individual'nykh Veshchestv. Spravochnik (Thermophysical Properties of Individual Compounds. Handbook)*, Academy of Sciences,USSR Press, Vol. II, Moscow, 1962.

12. Arai, T. and M. Sakamoto: *J. Chem. Phys.*, Vol. 28, p. 32, 1958.

13. Keys, R.: *Nature*, Vol. 182, p. 43, 1958.

COEFFICIENT OF VISCOSITY OF COMPRESSED GAS AND ITS RELATIONSHIP WITH THERMAL PROPERTIES

P. M. Kessel'man and V. R. Kamenetskiy

Establishing the relationship between viscosity coefficients and thermal properties of a compressed gas is one of the urgent problems of present-day heat physics. The solution of this problem would afford the possibility based on existing compressibility data to obtain all the information on the viscosity coefficient of the compound under study for a wide range of temperatures and pressures without resorting to direct experimentation.

The first attempt in this direction was made by Enskog [1], who obtained an equation establishing the relationship between the reduced viscosity η/η_0 and the equation of state.

The Enskog equation was theoretically justified, however it is valid only for the model of rigid spheres, since it was derived on the assumption of elastic interaction among molecules. Accordingly, this equation is only of historic interest and naturally has not found practical application.

Well known attempts to modify this equation suitably for real molecular models have not yielded results owing to specific shortcomings inherent in the original Enskog equation.

Even existing empirical equations do not correspond to the problem posed, since their use necessitates availability of experimental data on the viscosity coefficient of the compound under study. We note that for the range of moderate pressures, when viscosity is practically independent of pressure, the problem posed has found solution in [2, 3]. Since a single mechanism of intermolecular interaction is responsible for thermal and transport properties, in solving such a problem it appears reasonable to use some potential of interaction capable of comprehensively describing all thermophysical properties of a compound.

In this respect, the potential function (6-12) with variable parameters introduced for consideration in [2, 3] appears highly effective.

This function is of the form

$$U = 4\varepsilon(T)\left[\left(\frac{\sigma(T)}{r}\right)^{12} - \left(\frac{\sigma(T)}{r}\right)^{6}\right], \qquad (1)$$

where the parameters σ and ε provisionally depend on temperature.

Without dwelling in detail on the various advantages of the introduced potential function (1), we note that by means of it it is possible to comprehensively describe using a single set of potential parameters σ(T) and ε(T), both the thermal and transport properties of a compound under study. In particular, a method of determining σ(T) and ε(T) from compressibility data is elaborated in [2, 3] and it is shown that the parameters obtained can serve as a basis for satisfactory description of viscosity coefficient $\eta_0(T)$ for any compound, independent of its molecular structure.

The aim of this present study is to establish a relationship between thermal properties and the viscosity of a dense gas η(P, T) based on the potential function (1) described.

It is convenient to seek this function in the form

$$\eta/\eta_0 = f(\rho, T), \qquad (2)$$

where the density of gas ρ at given temperature and pressure is known from the equation of state ρ = ρ(P, T) or from tables of thermodynamic properties of the compound investigated. A breakdown of the righthand member of equation (2) appears possible if we make use of the methods of thermodynamic similarity, employing here the potential function (1) which is universal in the sense of applicability for any complex compound.

Actually, it follows from the principles of thermodynamic similarity that if compounds are similar in thermal properties, they must be similar also in coefficients of viscosity. In this way, if similarity exists with respect to compressibility $Z = PV/RT$ in some system of dimensionless parameters ω^* and T^* for all compounds, then for the same ω^* and T^* the values of the reduced viscosity coefficient η/η_0 must be equal for these compounds.

In this case we could obtain from experimental values of η/η_0 for some limited number of compounds a generalized diagram $\eta/\eta_0 = \phi(\omega^*, T^*)$, (valid for all gases), the analytic description of which would lead us to the goal we seek.

Let us show here that by using the potential function (1), we can find such a system of dimensionless coordinates ω^* and T^* in which all compounds will be thermodynamically similar. Actually, describing the equation of state in the form

$$Z = 1 + \frac{B(T)}{V} + \frac{C(T)}{V^2} + \dots \qquad (3)$$

and using the functions

$$B = b_0 \cdot B^*(T^*)$$
$$C = b_0^2 \cdot C^*(T^*)$$

where $T^* = kT/\varepsilon$, $b_0 = 2/3(\pi N \sigma^3)$, we get

$$Z = 1 + \frac{b_0}{V} B^*(T^*) + \frac{b_0^2}{V^2} C^*(T^*) + \dots \qquad (4)$$

If we take a point with characteristic values of volume and temperature equal, respectively, to b_0 and ε/k, as the support point, equation (4) becomes

$$Z = 1 + B^*(T^*)\omega^* + C^*(T^*)\omega^{*2} + \dots, \qquad (5)$$

where the dimensionless quantities ω^* and T^* are determined by coordinates of the support point by the relationships

$$\omega^* = \frac{B_0}{V}, \quad T^* = \frac{\kappa T}{\varepsilon}. \tag{6}$$

Since B(T), C(T), etc. are universal functions for all compounds (theoretical reduced virial coefficients for the potential (6-12)[1], equation (5) in the system of coordinates Z, ω* and T* is general for all compounds, which demonstrate the assertion made. Thus, all compounds are thermodynamically similar in this system of dimensionless coordinates. Therefore, in the system of coordinates η/η_0, ω* and T*, they must also be similar, that is, the general equation must hold for all gases

$$\eta/\eta_0 = \varphi(\omega^*, T^*) \tag{7}$$

The distinguishing feature of this established fact is that in this system of coordinates, the parameters of reduction (support point parameters) are not constant, but vary from isotherm to isotherm. Treatment in these coordinates of experimental data for many compounds (Ar, Kr, Xe, He, N_2, O_2, CO_2, H_2, CH_4, C_2H_4, C_2H_6, C_3H_8, NH_3, H_2O and CO), belonging to different molecular models (from spherical to complex polar molecules), confirmed that they are actually similar, since the isotherms of the reduced viscosity η/η_0 for these compounds practically speaking coincide. This fact is selectively shown in Figure 1.

Further, the maximum scatter of points did not exceed 7 percent.

In plotting the isotherms of reduced viscosity, use was made of experimental data in [6] for CH_4, C_2H_4, C_2H_6, CO, CO_2, O_2 and NH_3, data in [7] for H_2 and D_2, data in [8] for N_2, data in [9] for He, and data in [10] for Ar, Kr and Xe.

Values of reduced viscosity for H_2O were calculated from data in the International Steam Table [11].

---

[1] See p. 125

The corresponding density values were taken from [12], and also from original studies, while the values of the potential parameters $\sigma(T)$ and $\varepsilon(T)$ -- from [3] and [13-15], where they have been tabulated for a large number of compounds.

Smoothing out and mutual agreement of experimental values of η/η_0 according to the lines $T^* = \text{const}$ and $\omega^* = \text{const}$ allowed us to obtain a network of support values of $\eta/\eta_0 = \phi(\omega^*, T^*)$, which is general for all compounds, since in the established system of coordinates all compounds are similar.

To obtain the analytical function (7), the network of support values of η/η_0 we have arrived at was approximated by an equation according to the method. This equation is of the form

$$\eta/\eta_0 = 1 + \sum_{i=1}^{n} a_i \omega^{*i} + \frac{1}{T^*}\sum_{i=1}^{n} b_i \omega^{*i} + \frac{1}{T^{*2}}\sum_{i=1}^{n} c_i \omega^{*i} + \frac{1}{T^{*3}}\sum_{i=1}^{n} d_i \omega^{*i} + \frac{1}{T^{*4}}\sum_{i=1}^{n} e_i \omega^{*i}. \tag{8}$$

Numerical values of the coefficients in equation (8) are given in Table 1.

Table 1. Values of the Coefficients in Equation (8)

i	a_i	b_i	c_i	d_i	e_i
1	-0,126297	2,48252	-2,12956	1,04265	-0,199718
2	0,280292	0,101319	0,273418	-1,46498	0,980365
3	0,422594	-2,94345	7,69111	-5,32324	1,40170
4	0,222556	2,68969	-5,34702	4,04629	-1,28964

Equation (8) was verified by us from experimental data for a large number of compounds. Further, the mean error did not exceed 5 percent, and the maximum error -- 7 percent. We present Tables 2 and 3 as selective illustrations.

The region of applicability for equation (8) is

$$\omega^* = 0\text{-}1.20,\ T^* = 1\text{-}25,$$

which in terms of the usual parameters is approximately

$$\rho/\rho_k = 0\text{-}1.8,\ T/T_k = 0.8\text{-}20.$$

The values of the experimental parameters $\sigma(T)$ and $\varepsilon(T)$ required for the calculation can be found from compressibility data using the method set forth in [3]. Thus, equation (8) affords calculation of the viscosity of unstudied compounds for a wide range of parameters of state with an adequate precision. Further, it is enough to have available as the original values data on density as a function of pressure and temperature or the equation of state of a real gas.

Table 2. A Comparison of Calculated Values of the Cited Krypton Viscosity (Column I) with Experimental Viscosities [10] (Column 2)

p, atm	100°C		150°C	
	I	2	I	2
71,II	I,I07	I,082	I,083	I,076
I33,I	I,240	I,2I3	I,I67	I,I74
207,2	I,402	I,4I8	I,287	I,3I0
279,4	I,578	I,655	I,4I3	I,456
34I,9	I,763	I,862	I,546	I,6I8
4II,3	I,945	2,068	I,668	I,770
478,7	2,I4I	2,28I	I,804	I,922
546,7	2,39I	2,480	I,937	2,058
6I4,8	2,49I	2,665	2,05I	2,I90
683,5	2,653	2,846	2,I83	2,3I8
752,6	2,8I7	3,0I7	2,302	2,420
8I9,6	3,006	3,I87	2,4I2	2,529
δ_{ay}, %	5,0		4,I	
δ_{max}, %	- 6,8		- 6,I	

Table 3. A Comparison of Calculated Values of the Cited Viscosity of Water Vapor (Column I) with Data of [II] (Column 2)

P , bar	500°C		650°C	
	1	2	I	2
I0	I,004	I,004	I,003	I,003
25	1,0II	I,0I0	I,008	I,006
30	I,022	I,0I8	I,0I6	I,012
100	I,047	I,039	I,032	I,026
I50	1,075	1,063	I,050	I,04I
200	I,I08	I,095	I,069	I,058
250	I,I45	1,130	1,088	1,075
300	1,190	1,I76	I,109	1,093
400	1,3I2	1,299	1,156	2,136
500	I,497	1,497	1,2I0	1,I88
600	I,734	1,708	I,270	I,246
700	1,978	I,9I9	I,338	1,313
800	2,196	2,099	1,4I3	1,386
δ_{ay}, %	I,2		I,2	
δ_{max}, %	+ 4,6		+ I,9	

Symbols

η = coefficient of dynamic viscosity at temperature T and pressure P; η_o = coefficient of dynamic viscosity at temperature T and atmospheric pressure; σ and ε = parameters of the potential (6-12); k = Boltzmann constant; N = Avogadro's number; ρ = density; ρ_k = critical density; T_k = critical temperature; $T^* = T/(\varepsilon/k)$, reduced temperature; B, C,... = = second, third, etc. virial coefficients.

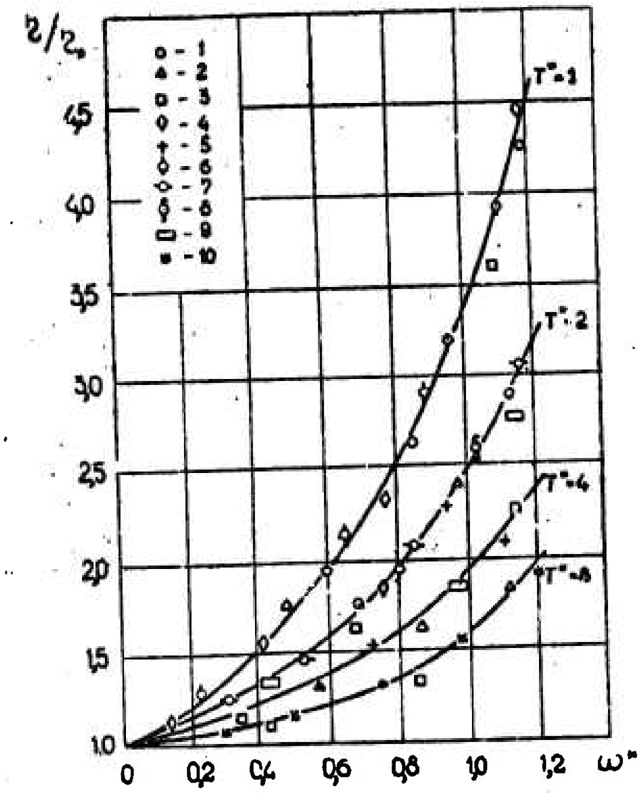

Figure 1. Isotherms of the reduced viscosity in the coordinates η/η_0, ω^* and T^*: 1, Xe; 2, CO; 3, N_2; 4, H_2O; 5, CO_2; 6, NH_3; 7, CH_4; 8, C_2H_4; 9, C_2H_6; 10, H_2

Footnotes

1. To p. 120 At present, the first four virial coefficients B, C, D and E have been tabulated for the potential (6-12) as a function of T* [4, 5].

References

1. Enskog, D.: *Kingl. Svenska Vetenkapsakad. Handlingar*, Vol. 68, p. 4, 1922.
2. Kessel'man, P. M.: *Teplofizika Vysokikh Temperatur*, Vol. 2, No. 6, p. 879, 1964.
3. Kessel'man, P. M.: *Doktorskaya Dissertatsiya (Doctoral Dissertation)*, Odessa Technological Institute imeni M. V. Lomonosov Press, Odessa, 1966.
4. Hirschfelder, J.; C. Curtis. and R. Byrd : *Molekulyarnaya Teoriya Gazov i Zhidkostev (Molecular Theory of Gases and Liquids)*, IL Press, Moscow, 1961.
5. Barker, J. A., P. J. Leonard and A. Pompe: *J. Chem. Phys.*, Vol. 44, II, p. 4206, 1966.
6. Golubev, I. F.: *Vyazkost' Gazov i Gazovykh Smesey (Viscosity of Gases and Gas Mixtures)*, Gizmatgiz Press, Moscow, 1959.
7. Michels, A., A. Shipper and W. Rintoul: *Physica*, Vol. 19, No. 10, p. 1011, 1953.
8. Michels, A. and R. Gibson: *Proc. Roy. Soc.*, A 134, p. 288, 1931.
9. Ross, J. F. and G. M. Brown: *Ind. Eng. Chem.*, Vol. 49, p. 2026, 1957.
10. Reynes, E. G. and G. Thodca: *G. Physica*, Vol. 30, p. 1529, 1964.
11. Vukalovich, M. P. and N. B. Vargaftik: *Teploenergetika*, No. 12, p. 55, 1965.
12. *Teplofizicheskiye Svoystva Gazov i Zhidkostey. Spravochnik pod redaktsiyey N. B. Vargaftika (Thermophysical Properties of Gases and Liquids. Handbook edited by N. B. Vargaftik)*, Fizmatgiz Press, Moscow, 1963.
13. Kessel'man, P. M. and S. K. Chernyshev: *Teplofizika Vysokikh Temperatur*, Vol. 3, No. 5, p. 700, 1965.
14. Kessel'man, P. M. and A. S. Litvinov: *IFZh*, Vol. 10, No. 3, p. 385, 1966.
15. Kessel'man, P. M., A. S. Litvinov and S. K. Chernyshev: *Sb. Obshchiye voprosy teploobmena (Collection: General Problems of Heat Transfer)*, Nauka i Tekhnika Press, Minsk, 1966.

VISCOSITY AND THERMAL CONDUCTIVITY OF COMBUSTION PRODUCTS OF ORGANIC FUELS

P. M. Kessel'man and A. S. Litvinov

Study and practical use of high-temperature processes has necessitated the determination of transport coefficients for the combustion products of various fuels at temperatures up to 5000-6000°K upon their combustion in air and oxygen-air mixtures with different oxygen content.

Direct experimental study of thermophysical properties at high temperatures is difficult, therefore theoretical calculation is widely used in these cases. As we know, statistical mechanics of nonequilibrium systems gives an expression for the viscosity and thermal conductivity of single-atom gases and their mixtures, presented in [1]. Strictly speaking, this theory is applicable only for single-atom gases. For multiatomic gases, whose molecules also exhibit internal degrees of freedom, inelastic collisions are possible. Further, kinetic energy is no longer preserved, while momentum is preserved. Therefore, viscosity depends only slightly on the existence of internal degrees of freedom, and the theory of single-atom gases has been successfully applied to multiatomic gases and to gas mixtures. Taking account of the influence of internal degrees of freedom and calculating thermal conductivity of combustion products of fuels will be considered below.

To calculate the coefficients of viscosity of combustion products according to formulas of kinetic theory, we must know the mole fraction of components and the component coefficients of viscosity.

In the general case, at low temperatures combustion products of organic fuels contain H_2O, CO_2, N_2 and O_2 (for sulfurous fuels SO_2 can be related to carbon dioxide). At high temperatures combustion products constitute a chemical reacting mixture in which, in addition to dissociation, formation of new molecular species takes place (at the indicated P and T, ionization is insignificant), as the result of which they have a very complex composition (H_2O, CO_2, N_2, O_2, H_2, CO, NO, OH, H, O, N and C), dependent on the original composition of the fuel, oxidizer, coefficient of excess oxidizer α, temperature and pressure. Dissociation of combustion products having the composition described is determined by the following chemical reactions:

$$CO_2 \rightleftharpoons CO + \frac{1}{2} O_2; \quad H_2O \rightleftharpoons H_2 + \frac{1}{2} O_2; \quad H_2O \rightleftharpoons OH + \frac{1}{2} H_2;$$
$$H_2 \rightleftharpoons 2H; \quad O_2 \rightleftharpoons 2O; \quad \frac{1}{2} N_2 + \frac{1}{2} O_2 \rightleftharpoons NO; \quad N_2 \rightleftharpoons 2N;$$
$$CO \rightleftharpoons C + O.$$

To determine the equilibrium composition of combustion products of fuels, a system of twelve nonlinear algebraic equations was derived, which consists of eight equations for chemical equilibrium corresponding to the reactions presented above, three equations obtained from the equations of the material balance of atoms, and the equation of Dalton's law. This system was solved by a method similar to that set forth in [2]. The equilibrium constants were taken from [3].

Due to the slight carbon content in the combustion products, when we calculated the transport coefficients the carbon content was included with the CO.

Component coefficients of viscosity were expressed by the collision integrals $\Omega^{(2.2)*}$, in the calculation of which we must know about the potential function of interaction among similar and dissimilar molecules and atoms.

In this study, to describe the coefficients of viscosity of the "pure" components, we used the potential of interaction (6-12) that contained variable potential parameters σ(T) and ε(T)

$$U = 4\varepsilon(T)\left\{\left[\frac{\sigma(T)}{r}\right]^{12} - \left[\frac{\sigma(T)}{r}\right]^{6}\right\} \qquad (1)$$

The method of determining potential parameters is described in [4, 5]. The collision integrals are tabulated in [1].

The reliability of this method of describing thermophysical properties of gases was verified for many multiatomic and polar gases [5-8]. This same method was successfully used in [5, 9] in calculating the transport coefficients and the second virial coefficient of the atomic components O, N and H. Thus, potential parameters and the coefficients of viscosity of all components of the combustion products of fuels can be found in [5-7, 9].

In describing the interaction among dissimilar molecules and atoms, potential parameters are found by combining the corresponding parameters for the "pure" components.

These combining rules, when the potential (1) was used, proved to be reliable in calculating the viscosity of mixtures consisting of molecular components [7]. Collision integrals for the interaction N-O, O-H, H-H_2 O-O_2, etc. have been calculated in [10-12]. Comparison of the latter with collision integrals found by combination of potential parameters gives a maximum deviation of 15-20%, which does not overreach the limits of precision of the calculations made in [10-12].

Thus, with the mole fractions of components and component coefficients of viscosity, the coefficients of viscosity of the combustion products of twelve fuels (Saratov gas, kerosene, etc.) were calculated from formula [1, p. 422] in the temperature range 400-6000°K and the pressure range 0.1-100 bar. The coefficient of oxidizer excess $\alpha = 1.0$ (for Saratov gas 1.0, 1.1, 1.2 and 1.5), and the oxygen content O_o = 23.15, 40, 60, 80 and 100% (composition by weight). As an illustration, Figure 1 presents the function of the viscosity of the combustion products of Saratov gas when $\alpha = 1.0$ and O_o = 23.15% at several pressures, from which it is clear that η varies insignificantly with rise in pressure and only at high temperatures does this change amount to 15%. The function of the coefficient of viscosity of combustion products of Saratov gas is shown in Table 1 a. The maximum variation was observed at low temperatures and is 20% when O_o is varied from 23.15 to 100%.

When the coefficient of oxidizer excess α rises from 1.0 to 1.5, values of η vary by no more than 3%. A similar picture is observed for combustion products of other fuels.

At high reaction rates, the effective thermal conductivity of a dissociating gas mixture can be described as the sum of the member λ_{froz} for the thermal conductivity of the "chemically frozen" mixture and the member λ_{reac}, caused by the chemical reactions

$$\lambda_{CM} = \lambda_{з} + \lambda_{p} \qquad (2)$$

Table 1 a. Coefficient of Viscosity of Combustion Products of Saratov Gas ($\eta \cdot 10^8$ n·sec/m^2) As a Function of Oxidizer O_o for α = 1.0 and p = 1.0 bar

T, °K \ O_o, %	23,15	40	60	80	100
500	2394	2294	2175	2060	1951
1000	3991	3960	3916	3866	3814
2000	6393	6447	6506	6508	6506
3000	8363	8467	8569	8660	8741
4000	10386	10622	10834	11000	11137
5000	12303	12728	13120	13425	13655
6000	14587	15157	15543	15772	15780

Table 1 b. Coefficient of Viscosity of Combustion Products of Saratov Gas ($\eta \cdot 10^8$ n·sec/m^2) As a Function of the Coefficient of Oxidizer Excess α for O_o = 23.15% and p = 1.0 Bar

T, °K \ α	1,0	1,1	1,2	1,5
500	2394	2413	2429	2465
1000	3991	4007	4020	4048
2000	6393	6406	6417	6441
3000	8363	8389	8404	8437
4000	10386	10419	10447	10510
5000	12303	12342	12375	12448
6000	14587	14728	14757	14831

A formula for calculation of thermal conductivity of a mixture of nonreacting gases that includes effects of inelastic collisions was recently derived in [13]. However, calculation using this formula when there is a large number of components in the mixture is laborious and indeterminate owing to the absence of data on the transient relaxation of dissimilar molecules. Moreover, correction for the inelasticity is small, therefore the Hirschfelder-Eichen formula [14] proves satisfactory in calculating the thermal conductivity of a mixture

$$\lambda_{\text{з}} = \lambda^{0}_{\text{з}} + \sum_{\kappa} \frac{\lambda_{\kappa} - \lambda^{0}_{\kappa}}{1 + \sum\limits_{\ell \neq \kappa} \frac{x_{\ell}}{x_{\kappa}} \cdot \frac{\mathcal{D}_{\kappa\kappa}}{\mathcal{D}_{\kappa\ell}}} \qquad (3)$$

But, here, inelastic effects must be included in calculations of the thermal conductivity of the "pure" components λ_k.

Table 2. Number of Collisions for Rotational Relaxation

Gas	H_2O	CO_2	O_2	N_2	CO
Z_{rot}	4,0	5,0	7,0	6,0	7,0

Calculation of the translational component of the thermal conductivity of a mixture λ^{o}_{froz} and calculation of the components λ^{o}_{k} similar to the calculation of viscosity [1, p. 426] was made based on potential parameters in the potential (1) found above.

Calculation of the thermal conductivity λ_k for H_2O, CO_2, O_2, N_2 and CO was carried out using the Mason and Monchick formula [15].

$$\frac{\lambda M}{\eta} = \frac{15}{4} R + \left(c_v - \frac{3}{2} R\right) \frac{\rho \mathcal{D}}{\eta} - \frac{2}{\pi} \left(\frac{5}{2} - \frac{\rho \mathcal{D}}{\eta}\right)^2 \left(\frac{c_{\text{вр}}}{Z_{\text{вр}}} + \frac{c_{\text{кол}}}{Z_{\text{кол}}}\right) \qquad (4)$$

The last member in (4) allows for the contrution of internal degrees of freedom to the thermal conductivity by introducing the number of collisions Z_{rot} and Z_{vib} for rotational and vibrational relaxation. The number Z_{vib} has a fairly large value, owing to which the contribution to the thermal conductivity of vibrational relaxation was neglected. Theoretical calculations of the exchange of rotational energy are still inadequate, and experimental values of various authors differ widely. Accordingly, Z_{rot} was determined on the basis of experimental data for thermal conductivity and was adopted as average values not dependent on temperature (Table 2). The rotational contribution to heat capacity c_{rot} is taken as follows: R = for linear molecules and $\frac{3}{2}R$ = for nonlinear molecules (for H_2O, the values $c_{int} = C_v - \frac{3}{2}R$ were substituted for c_{rot}). For nonpolar multiatomic molecules, the relationship was $\rho D/\eta = \frac{6}{5}A^*$. For water vapor, the resonance exchange of rotational energy $\rho D/\eta = \frac{6}{5}A^*(1 + Z'/Z_0)^{-1}$ was taken into account. The expression Z'/Z_0 was obtained in [15] for different types of polar molecules.

The values of the coefficient of thermal conductivity of the "pure" components of the fuel combustion products calculated by formula (4) are given in Table 3. Comparison with available experimental data for these compounds gives good agreement.

Calculation of the thermal conductivity of combustion products caused by chemical reactions is made on the basis of formulas derived in [16, 17].

$$\lambda_p = -\frac{1}{RT^2}\,\frac{\begin{vmatrix} A_{11} & A_{12} & \dots & A_{1\nu} & \Delta H_1 \\ A_{12} & A_{22} & \dots & A_{2\nu} & \Delta H_2 \\ \cdot & \cdot & \cdot & \cdot & \cdot \\ A_{1\nu} & A_{2\nu} & \dots & A_{\nu\nu} & \Delta H_\nu \\ \Delta H_1 & \Delta H_2 & \dots & \Delta H_\nu & 0 \end{vmatrix}}{\begin{vmatrix} A_{11} & A_{12} & \dots & A_{1\nu} \\ A_{12} & A_{22} & \dots & A_{2\nu} \\ \cdot & \cdot & \cdot & \cdot \\ A_{1\nu} & A_{2\nu} & \dots & A_{\nu\nu} \end{vmatrix}} \qquad (5)$$

where

$$A_{ij} = A_{ji} = \sum_{k=1}^{\mu-1}\sum_{l=k+1}^{\mu} \frac{RT}{D_{kl}P}\, x_k x_l \left(\frac{n_{ik}}{x_k} - \frac{n_{il}}{x_l}\right)\left(\frac{n_{jk}}{x_k} - \frac{n_{jl}}{x_l}\right) \qquad (6)$$

Seven of the first reactions given above are taken into account in calculation of λ_{reac}. The heats of reaction ΔH_ν have been calculated from data in [3].

Table 3. Coefficients of Thermal Conductivity of "Pure" Components of Combustion Products of Fuels, $\lambda \cdot 10^8$ kw/m·deg

Gas / T, °K	H_2O	CO_2	N_2	O_2	H_2	CO	NO	OH	O	H
400	2663	2449	3161	3329	22931	3144	3391			
500	3559	3211	3747	4053	26645	3747	4074			
600	4605	3965	4329	4739	30116	4346	4744			
700	5820	4698	4907	5405	33499	4932	5397			
800	7109	5372	5481	6042	36794	5510	6033			
900	8462	6016	6037	6657	40135	6079	6649			
1000	9881	6644	6586	7247	43430	6628	7247			
1200	12841	7846	7641	8369	50083	7687	8382			
1400	15797	8956	8642	9424	56765	8683	9437			
1600	18548	10006	9596	10429	63439	9852	10429	9380	14139	82647
1900	21194	10995	10505	11401	70158	10526	11371	10770	15432	90661
2000	23752	11932	11371	12355	76765	11376	12259	11840	16684	98834
2200	26209	12828	12192	13301	83213	12196	13117	12866	17936	107009
2400	28600	13699	12987	14259	89526	12971	13942	13858	19167	115489

Table 3 [continued].

gas T, °K	H_2O	CO_2	N_2	O_2	H_2	CO	NO	OH	O	H	
2600	40907	14537	13758	15105	95748	13728	14746	14825	20377	123546	
2800	33172	15353	14486	16094	101773	14470	15520	15776	21587	132387	
3000	35408	16153	15211	17007	107672	15181	16710	16710	22810	140095	[illegible]
3200	37597	16936	15914	17899	113487	15885	17028	17635	24036	149036	[illegible]
3400	39787	17706	16609	18795	118834	16576	17760	18548	25267	158016	[illegible]
3600	41935	18460	17279	19657	124549	17250	18472	19460	26532	166651	32737
3800	44095	19201	17949	20503	130197	17911	19167	20360	27796	175473	[illegible]
4000	46264	19933	18606	21323	135878	18560	19850	21252	29098	184255	[illegible]
4200	48433	20649	19251	22131	141526	19205	20515	22140	30438	192935	[illegible]
4400	50593	21348	19883	22927	147158	19824	21173	22986	31762	201661	41273
4600	52712	22056	20503	23722	152709	20440	21822	23810	33109	210236	43763
4800	54818	22747	21106	24514	158202	21043	22471	24597	34453	219024	46356
5000	56920	23442	21700	25305	163528	21637	23120	25334	35810	227569	49032
5200	59013	24166	22286	26084	168720	22232	23764	26050	37162	236391	51950
5400	61106	24874	22877	26796	173915	22831	24405	26741	38493	245058	54935
5600	63200	25573	23480	27549	179007	23442	25045	27465	39821	253724	58016
5800	65299	26201	24112	28253	184378	24074	25698	28324	41152	262517	61090
6000	67374	26749	24803	28931	190319	24744	26080	29433	42471	271275	64318

Calculation of thermal conductivity was made for the same fuels, oxidizers, coefficients of oxidizer excess and parameters P and T as for viscosity. Figure 2 presents the function of the effect of thermal conductivity of Saratov gas combustion products for $\alpha = 1.0$, $O_o = 23.15$ percent for the pressures 0.1, 1.0, 10 and 100 bar. For comparison, the thermal conductivity of the "chemically frozen" mixture λ_{froz} at a pressure of 0.1 bar is plotted on the dot-dash line. The contribution of the coefficient of thermal conductivity λ_{reac} caused by chemical reactions is several times greater than λ_{froz}.

We must also note that in contrast to the viscosity the coefficient of thermal conductivity varies sharply as a function of pressure and temperature (when $T > 2000°K$). This is accounted for by the change in the composition of the fuel combustion products as a result of dissociation and formation of new molecular species. Thus, for example, the existence of maxima is caused by the dissociation of H_2O, CO_2, H_2 and O_2, and the rise in the coefficient of thermal conductivity at low pressures for temperatures greater than 4000°K is associated with the dissociation of N_2.

Symbols

P = pressure; T = temperature; M = molecular weight; R = universal gas constant; u = intermolecular potential; σ and ε = force constants of the intermolecular potential; r = intermolecular distance; η = coefficient of dynamic viscosity; λ = coefficient of thermal conductivity; D_{kl} = binary coefficient of diffusion; c_v = specific heat capacity at constant volume; c_{int} = internal heat capacity; c_{rot} and c_{vib} = rotational and vibrational heat capacities, respectively; Z_{rot} and Z_{vib} = number of collisions for rotational and vibrational relaxations, respectively; ρ = density; $A^* = \frac{\Omega^{(2.2)*}}{\Omega^{(1.1)*}}$; $\Omega^{(1.1)*}$ and $\Omega^{(2.2)*}$ = reduced collision integrals; $1 + Z'/Z_o$ = correction for resonance collisions for polar molecules; x_k and x_l = mole fraction of the k-th and l-th components; μ = total number of components in gas mixture; ν = total number of chemical reactions; ΔH_i = heat of the i-th reaction; n_{ik} = stoichiometric coefficient for the k-th component in the i-th reaction; O_o = oxygen content in oxidizer; α = coefficient of oxidizer excess.

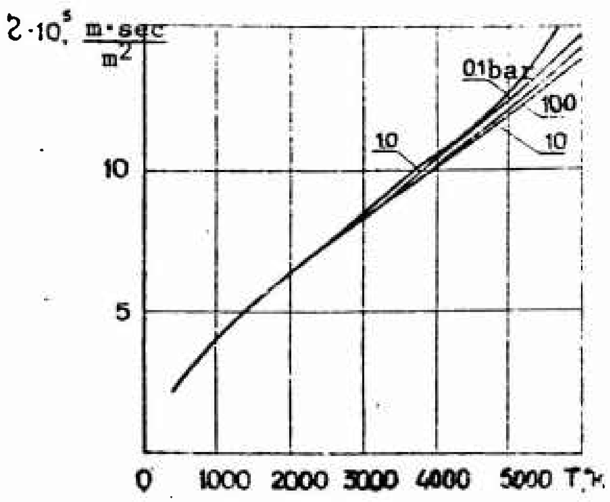

Figure 1. Coefficient of viscosity of Saratov gas combustion products as a function of temperature ($\alpha = 1.0$, ($\alpha = 1.0$, $O_o = 23.15$ percent).

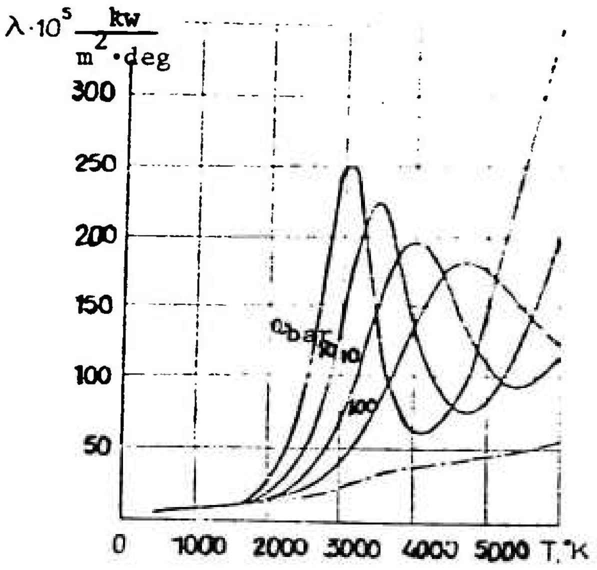

Figure 2. Coefficient of thermal conductivity of Saratov gas combustion products as a function of temperature ($\alpha = 1.0$, $O_o = 23.15$ percent): ——— = effective coefficient of thermal conductivity; —·—·—· = = coefficient of thermal conductivity of the "chemically frozen" mixture.

References

1. Hirschfelder, J.; C. Curtis, and R. Byrd : *Molekulyarnaya Teoriya Gazov i Zhidkostey (Molecular Theory of Gases and Liquids)*, IL Press, Moscow, 1961.

2. Lapshov, V. N., V. I. Borshchov and G. S. Saprykin: *Tablitsy Termodinamicheskikh Svoystv Produktov Sgoraniya Saratovskogo Priprodnogo Gaza pri Vysokikh Temperaturakh (Tables of Thermodynamic Properties)*, Saratov University Press, Saratov, 1964.

3. Gurvich, L. V., G. A. Khachkaruzov, V. A. Medvedev, et al: *Spravochnik. Termodinamicheskiye Svoystva Individual'nykh Veshchesty (Handbook. Thermodynamic Properties of Individual Compounds)*, Academy of Sciences, USSR Press, Moscow, 1962.

4. Kessel'man, P. M.: *Teplofizika Vysokikh Temperatur*, Vol. 2, p. 879, 1964.

5. Kessel'man, P. M.: *Doktorskaya Dissertatsiya (Doctoral Dissertation)*, Odessa Technological Institute imeni Lomonosov, Odessa, 1966.

6. Kessel'man, P. M., A. S. Litvinov and S. K. Chernyshev: *Sb. Obshchiye Voprosy Teplo- i Massoobmena (Collection: General Problems of Heat and Mass Transfer)*, Nauka i Tekhnika Press, Minsk, 1966.

7. Kessel'man, P. M. and A. S. Litvinov: *IFZh*, Vol. 10, p. 385, 1966.

8. Kessel'man, P. M. and S. K. Chernyshev: *Teplofizika Vysokikh Temperatur*, Vol. 3, p. 700, 1965.

9. Kessel'man, P. M., A. S. Bestuzhev, Yu. I. Blank and A. S. Litvinov: *Teplo- i Massoperenos, Tom 7 (Heat and Mass Transfer, Volume 7)*, Energiya Press, Moscow-Leningrad, 1968.

10. Yun, K. S. and E. A. Mason: *Phys. Fluids*, Vol. 5, p. 380, 1962.

11. Vanderslice, J. T., S. Weissman, E. A. Mason and R. J. Fallon: *Phys. Fluids*, Vol. 5, p. 155, 1962.

12. Krupenie, P. H., E. A. Mason and J. T. Vanderslice: *J. Chem. Phys.*, Vol. 39, p. 2399, 1963.

13. Monchick, L., A. N. G. Pereira and E. A. Mason: *J. Chem. Phys.*, Vol. 42, p. 3241, 1965.

14. Hirchfelder, J. O.: *J. Chem. Phys.*, No. 26, p. 282, 1957; *Symp. Combust. 6th Yale Univ.*, p. 351, 1956, 1957; *Proceedings of the Joint Conference on Thermodynamic and Transport Properties of Fluids (Institution of Mechanical Engineers)* London, p. 133, 1958.

15. Mason, E. A. and L. Monchick: *J. Chem. Phys.*, Vol. 36, p. 1622, 1962.

16. Butter, J. N. and R. S. Brokaw: *J. Chem. Phys.*, Vol. 26, p. 1696, 1957.

17. Brokaw, R. S.: *J. Chem. Phys.*, Vol. 32, p. 1005, 1960.

TRANSPORT COEFFICIENTS OF WATER VAPOR AND AIR AT T = 1000-6000°K WITH ACCOUNT OF THEIR THERMAL DISSOCIATION

P. M. Kessel'man, A. S. Bestuzhev, Yu. I. Blank, and
A. S. Litvinov

A considerable number of studies have dealt with determination of transport coefficient of air [1-3]. Results of refined calculation of coefficients of viscosity and thermal conductivity of air with account taken of thermal dissociation are given in this present paper. The following bulk composition of air was adopted: N_2 = 78.084 percent, O_2 = 20.946 percent and Ar = 0.97 percent. For the temperature range studied at pressures 0.1-100 bar air contains the following components: N_2, O_2, Ar, NO, N and O. Estimates show that formation of NO_2, N_2O and N_2O_4, and also ionization at the indicated p and T may not be taken into account. In this case, when we calculate the compositions of air it is necessary to pay attention to the following chemical reactions:

$$N_2 \rightleftarrows 2N; \quad O_2 \rightleftarrows 2O; \quad \frac{1}{2} N_2 + \frac{1}{2} O_2 \rightleftarrows NO.$$

It must be noted that there is considerably less data on coefficients of viscosity and thermal conductivity of water vapor, and in the temperature range under study they are practically totally lacking with the exception of [4]. Dissociation of water vapor[1] is determined by four independent equations: $H_2O \rightleftarrows H_2 + 1/2\ O_2$; $H_2O \rightleftarrows OH + 1/2\ H_2$; $O_2 \rightleftarrows 2O$; and $H_2 \rightleftarrows 2H$.

H_2O, H_2, O_2, OH, H and O can be present in the mixture.

The equilibrium composition of air and water vapor is found by solving systems of nonlinear algebraic equations derived from the law of active masses, equations of material balance of atoms, and the condition $\Sigma x_i = 1$.

---

[1] See p. 149

Since the solution of the above-indicated systems in general form does not appear possible, they were solved by an iterative method on the M-20 electronic digital computer for specified values of p and T. The values of the equilibrium constants were taken from data in [5].

As we know, transport coefficients can be calculated from rigorous formulas of kinetic theory if the potentials of interaction among particles have been determined. The potential (6-12) with variable potential parameters σ and ε dependent on temperature [6] was used for molecular components (H_2O, N_2, O_2, H_2, NO, and Ar). Potential parameters and the coefficient of viscosity for H_2O, N_2 and O_2 to 3000°K are given in [7]. Extrapolation of data to 6000°K does not present any difficulties and was carried out by the method given in [6]. Parameters for H_2, NO and Ar obtained from experimental data proved to be practically independent of temperature and were taken as constant (for H_2, $\sigma = 2.934$ Å, $\varepsilon/k = 34.1$°K; NO, $\sigma = 3.495$ Å, $\varepsilon/k = 124.2$°K; Ar, $\sigma = 3.408$ Å; $\varepsilon/k = 119.4$°K). The potential energy of interaction and the collision integrals $\sigma^2\Omega^{(2.2)*}$ for hydroxyl were obtained in [8] to the complete pairing approximation. The second virial coefficient of OH, the values of which are given in Table 1, were also calculated with account taken of the dispersional member ($58.4/r^6$ ev)[2] based on the potential indicated. The integrals $\sigma^2\Omega^{(2.2)*}$ were obtained in the same way.

The potentials of interaction of atomic components (N, O and H) are given in [10-12]; collision integrals for these are in fact calculated in [11, 12]. The indicated data was used in our present study.

Potentials of interaction of dissimilar particles were determined by using the customary combining rules. For this purpose, the interactions N-N, O-O, H-H, and OH-OH were approximated by the potential in [6]. Data on the second virial coefficients and the collision integrals were used at an approximation. Table 1 presents the second virial coefficients obtained from the method given in [13] and the potential parameters σ and ε/k found as a result of approximation.

---

[2] See p. 149

Table 1. Second Virial Coefficients and Potential Parameters for N-N, O-O, H-H and OH-OH Interactions

T, °K	N - N			0 - 0			H - H			OH - OH			
	B, $\frac{cm^3}{mole}$	σ, Å	$\frac{\varepsilon}{\kappa}$, °K	B, $\frac{cm^3}{mole}$	σ, Å	$\frac{\varepsilon}{\kappa}$, °K	B, $\frac{cm^3}{mole}$	σ, Å	$\frac{\varepsilon}{\kappa}$, °K	$\sigma^2\Omega^{(2,2)3}$, Å^2	B, $\frac{cm^3}{mole}$	σ, Å	$\frac{\varepsilon}{\kappa}$, °K
2000	-	-	-	I4,62	2,820	II8,3	0,67	2,I89	547,8	I2,2I4	39,35	3,954	I47,5
2400	-	-	-	I4,48	2,795	II8,3	I,04	2,I33	627,8	II,775	38,67	3,9I4	I62,5
2800	-	-	-	I4,2I	2,774	II8,I	I,30	2,085	70I,7	II,399	38,0I	3,873	I72,8
3200	-	-	-	I3,94	2,756	II7,8	I,5I	2,045	770,7	II,085	37,37	3,846	I80,8
3600	-	-	-	I3,67	2,74I	II7,6	I,67	2,0I4	835,3	I0,8I9	36,77	3,8I8	I87,7
4000	4,76I	2,3I8	688	I3,42	2,728	II7,3	I,8I	I,988	896,9	I0,565	36,23	3,794	I94,0
4400	4,837	2,288	737	I3,I5	2,7I5	II7,I	I,92	I,965	955,5	I0,365	35,72	3,773	I99,8
4800	4,904	2,264	778	I2,9I	2,704	II6,8	2,00	I,943	I0II,8	I0,I65	35,22	3,754	204,9
5200	4,962	2,244	8I4	I2,67	2,693	II6,6	2,07	I,923	I065,6	9,979	34,78	3,737	208,9
5600	5,0I3	2,226	848	I2,45	2,684	II6,4	2,I2	I,902	III6,9	9,8I3	34,34	3,72I	2I2,2
6000	5,053	2,2I0	879	I2,24	2,675	II6,2	2,I7	I,882	II65,7	9,654	33,92	3,707	2I5,0

---

[3] See p. 149

The reliability of the combining rules for molecular interactions when use is made of the potential with variable parameters is shown in [1]. The suitability of the above-described method for the atom-atom and atom-molecule systems was verified by comparing collision integrals determined on the basis of combining rules with those determined from curves of potential energies taken from [11, 12]. Examples of such comparison are given in Table 2.

Determining all component viscosities in the above-described way (corresponding to the different possible interactions among gas particles) at a known composition using formulas in [14, p. 422], the coefficients of viscosity were calculated for water vapor and air, and they are shown graphically in Figures 1 and 2, respectively.

The method of calculating the coefficient of thermal conductivity of chemically reacting systems is set forth in [15]. Also found there are values of the coefficients of thermal conductivity of all components present in dissociating water vapor and air. Therefore, this present study gives only the results of the corresponding calculations relevantly for water vapor and air (Figures 3 and 4).

It was of interest to compare the results of calculations made in the present study with the data of other authors. Figure 5 presents a comparison of our calculated data with experiments and theoretical calculations by Tomas, Nansen, Stupochenko, etc. borrowed from [16]. As we see from the figure, our calculated data qualitatively best agrees with the experiment. However, quantitative deviations do exist, which can be seen in Figure 5. The results of other authors presented on the same graph do not agree even qualitatively, since maximum and minimum of the coefficient of thermal conductivity caused by dissociation of oxygen is absent. It must also be pointed out that experimental points [16] lie with a marked scatter and the curve given in Figure 5 as experimental has actually been determined in [16] not precisely enough (with a 20-percent error).

Table 2. Comparison of Collision Integrals $\sigma^2\Omega^{(2.2)}$[4] Obtained in the Present Study with Data in [11]

T, °K	O - N		O - N_2		N - N_2		O - O_2	
	I	2	I	2	I	2	I	2
2000	-	6,494	7,899	8,926	-	8,272	7,451	7,624
3000	5,345	5,606	7,317	7,998	7,320	7,427	6,900	6,985
4000	4,944	5,075	6,934	7,374	6,918	6,850	6,528	6,548
5000	4,651	4,745	6,649	6,899	6,646	6,419	6,254	6,219
6000	4,442	4,490	6,418	6,535	6,398	6,080	6,042	5,956

---

[4] See p. 149

Symbols

T = absolute temperature; p = pressure; σ and ε = potential parameters; k = Boltzmann constant; B = second virial coefficient; $\Omega^{(2.2)*}$ = reduced collision integral.

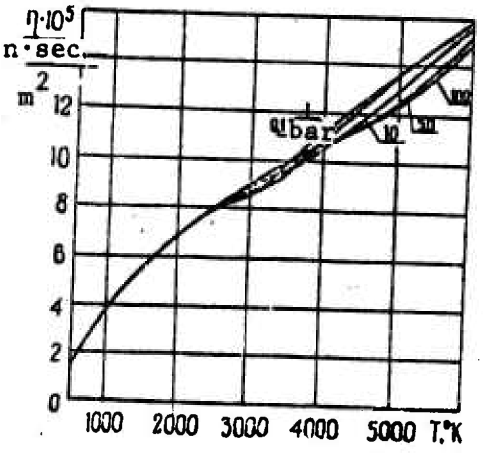

Figure 1. Coefficient of viscosity of water vapor

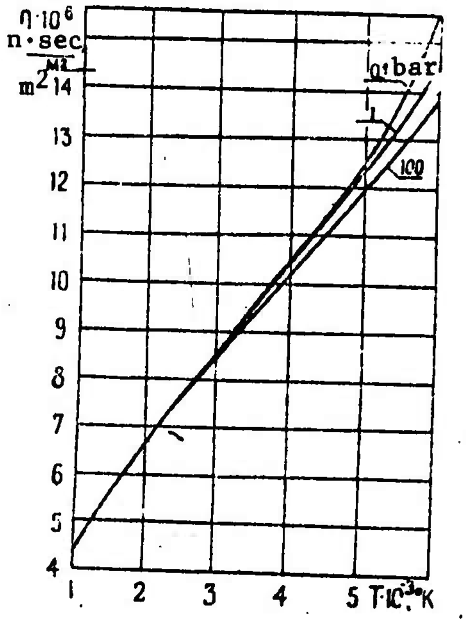

Figure 2. Coefficient of viscosity of air

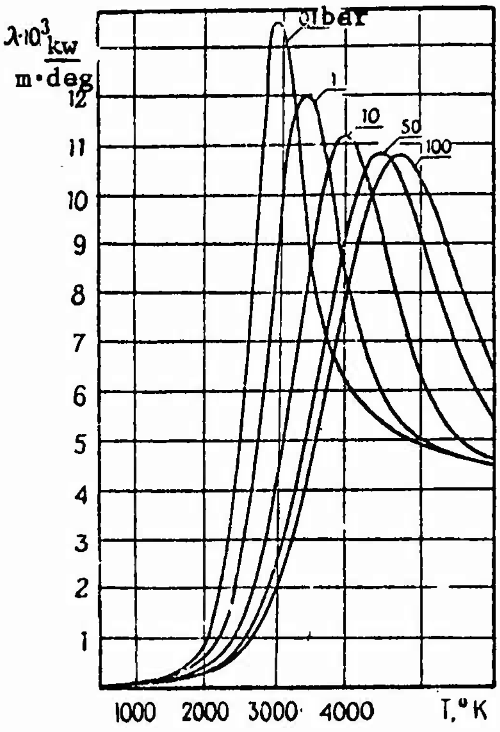

Figure 3. Coefficient of thermal conductivity of water vapor

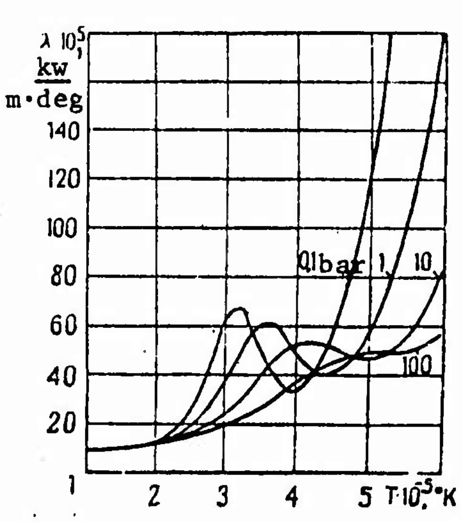

Figure 4. Coefficient of thermal conductivity of air

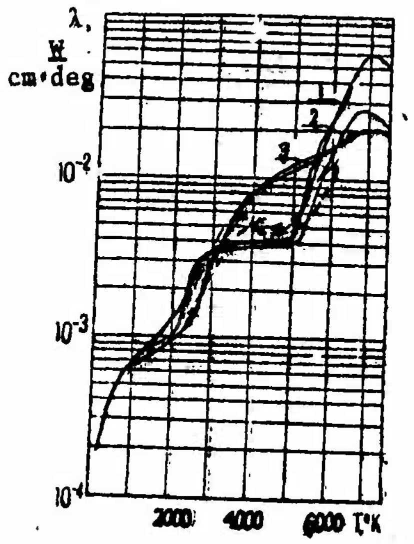

Figure 5. Comparison of results on coefficient of thermal conductivity of air: — — —, Experiment when $\rho = 0.1\ \rho_N$ [16]; —·—·—, Results of the present study when $\rho = 0.1\ \rho_N$; ——, Theoretical calculations at atmospheric pressure: 1, 2, 3, From [16].

Footnotes

1. To p.140 Calculation of transport coefficients of water vapor was made for the same pressure range as for air.

2. To p. 141 Polarizability values needed in calculating the dispersional energy were obtained according to the method given in [9].

3. To p. 142 Note. For atomic nitrogen, the second virial coefficient and the potential diameters are given, beginning with T = 4000°K, since at lower temperatures its dissociation is practically absent, even at p = 0.1 bar. Thus, at p = 0.1 bar and T = 4000°K, the mole fraction of nitrogen $x_N = 0.004$.

4. To p. 144 Note. 1 -- Data of the present study obtained using combining rules for potential parameters; 2 -- data of the study [11].

References

1. *P'eng Tsai-ch'eng, Pindrokh, Voprosy Raketnoy Tekhniki,* Vol. 12, p. 3, 1962.

2. Vasserman, A. A., Ya. Z. Kazavchinskiy and V. A. Rabinovich: *Teplofizicheskiye Svoystva Vozdukha i Yego Komponentov (Thermophysical Properties of Air and Its Components),* Nauka Press, Moscow, 1966.

3. Mathur, G. P. and G. A. Thodos: *A. I. Ch. E. Journal,* Vol. 9, p. 596, 1963.

4. Bonilla, C. F., R. D. Brooks and P. C. Wolker: *Proceedings of General Discussion of Heat Transfer,* Inst. Mech. Eng. Lond., p. 167, 1951.

5. Gurvich, L. V., G. A. Khachkuruzov, et al.: *Termodinamicheskiye Svoystva Individual'nykh Veshchestv (Thermocynamic Properties of Individual Properties),* Vol. II, Academy of Sciences USSR Press, Moscow, 1962.

6. Kessel'man, P. M., *TVT,* No. 2, p. 879, 1964.

7. Kessel'man, P. M. and A. S. Litvinov: *IFZh,* Vol. 10, p. 385, 1966.

8. Kessel'man, P. M., Yu. I. Blank and Ye. G. Taratunin: *Vsesoyuznaya Konferentsiya po Teplofizicheskim Svoystvam Veshchestv pri Vysokikh Temperaturakh. Tezisy Dokladov (All-Union Conference on Thermophysical Properties of Compounds at High Temperatures. Abstracts of Papers),* Novosibirsk, 1966.

9. Lippincott, E. R. and J. M. Stutman: *J. Phys. Chem.*, Vol. 68, p. 10, 1964.

10. Kessel'man, P. M., A. S. Bestuzhev, Yu. I. Blank and S. A. Shchekatolina: *Teplofizika Vysokikh Temperatur,* Vol. 4, p. 801, 1966.

11. Yun, K. S. and E. A. Mason: *Phys. Fluids,* Vol. 5, p. 380, 1962.

12. Vanderslice, J. T., S. Weissman, E. A. Mason and R. J. Fallon: *Phys. Fluids,* Vol. 5, p. 155, 1962.

13. Kassel'man, P. M.: *Doktorskaya Dissertatsiya (Doctoral Dissertation),* Odessa Technological Institute imeni Lomonosov, Odessa, 1966.

14. Hirschfelder, J.; curtis, C. and Byrd, R. : *Molekulyarnaya Teoriya Gazov i Zhidkostey (Molecular Theory of Gases and Liquids),* IL Press, Moscow, 1961.

15. Kessel'man, P. I. and A. S. Litvinov: *Teplo- Massoperenos, t. 7 (Heat and Mass Transfer, Volume 7)*, ITiMO Press, Minsk, 1968.

16. Smeets, G.: *Z. Naturforsch.*, Vol. 20-A, p. 683, 1965.

HEAT CAPACITY OF GASES AT ELEVATED TEMPERATURES WITH ACCOUNT OF THEIR NONIDEALITY AND THERMAL DISSOCIATION (H_2O, CO_2, F_2, AIR, LITHIUM AND FUEL COMBUSTION PRODUCTS)

P. M. Kessel'man, M. M. Afanas'yev, A. S. Bestuzhev,
Yu. I. Blank, S. F. Gorykin, P. A. Kotlyarevskiy,
S. K. Chernyshev and S. A. Shchekatolina

Knowledge of heat capacity of dissociated gases as we know is necessary in solving several problems in heat transfer.

This paper considers a method of calculating the heat capacities C_p and C_v of chemically reacting gases with account of their nonideality. Deviation from nonideality when calculations are made of properties of pure components, equilibrium compositions, and compositions of mixtures is allowed for by the second and third virial coefficients, which ensures adequate precision of results for the entire range of parameters investigated. Virial coefficients (N_2, O_2, H_2, CO, CO_2, NO, H_2O and Ar) of molecular components have been obtained on the basis of experimental thermal data by the method in [1], and virial coefficients for F_2, Li_2 and OH have been borrowed from [2, 4].

For the atomic components O, H, N, F and Li, the second virial coefficients are relevant, the method and results of calculation of which have been presented in [3, 4].

Calculation of equilibrium compositions has been carried out by solving a system of nonlinear algebraic equations, a specific form of which is determined in the individual case by the equations of the corresponding chemical reactions, equations of material valance of atoms, and the condition $\Sigma x_i = 1$.

Since in the general form solution of this system does not appear possible, equilibrium compositions were determined by the iterative method on an electronic digital computer at specified values of T and p.

Further, the equilibrium constant was calculated from the formula

$$K_p = \frac{K_{p_0}}{K_\gamma} , \tag{1}$$

in which k_γ is determined by the expression

$$\ln K_\gamma = \sum \nu_i \ln \gamma_i , \tag{2}$$

where

$$\ln \gamma_i = \frac{1}{RT}\left(\tilde{B}_i p + \frac{\tilde{C}_i - \tilde{B}_i^2}{RT} \cdot \frac{p^2}{2}\right). \tag{3}$$

Values of the constant k_{p_o} were borrowed from [5]. Determining the equilibrium composition by the method described and using the equation of state for a mixture in the form found in [6]

$$\tilde{V}_{cm} = \sum \tilde{V}_i x_i + \sum \sum x_i x_j \Delta \tilde{V}, \tag{4}$$

where

$$\Delta \tilde{V} = \tilde{\delta}_{ij} + \frac{(B_i - B_j)^2}{RT} p , \tag{5}$$

and

$$\tilde{\delta}_{ij} = 2 \tilde{B}_{ij} - \tilde{B}_j - \tilde{B}_i \tag{6}$$

We determine B_{ij} by the usual combining rules [3].

Based on the equation of state for a mixture [4], it is not difficult to obtain an expression for the enthalpy of a chemically reacting gas mixture

$$\tilde{H}_{\text{см}} = \sum \tilde{H}_i x_i + \sum\sum x_i x_j \Delta\tilde{H}_{ij} \,, \tag{7}$$

$$\Delta\tilde{H}_{ij} = \int\left[\Delta\tilde{V} - T\left(\frac{\partial\Delta\tilde{V}}{\partial T}\right)_p\right]dp \tag{8}$$

Substituting in (8) the expressions (5) and (6), after integration with respect to p, we get

$$\Delta\tilde{H}_{ij} = \left(\tilde{\delta}_{ij} - T\frac{d\tilde{\delta}_{ij}}{dT}\right)p + \frac{(\tilde{B}_i - \tilde{B}_j)}{RT}p^2\left[\left(B_i - T\frac{dB_i}{dT}\right) - \left(B_j - T\frac{dB_j}{dT}\right)\right]. \tag{9}$$

The formulas (3)-(9) presented above involve mole quantities.

The specific isobaric heat capacity of a mixture of variable composition was calculated from the formula

$$C_{P_{\text{см}}}^{\text{уд}} = \frac{\partial}{\partial T}\left(\frac{\tilde{H}_{\text{см}}}{\mu_{\text{см}}}\right), \tag{10}$$

which takes into account properties of the frozen mixture and the effect of the heat of chemical reaction. In (10) $\mu_{mix} = \Sigma\mu_i x_i$, and $\bar{H}_{mix}$ is given by expression (7).

The specific heat capacity C_{vmix}^{spec} is calculated from the formula

$$C_{V_{\text{см}}}^{\text{уд}} = C_{P_{\text{см}}}^{\text{уд}} + T\left(\frac{\partial V_{\text{см}}^{\text{уд}}}{\partial T}\right)_p^2 \Big/ \left(\frac{\partial V_{\text{см}}^{\text{уд}}}{\partial p}\right)_T . \tag{11}$$

The partial derivatives $(\partial x_i/\partial T)_p$ and $(\partial x_i/\partial p)_T$ that are part of (10) and (11) were obtained from a system of equations determining the equilibrium composition, which after uncomplicated transformations (taking the logarithm of and differentiating with respect to the appropriate variable) is reduced to a linear system with respect to the derivatives sought for.

The authors used the above-described method to calculate detailed tables of isobaric and isochoric heat capacities for water vapor, carbon dioxide, fluorine, air, lithium and the combustion products of thirteen organic fuels throughout the entire range of temperatures and pressures of practical importance (up to 6000°K and 0.1-1000 bar). The isobars of the specific heat capacity C_p for one of the most complex systems of the groups under study (combustion products of a stoichiometric mixture of Saratov gas and air) are given in the figure by way of example.

Symbols

T = absolute temperature; p = pressure; K_p and K_{p_o} = equilibrium constants for the real and the ideal gas, respectively; γ_i = activity of component; ν_i = stoichiometric number of components participating in the reaction; B_i and C_i' = second and third virial coefficients of the i-th component; $\overline{V}$ = molar volume; $\overline{H}$ = molar enthalpy; x = mole fractions of components; μ_i = molecular weight; R = universal gas constant.

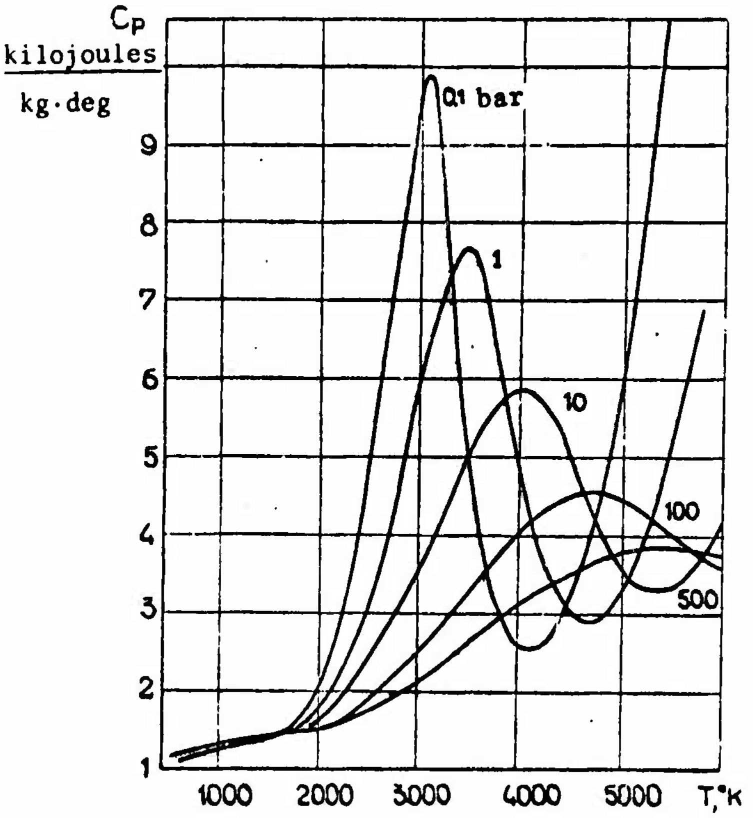

Figure 1. Isobaric heat capacity of Saratov gas combustion products in air

References

1. Kessel'man, O. M., TVT, Vol. 2, p. 879, 1964.
2. Kessel'man, P. M., A. S. Bestuzhev, Yu. I. Blank, and A. S. Litvinov, *Teplo- i Massoperenos, (Heat and Mass Transfer)*, Vol. 7, ITiMO Press of the Academy of Sciences, Belorussian SSR, Minsk, 1968.
3. Kessel'man, P. M., *Doktorskaya Dissertatsiya, (Doctoral Dissertation)*, Odessa Technological Institute imeni Lomonosov, Odessa, 1966.
4. Kessel'man, P. M. and S. F. Gorykin, *Teplo- i Massoperenos, (Heat and Mass Transfer)*, Vol. 7, ITiMO Press of the Academy of Sciences Belorussian SSE, Minsk, 1968.
5. Gurvich, L. V., G. A. Khachkuruzov, V. A. Medvedev, et al., *Teplo-fizicheskiye Svoystva Individual'nykh Veshchestv. Spravochnik, (Thermo-physical Properties of Individual Compounds. Handbook)*, Academy of Sciences USSR, Vol. 2, 1962.
6. Kessel'man, P. M., *Sb. Teplofizika i Teplotechnika, (Collection: Heat Physica and Heat Engineering)*, Naukova Dumka Press, Kiev, 1964.

TRUE AND TRACE DIFFUSION COEFFICIENTS OF GASES

N. D. Kosov and L. I. Kurlapov

When there is mutual diffusion of gases in closed instruments, the diffusional baro-effect arises [1, 2], which is the cause for the phenomenon of hydrodynamic flow of the gas mixture. This flow superimposed on diffusion currents, equalizes the transport of the number of molecules of each gas. The mutual diffusion coefficient of gases measured under these conditions is a characteristic of overall mass transport -- transport by chaotic thermal movement (diffusion proper) and transport by hydrodynamic current generated in the course of diffusion.

If measurements are made with strict observance of the isobaricity of conditions [3] (that is, in the absence of the baro-effect and the hydrodynamic flow it generates), the diffusion coefficient determined by Fick's law will characterize transport caused only by thermal movement (diffusion proper), and it is conveniently called the true diffusion coefficient. In the general case, the true diffusion coefficient of the first gas into the second does not equal the true diffusion coefficient of the second gas into the first.

An expression of true diffusion coefficients using molecular-kinetic parameters (for the model of solid spheres, using effective molecular diameters, molecular masses and the density of the number of molecules of each species) had been given already by L. Boltzman [4], and the relationship of the true diffusion coefficients with the coefficient of mutual diffusion by O. Meyer [5]. In the Boltzmann-Meyer theory, diffusion coefficients (true and mutual) depend on the concentration of the diffusion gases even for the simplest gas model -- solid spheres (the concentration explicitly enters into the formulas). In the Chapman-Enskog theory [6], the coefficient of mutual diffusion for this model does not depend on concentration, to the first approximation. Weak dependence on concentration was found only in the second approximation. The nondependence on concentration of the mutual diffusion coefficient in the Chapman-Enskog theory can be accounted for by the fact that this theory does not take account of the effect on diffusion of the collision of molecules of a given species. When the concentration of one of the diffusing gases is low (so-called trace diffusion), then in the Boltzmann theory the effect of homogeneous collisions can be neglected. However, both these theories lead to different values for the ratio of mutual diffusion coefficients for the two extreme cases (when the concentration of the first gas is small, and when the concentration of the second gas is small). Hence, it was of interest to investigate mutual diffusion of gases for these extreme cases. Below are given the results of measurements of trace diffusion coefficients of four systems.

True and Trace Coefficients

According to Boltzmann [4], the true coefficient of the i-th gas in the j-th gas with account taken of the persistency of velocities [6, 7] and the mean free path as a function of velocity [7] is written as follows:

$$\mathcal{D}_i = \frac{1{,}051\sqrt{8\kappa T}}{3\pi\sqrt{\pi m_i}\left\{(1-\omega_{ii})n_i\sqrt{2}\sigma_i^2+(1-\omega_{ij})n_j\sigma_{ij}^2\sqrt{\frac{m_i+m_j}{m_j}}\right.} \tag{1}$$

The coefficient of mutual diffusion is associated with the true coefficients by the O. Meyer formula:

$$\mathcal{D}_{ij} = c_i\mathcal{D}_j + c_j\mathcal{D}_i \tag{2}$$

The diffusion coefficients, as is seen from formulas (1) and (2), depend on concentration. In the limiting cases (when $c_1 \to 0$ or $c_2 \to 0$, the true diffusion coefficient of the first gas in the second varies from the self-diffusion coefficient D_{11} to the trace coefficient D^*_1,

$$\mathcal{D}_1(c_2 \to 0) = \frac{1{,}051 \cdot 2(\kappa T)^{3/2}}{3\pi\sqrt{\pi m_1}(1-\omega_{11})p\sigma_1^2} \equiv \mathcal{D}_{11} \tag{3}$$

$$\mathcal{D}_1(c_1 \to 0) = \frac{1{,}051(2\kappa T)^{3/2}}{3\pi\sqrt{\pi m_1}(1-\omega_{12})p\sigma_{12}^2\sqrt{\frac{m_1+m_2}{m_2}}} \equiv \mathcal{D}_1^* \quad (4) \tag{4}$$

Similar expressions have been obtained also for extreme values of the true diffusion coefficient of the second gas into the first:

$$\mathcal{D}_2(c_2 \to 0) = \frac{1{,}051(2\kappa T)^{3/2}}{3\pi\sqrt{\pi m_2}(1-\omega_{21})p\sigma_{12}^2\sqrt{\frac{m_1+m_2}{m_1}}} \equiv \mathcal{D}_2^* \tag{5}$$

$$\mathcal{D}_2(c_1 \to 0) = \frac{1{,}051 \cdot 2(\kappa T)^{3/2}}{3\pi\sqrt{\pi m_2}(1-\omega_{22})p\sigma_2^2} \equiv \mathcal{D}_{22} \tag{6}$$

The coefficient of mutual diffusion determined by formula (2) at extreme concentration values intergrades into the trace coefficient of the first gas and the second gas, respectively:

$$\mathcal{D}_{12}(c_1 \to 0) = \mathcal{D}_1(c_1 \to 0) = \mathcal{D}_1^* \tag{7}$$

$$\mathcal{D}_{12}(c_2 \to 0) = \mathcal{D}_2(c_2 \to 0) = \mathcal{D}_2^* \tag{8}$$

The relationship of mutual diffusion coefficients for these extreme cases is:

$$\frac{\mathcal{D}_{12}(c_1 \to 0)}{\mathcal{D}_{12}(c_2 \to 0)} = \frac{\mathcal{D}_1^*}{\mathcal{D}_2^*} \quad \frac{m_2(1-\omega_{21})}{m_1(1-\omega_{12})} \, . \tag{9}$$

We note that when the persistency of velocities is left out of the picture, the relationship (9) equals the ratio of molecular masses, which does not agree with experiment. This fact once served as one of the main reasons for nonacceptance of the Boltzmann diffusion theory (cf., for example, [6-8]] in this respect).

The Chapman-Enskog theory of diffusion gives the following expression for the relationship of trace coefficients of mutual diffusion in the second approximation for the model of solid elastic spheres [6]:

$$\frac{[D_{12}(c_1 \to 0)]_2}{[D_{12}(c_2 \to 0)]_2} = \frac{1 - \dfrac{m_1^2}{13m_1^2 + 30m_2^2 + 16m_1m_2}}{1 - \dfrac{m_2^2}{13m_2^2 + 30m_1^2 + 16m_1m_2}} \tag{10}$$

The concept of trace diffusion coefficient has a quite definite physical meaning in the Boltzmann theory of diffusion. As we can see from formula (1), trace coefficients characterize diffusion under such conditions when collisions of dissimilar molecules play an essential role and when collisions of molecules of the "trace" gas among each other can be neglected, that is, when

$$\frac{1-\omega_{ij}}{1-\omega_{ii}} \cdot \frac{C_j}{C_i}\left(\frac{\sigma_{ij}}{\sigma_i}\right)^2 \sqrt{\frac{m_i+m_j}{2m_j}} >> 1 \tag{11}$$

From relationship (11), it is clear that trace diffusion occurs not only when $C_i \ll C_j$, but also when masses of molecules and their effective diameters at commensurable values of the concentrations of diffusing gases satisfy relationship (11).

Measurement of Trace Diffusion Coefficients by a Steady-State Method

Usually, trace diffusion coefficients are determined by a steady-state method using a double-flask instrument, when its radioactive isotope is added to the gas under study. We used an earlier proposed steady state method of measuring mutual diffusion coefficients [9] for the measurement of trace coefficients. Essentially the method amounts to the following. Let the pure gas 1 move at a specific bulk velocity v through the upper tubing (Figure 1), and traces 2* of the second gas through the lower tubing with the same velocity of gas 1. The tubings are connected by a capillary. A set of identical capillaries is used to increase precision of measurement. Tubing and the capillary set form a diffusion cell. Diffusion will take place in capillaries connecting the tubings. In mutual diffusion of gases the overall flow q_1 of the first gas will equal the overall flow q_2 of the second gas, as has been indicated above.

Before the gases are admitted into the tubings, they are passed through identical halves (only the left, or only the right) of two successively arranged identical interference cells. After diffusion, the gases pass through the other halves of the interference cells. Upon attaining the conditions $q_1 = q_2 = q$, that is, when mutual diffusion occurs, the optical difference of the path of the interferometer rays will equal zero, and the readings of the interferometer compensator cylinder will be zero. Then one of the halves of the cell is swept through with the same gas (or gas mixture) which is present in the other half of the same cell, and an analysis of the gas mixture in the other cell is made in the usual way. From the concentration of the gas following diffusion, the geometric dimensions of the capillary set, the coefficient of mutual diffusion is found from Fick's law

$$D_{12} = \frac{cvL}{S\Delta c} . \qquad (12)$$

In deriving formula (12), it is assumed that linear distribution concentration holds in the cylinder, and the difference in concentrations Δc at the capillary ends is calculated from the known initial and final concentrations with allowance of its variation over the capillaries along the flow.

Equating the flows q_1 and q_2 is achieved by varying the gas pressure in one of the tubings [3].

The bulk velocity of gases v is measured by liquid rheometers. Their relative calibration by means of the interferometer [10] makes it possible to satisfy the condition of equality of v in both tubings with a high degree of precision (0.05 percent).

The apparatus as a whole does not differ from that previously described [3, 9, 11] for measuring true diffusion coefficients. To increase measurement precision, the main assemblies of the apparatus (diffusion cell, rheometers, and interference cells) are thermostated.

Here is some data characterizing the apparatus. The capillary set consists of 930 identical stainless steel tubes, with an overall area of 2.03×10^{-4} m^2 and 7.16×10^{-2} m long. The velocity with which the gases are swept through the tubings is kept constant throughout the experiment to a precision of 0.1 percent and was 0.862×10^{-6} m^3/sec in all the experiments. Special verification of the equality of gas volumes after diffusion was made prior to measurement of trace coefficients. For this purpose, the bulk gas velocities were measured at the outlet from the diffusion cell after a steady-state condition was established with zero reading on the interferometer. Within the limits of experimental error, bulk velocities measured by the displacement method proved to be the same, confirming the equality of the flows q_1 and q_2.

Table 1 presents the results of measuring trace coefficients for four systems of gases at a temperature of 298.2°K. Each value of the trace coefficient is the mean of four to six measurements. The error in determination of trace coefficient was 3-5 percent and was mainly due to error in determination of the absolute value of the velocity with which the gases were swept through the tubings and error in measuring the area of the capillary set. The relationship of coefficients calculated directly from measured values $q = cv$ was determined more precisely (the error was 1-2 percent), since it did not depend on the absolute value of the velocity, b· depends only on the ratio of velocities in the tubings.

The values of the customary mutual diffusion coefficients of systems investigated [12] lie between trace coefficients, as is to be expected.

The measured relationship of trace coefficients for three systems agreed within limits of experimental error with those calculated from the Boltzmann theory. For the third system ($He-O_2$), it proved to be less than is to be expected from formula (9). The relationship of the trace coefficients calculated from the Chapman-Enskog theory for solid elastic spheres was 7-16 percent less than the experimental. This theory gave still smaller relationships for other potentials [6].

Table 1. Trace Diffusion Coefficients at 298.2°K

System	Pure gas	Concentration in mixture, %	$\rho \, 10^{-2}$ n/m²	$D_i^* 10^4$ m²/sec	$D_{12} 10^4$ m²/sec	Relationship of trace coefficients		
						Experiment	Calculated from formulas indicated below	
							(9)	(I0)
He-Ar	Ar	4,94	925,8	0,88	0,788	I,I8	I,20	I,072
	He	94,70	928,2	0,74				
He-CO_2	CO_2	3,98	924,4	0,7I	0,658	I,29	I,32	I,073
	He	97,64	924,I	0,55				
He-O_2	O_2	4,I6	929,3	0,80		I,I6	I,25	I,068
	He	95,72	924,5	0,69				
He-N_2	N_2	5,70	925,0	0,83	0,775	I,26	I,2I	I,066
	He	96,70	928,4	0,66				

Measurement results show that the mutual diffusion coefficient depends on concentration more strongly than was commonly believed [13]. The Boltzmann diffusion theory (taking account of persistence of velocities) better describes extreme values of the mutual diffusion coefficients than does the Chapman-Enskog theory.

We note that Westenberg and coworkers [14] obtained values differing little from those calculated by the Chapman-Enskog theory for the relationship of trace coefficients of the He-N_2 and He-Ar systems. The difference between the data we obtained and the Westenberg data can be accounted for by the fact that the latter used a relative method of measurement, graduating the apparatus beforehand with the He-Ar system, the mutual diffusion coefficient of which was adopted as a standard and did not depend on concentration. When graduating the apparatus, it is necessary to bear in mind that at the point of the concentration field where trace coefficients are measured the numerical value of the standard coefficient must also be a trace coefficient.

Symbols

D_i, D_{ij}, D^*_i and D_{ii} = true, mutual, and trace diffusion coefficient, and self-diffusion coefficient; ω = persistence of velocities; m and σ = mass and effective diameter of molecule; $\sigma_{ij} = (\sigma_i + \sigma_j)/2$; k and n = Boltzmann constant at number of molecules per unit volume; $c_i = n_i/\Sigma n_i$ = relative concentration; T = absolute temperature; p = pressure; L and S = length and overall area of capillary set; q_1 and q_2 = overall flows of first and second gases; v = bulk velocity of gas in diffusion cell tubing.

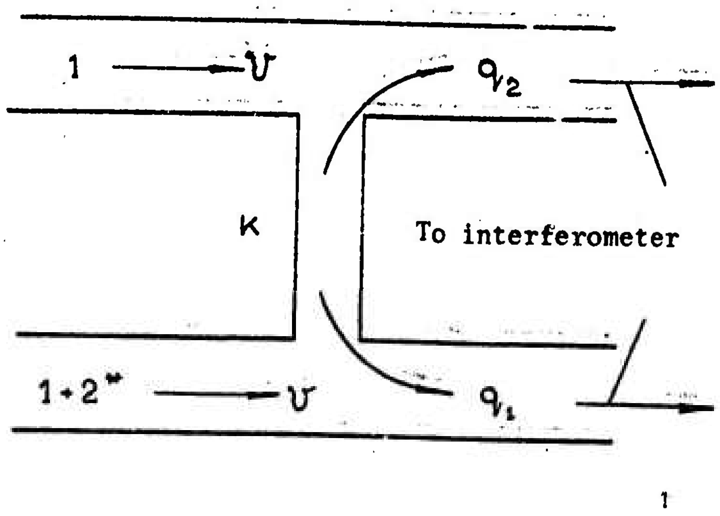

Figure 1. Diagram of diffusion cell

References

1. Waldman, L. and K. H. Schmitt, Naturforschung, Vol. 16 a, 1961.
2. Suyetin, P. Ye. and P. V. Volobuyev, *ZhTF*, Vol. 34, p. 1107, 1964.
3. Kosov, N. D. and L. I. Kurlapov, *ZhTF*, Vol. 35, p. 2120, 1965.
4. Boltzmann, L., *Lektsii po Teorii Gasov, (Lectures on the Theory of Gases)*, GITTL Press, Moscow, 1956.
5. Meyer, O. R., *Die kinetische Theorie der Gase, (The Kinetic Theory of Gases)*, Breslau, 1877.
6. Chapman, S. and T. Cowling, *Matematicheskaya Teoriya Neodnorodnykh Gasov, (Mathematical Theory of Nonhomogeneous Gases)*, IL Press, Moscow, 1960.
7. Jeans, J. H., *The Dynamical Theory of Gases*, 4th ed, New York, 1925.
8. Furry, W. H., *American Journal of Physica*, Vol. 16, p. 63, 1948.
9. Kurlapov, L. I. and N. D. Kosov, *Sb. Trudov i Soiskateley, (Collection of Works of Graduate Students and Degree-Seekers)*, MVSSO Kazakh SSR Press, No. 3, Alma-Ata, 1967.
10. Kurlapov, L. I., *Zavodskaya Laboratoriya*, Vol. 33, p. 121, 1967.
11. Kosov, N. D. and L. I. Kurlapov, *Nekotoryye Voprosy Obshchey i Prikladnoy Fiziki, (Several Problems of General and Spplied Physics)*, Proceedings of the City Conference on Problems of General and Applied Physics, 25-29 October, 1965, Nauka Kaz. SSR Press, Alma-Ata, 1966.
12. Vargaftik, N. B., *Spravochnik po Teplofizicheskim Svoystvam Gasov i Zhidkostey, (Handbook on Thermophysical Properties of Gases and Liquids)*, Fizmatgiz Press, Moscow, 1963.
13. Joshi, R. K., B. P. Mathur and S. C. Saxena, *Molecular Physics*, Vol. 12, p. 249, 1967.
14. Walker, R. E. and A. A. Westenberg, *J. Chem. Phys.*, Vol. 29, p. 1139, 1958; Vol. 29, p. 1147, 1958; Vol. 31, p. 519, 1959.

STUDY OF THE TEMPERATURE DEPENDENCE OF BODY LENGTH FROM CHANGES IN HEAT CAPACITY IN QUANTITIES CHARACTERIZING BODY STRUCTURE

N. N. Medvedev and L. G. Savel'yeva

Precision measurements show that body length is a nonlinear function of temperature. Body length as a function of temperature is usually expressed by the empirical formula:

$$l = l_0(1 + \alpha t + \beta t^2) \qquad (1)$$

We note that a physical quantity determined by the following expression is called the true temperature coefficient of body elongation:

$$\alpha_t = \frac{1}{l_0} \cdot \frac{dl}{dT} \qquad (2)$$

where $t = T - T_0$, $T_0 = 273°K$. Using expression (2) for formula (1), we get

$$\alpha_t = \alpha + 2\beta t \qquad (3)$$

Formula (3) shows that the true temperature coefficient of elongation in contrast to the coefficients α and β is a function of temperature.

The empirical formula (1) can be viewed as an expansion of the unknown function $l = f(T_0 + t)$ in series in powers of t with a restricted number of members of this series.

Expansion of the function $l = f(T_0 + t)$ into a series can be represented as follows:

$$l = l_0\left[1 + \frac{t}{l_0}\left(\frac{dl}{dt}\right)_{t=0} + \frac{t^2}{2!\,l_0}\left(\frac{d^2l}{dt^2}\right)_{t=0} + \frac{t^3}{3!\,l_0}\left(\frac{d^3l}{dt^3}\right)_{t=0} + \cdots\right]$$

or

$$\ell = \ell_0(1 + \alpha t + \beta t^2 + \gamma t^3 + \zeta t^4 + \ldots)$$

where

$$\alpha = \frac{1}{\ell_0}\left(\frac{d\ell}{dt}\right)_{t=0}$$

$$\beta = \frac{1}{2!\,\ell_0}\left(\frac{d^2\ell}{dt^2}\right)_{t=0}$$

$$\gamma = \frac{1}{3!\,\ell_0}\left(\frac{d^3\ell}{dt^3}\right)_{t=0} \qquad (4)$$

Let us find the analytic expression of the function $l = f(T)$. For metal bodies, the energy of interaction of particles in the body is determined [1] by the expression

$$W = -\frac{a}{r} + \frac{b}{r^2} \qquad (5)$$

Equation (5) can be represented graphically (Figure 1).

From the graph (Figure 1) it is clear that when there is a rise in the body temperature, atomic oscillations make a transition to a higher energy level and become increasingly anharmonic, which is expressed by the asymmetry of the curve $W = W(r)$. The mean distance r between oscillating atoms increases nonlinearly with temperature rise, that is, $r = r(T)$ is a nonlinear function of temperature. This is also cause for the nonlinear expansion of bodies on heating.

It is plain from the graph (Figure 1) that to each set value of the function $W = W(r)$ there correspond two real values of the argument r, the arithmetic mean of which $\bar{r} = (r_1 + r_3)/2$ determines the geometric position of points having the coordinates $(W, \bar{r})$, that is, describe the curve $W = W[\bar{r}(T)]$. This fact can be used to find the function $\bar{r} = \bar{r}(T)$, and consequently, the function $l = f(T)$.

The constant b entering into equation (5) can be determined from the condition W = minimum [1]

$$b = \frac{a r^0}{2}$$

r^0 = value of r at T = 0°K. Substituting the value of b found into equation (5), we obtain

$$W = -\frac{a}{r} + \frac{ar^0}{2r^2} \quad (6)$$

On the other hand, a total energy of interaction of atoms in metal determined by formula (6) must be equated to the total internal energy of the body referred to a single atom. This energy can be found if we assume that its change depends not only on change in temperature, but also on change in heat capacity of the body, that is, if we assume that $dW = 1/N \, d(CT)$.

Heat capacity C is viewed as a function of temperature. In this case, it will be:

$$W = \frac{CT}{N} + W_0 \quad (7)$$

where W_0 = integration constant.

Comparing expression (6) and (7) and finding at T = 0°K, the value

$$W_0 = -\frac{a}{2r^0},$$

we get:

$$2\left(\frac{CT}{N} - \frac{a}{2r^0}\right)r^2 + 2ar - ar^0 = 0 \quad (8)$$

Equation (8) is a quadratic in terms of r. Hence, for each value of T there are two roots of this equation r_1 and r_2. The arithmetic mean of these roots determines the mean distance $\bar{r}$ between oscillating atoms, as a function of temperature, that is,

$$\bar{r} = \frac{r_1 + r_2}{2} = \bar{r}(T).$$

Using the properties of roots of a quadratic equation, we find:

$$\bar{r} = \frac{r^{\circ}}{1 - \frac{2r^{\circ}}{Na} CT}.$$

Noting that $\bar{r}/a = l/l_0$ and $r^{\circ}/r_0 \approx 1$, where r_0 = value of r at $T_0 = 273°K$, we get:

$$l = l_0 \frac{1}{1 - \frac{2r_0}{Na} CT} \tag{9}$$

In the general case of a polyvalent metal [1], we can adopt the following expression for the quantity a

$$a = 2Ae^2 z^{5/3}.$$

In this case, we will have

$$l = l_0 \frac{NAe^2 z^{5/3}}{NAe^2 z^{5/3} - r_0 CT} \tag{10}$$

Formula (10) is an analytic expression of the function $l = f(T)$.

Using formula (10) for the mean temperature of the interval $0 < \bar{T} < T$, where $\bar{T} = T/2$, based on the expressions (4) we obtain:

$$\bar{\alpha} = \frac{1}{l_0}\left(\frac{dl}{dT}\right)_{T=2\bar{T}} = \frac{r_0\left(C + 2T\frac{dC}{dT}\right)}{NAe^2 z^{5/3}\left[1 - \frac{2r_0 CT}{NAe^2 z^{5/3}}\right]^2} \tag{11}$$

$$\bar{\beta} = \frac{1}{2l_0}\left(\frac{d^2 l}{dT^2}\right)_{T=2\bar{T}} = \frac{NAe^2 z^{5/3} r_0\left[r_0\left(C + 2\bar{T}\frac{dC}{d\bar{T}}\right)^2 + \left(NAe^2 z^{5/3} - 2r_0 C\bar{T}\right)\frac{dC}{d\bar{T}}\right]}{\left(NAe^2 z^{5/3} - 2r_0 C\bar{T}\right)^3} \tag{12}$$

In obtaining formula (12) it was assumed that dC/dT = const. Formulas (11) and (12) show that the coefficients α and β depend on quantities characterizing the structure of the metal and its heat capacity.

Hence it follows that we can refer to constancy of the coefficients α and β in the empirical formula (1) only within the limits of preservation of a given type of structure, that is, in the absence of phase transitions. With a precision quite adequate for calculating the coefficients α and β when $\overline{T} = T_o$, formulas (11) and (12) can be represented in the following more convenient form

$$\alpha = \frac{r_0(C_0 + 2T_0 \frac{dC}{dT}}{NAe^2 z^{5/3}} \qquad (13)$$

$$\beta = \frac{r_0}{NAe^2 z^{5/3}} \frac{dC}{dT} + \alpha^2 \qquad (14)$$

Thus, the values of the coefficients α and β, and consequently, also the value of the true temperature coefficient $\alpha_t = \alpha + 2\beta t$ can be calculated theoretically for different metals and their alloys from known quantities characterizing their structure and heat capacity.

For most metals the value of the Madelung constant can be taken as equal to A = 1.75.

The value of the interatomic distance r_o can be found for various metals in handbooks [3, 5], and can be determined by X-ray structural methods of analysis or alloys.

The value of the heat capacity C and its change dC/dT can be calculated for a given metal from the known Debye characteristic temperature θ, using here the tables in [2] for $C = f(\theta/T)$.

If the Debye temperature is not known, for example, for alloys, it can be determined from the experimentally known value of the heat capacity and then dC/dT can be calculated. The values of the quantities N, e and z are generally accepted. If the valency is not known, it as an integral number always can be determined from the value of the coefficient of linear expansion [elongation] α that is known in approximate terms.

Table 1 presents the calculation of the coefficients α, β and α_t for different metals and gives a comparison of theoretical and experimental values of their coefficients of linear expansion. The distance r_o between nearest neighbors for the metals with a body centered cubic lattice has been calculated from the formula $r_o = \sqrt{3}a/2$ (where a = lattice parameter), and for metals with a hexagonal lattice $r_o = a$. For the series of metals that have a face-centered cubic lattice, the distance r_o was calculated from the formula $r_o = a/\sqrt{2}$, and for the series of metal with face-centered and rhombohedric cubic lattice (Ni, Bi, As, Al, Cu, Ag and Pb) the distance was calculated from the formula $r_o = \alpha\sqrt{2}$, that is, the distance is taken between corresponding oscillators [6].

The temperature coefficients of linear expansion were theoretically calculated for several metal alloys using the formulas derived. Table 2 presents a comparison of temperature coefficients of linear expansion [elongation] calculated by formulas (13), (14) and (3), and experimentally obtained for brass and steel. Interatomic distances for these alloys were determined by the Debye method on the URS-50 IM unit.

Word Symbols

l and l_o = body length at temperature t and t_o = 0°C, respectively; α and β = several coefficients constant for a given body; α_t = true temperature coefficient of linear expansion; T = absolute temperature; W = total energy of interaction per single atom; a and b = several constant quantities entering into the formula $W = f(r)$; r^o = value of r at T = 0°K; N = Avogadro's number; C = molar heat capacity; r_o = the value of r at T = 273°K; A = Madelung constant; e = electron charge; z = valency of metal; θ = characteristic temperature.

Table 1. Comparison of Theoretically Calculated and Experimentally Determined Coefficients of Linear Expansion [Elongation]

Element	$r_0 \cdot 10^{10}$, M	z	$C \cdot 10^{-4}$, $\frac{\text{J}}{\text{kg-atom}\cdot\text{deg}}$	$\frac{\Delta C}{\Delta T} \cdot 10^{-3}$, $(\frac{\text{J}}{\text{kg-atom}\cdot\text{deg}})$ Deg^{-1}	$\alpha \cdot 10^{6}$, Deg^{-1}	$\beta \cdot 10^{6}$, Deg^{-2}	$\alpha_t \cdot 10^{6}$, Deg^{-1}		t, °C
							Theoretical	Experimental	
I	2	3	4	5	6	7	8	9	IO
Lithium	3,04	I	22,8	0,033	52,2	0,043	54,3	56,0	25
Sodium	3,7I	I	26,9	0,035	69,9	0,053	72,6	72,I	25
Potassium	4,62	I	28,3	0,023	83,I	0,043	85,2	83,3	25
Rubidium	4,92	I	29,4	0,025	85,0	0,05I	87,5	90,0	25
Cesium	5,36	I	26,8	0,030	94,9	0,070	98,4	98,0	25
Thallium	3,45	I	24,8	0,00I	35,8	0,00I	35,9	33,6	50
Copper	5,05	2	24,3	0,004	I7,5	0,002	I7,7	I7,0	50
Silver	5,7I	2	24,2	0,004	I9,3	0,003	I9,6	I9,0	50
Gold	2,83	2	25,2	0,0I2	I2,I	0,005	I2,6	I4,2	50
Beryllium	2,87	2	I8,2	0,030	I0,3	0,009	I3,I	I3,0	I00
Magnesium	3,20	2	24,6	0,035	I9,3	0,0I6	22,5	25,0	I00
Calcium	3,93	2	24,3	0,0I2	I6,6	0,007	I8,7	22,0	I50
Strontium	4,30	2	27,2	0,005	I7,0	0,003	I7,6	20,0	I00
Zinc	7,50	2	2I,9	0,006	24,9	0,007	25,6	27,0	50
Aluminum	5,73	2	25,I	0,009	22,9	0,009	23,8	24,6	50
Indium	6,92	2	26,0	0,020	33,2	0,0I8	35,0	33,0	50
Tin	6,49	2	24,2	0,004	22,5	0,0I2	23,7	23,0	50
Lead	7,00	2	26,5	0,0II	29,7	0,0I0	30,7	29,4	50
Vanadium	2,62	2	23,8	0,003	9,6	0,002	I0,3	9,3	I50
Iron	2,48	2	2I,8	0,0I8	I0,3	0,006	I0,6	II,7	25
Cobalt	2,5I	2	26,2	0,020	I2,3	0,007	I3,0	I3,4	50
Nickel	4,90	2	25,8	0,0I5	II,0	0,005	II,5	I3,3	50
Palladium	2,75	2	26,I	0,005	I0,4	0,003	I0,5	II,7	25
Platinum	2,77	2	24,I	0,006	9,3	0,002	9,4	8,9	25
Bismuth	6,70	3	25,6	0,002	II,8	0,00I	II,9	I3,4	50
Chromium	2,49	3	23,9	0,0I5	5,4	0,003	5,7	6,2	I00
Molybdenum	2,72	3	22,I	0,008	4,8	0,002	5,0	5,8	50
Radium	5,32	3	25,4	0,0I0	I0,I	0,004	I0,5	8,5	50
Iridium	2,7I	3	25,I	0,0I6	6,03	0,003	6,3	6,5	I50
Cerium	3,64	3	26,7	0,003	6,3	0,00I	6,9	7,I	50
Zirconium	3,I2	4	25,2	0 003	5,60	0,00I	5,7	5,4	50
Germanium	4,00	4	22,8	0,004	4,92	0,003	5,8	6,I	I50
Tungsten	6,70	4	23,6	0,0I0	3,46	0,002	3,9	4,4	I50
Arsenic	5,77	5	24,0	0,04I	4,5	0,005	5,I	5,6	I50

Table 2. Comparison of Theoretically Calculated and Experimentally Determined Coefficients of Linear Expansion [Elongation] for Alloys

Material	$\alpha_t \cdot 10^6$, deg^{-1} Theoretical	$\alpha_t \cdot 10^6$, deg^{-1} Experimentel	$\bar{t}$, °C
Brass	I8,I	I8,4	50
Steel	II,7	I2,0	50

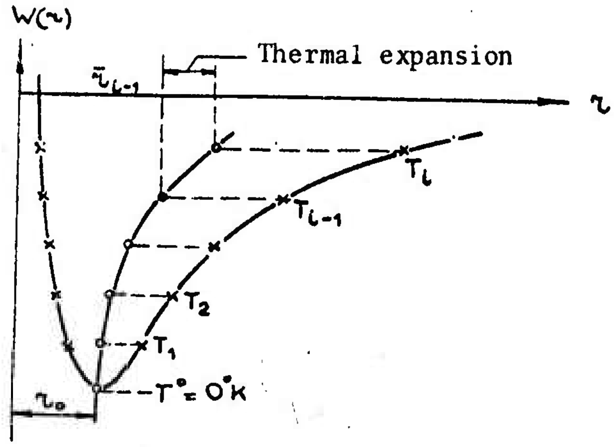

Figure 1. Graphic representation of the energy of interaction of particles in a body

References

1. Frenkel', Ya. I., *Vvedeniye v Teoriyu Metallov, (Introduction to the Theory of Metals)*, Gittl Press, Moscow, 1950.

2. Roberts, Dzh. *Teplota i Termodinamika, (Heat and Thermodynamics)*, Gittl Press, Moscow, 1950.

3. *Fizicheskiy Entsiklopedicheskiy Slovar', (Physics Encyclopedia Dictionary)*, Vol. 1-Vol. V, 1962-1965.

4. Zhdanov, G. S., *Fizika Tverdogo Tela, (Solid State Physics)*, Gittl Press, Moscow, 1962.

5. Kittel', Ch., *Vvedeniye v Fiziku Tverdogo Tela, (Introduction to Solid State Physics)*, Gittl Press, Moscow, 1957.

6. Kittel', Ch., *Elementarnaya Fizika Tverdogo Tela, (Elementary Solid State Physics)*, 1965.

THERMAL CONDUCTIVITY AND VISCOSITY OF A COMPRESSED LIQUID

R. S. Prasolov

In calculating various processes and in designing apparatus we must have data on the thermophysical properties of a liquid at pressures up to ~ 12,000 atm (~ 10^9 n/m^2). However, the unique experimental data of Bridgmen [1] are not very numerous, and well known methods of calculating thermal conductivity and viscosity of a liquid for these conditions, as shown in [2-5], are applicable only for pressures up to ~ 2000 atm ($2 \cdot 10^8$ n/m^2).

Using the concepts of the molecular-kinetic theory, we made a calculation estimate of λ and η of a homogeneous liquid at ultrahigh pressures. In the analysis, we introduced the following main assumptions, which are fairly well justified [2-6];

-- elastic smooth spheres (spherical intermolecular potentials of interaction) are the model concept of the molecules;

-- gradients of temperature and velocities in the liquid are small;

-- the velocity of all molecules is identical and is determined by the Maxwell distribution.

Essentially, the analysis consists in the fact that the transition to the liquid state is attained gradually from the model of ideal gases through the model of compressed (real) gases to the analogous model for liquid. Further, on analogy with the concepts of Enskog, but by an essentially different method, corrections are introduced into the transport by collisions (the greater rate of propagation of perturbations through the molecules themselves is taken into account). Moreover, corrections are introduced in the multiple interactions of particles, that is, consideration is given to the fact that in addition to binary, the interactions are ternary and quaternary, when three and four molecules collide simultaneously.

At first we explain how the classic relationship of the mean free path of molecules will change if we consider multiple particle interactions.

The number of binary collisions Z_2 by a single particle in the gas is determined by the following function [7]

$$Z_2 = \sqrt{2}\,\pi\sigma^2 nc \qquad (1)$$

and the total number of binary collisions S_2 of moving particles

$$S_2 = \frac{nZ_2}{2} \qquad (2)$$

since each interaction embraces two particles (and two mean free p Λ_0) in one second n molecules traverse $2Z_2$ mean free paths, which are confined into the segments nc equal to the overall path of n molecules in one second. From this follows the well known gas-kinetic relationship for an ideal gas

$$\Lambda_0 = \frac{nc}{2S_2} = \frac{nc}{nZ_2} = \frac{1}{\sqrt{2}\,\pi\sigma^2 n} \qquad (3)$$

where the multiplier $\sqrt{2}$ appears as a result of taking cognizance of molecular distribution by directions (including noncentral collisions) [6, 7].

We used the very same method of reasoning in taking account of multiple collisions. In addition to the cross section of binary collisions $F_2 = \pi\sigma^2$, we introduce the cross sections of ternary F_3 and quaternary F_4 collisions. Then the number of ternary and quaternary interactions of a single particle must be written in the form

$$Z_3 = \sqrt{2}\cdot F_3\cdot nc, \qquad Z_4 = \sqrt{2}\cdot F_4\cdot nc \qquad (4)$$

The total number of ternary and quaternary collisions, if we take into account the fact that each of them embraces three and four particles, respectively, amounts to

$$S_3 = \frac{n z_3}{3}, \quad S_4 = \frac{n z_4}{4} \tag{5}$$

As a result, we get the following relationship for the mean free path traversed by molecules with account taken of binary, ternary and quaternary collisions

$$\Lambda = \frac{nc}{2S_2 + 3S_3 + 4S_4} = \frac{nc}{n(z_2 + z_3 + z_4)} = \frac{1}{\sqrt{2}n(\pi\sigma^2 + F_3 + F_4} \tag{6}$$

in which the cross sections $\pi\sigma^2$, F_3 and F_4 are summed up. Determination of the relationship with the quantities F_3 and F_4 with the gas-kinetic diameter σ is the task of further calculation.

Quantum mechanical considerations indicate that in the general case wave fields (fields of interaction) are larger than molecular dimensions [5]. In particular, covalent radii proportional to the smallest distance between bound particles are smaller than the van der Waals radii of interaction (Lennard-Jones) [6]. Therefore it can be assumed that the transport cross sections associated with interaction potentials overlap in dense media (Figure 1, a). An impinging particle indicated in the figure by a point can fall in the zone of field overlapping and this will correspond to ternary interaction.

To find the doubled area of segments (overlapping zone) proportional to the cross section F_3, we find the distance l averaged over time between centers of oscillating neighboring particles of the liquid. For short-range order, particles in a liquid (a strongly compressed gas) lie in a tetrahedral three-dimensional pattern. The volume of the elementary equilateral tetrahedron can be found from the formula

$$v = \frac{\sqrt{2}}{12} l^3 \tag{7}$$

Summing up the volumes of these elementary tetrahedra, we can obtain the entire volume of the liquid, and consequently, express the elementary volume by the molar volume V and Avogadro's number, taking into account that 1/6 of a molecule is assigned to such a tetrahedron. Based on the foregoing we get

$$l = \sqrt[6]{2} \cdot \sqrt{\frac{V}{N}} \tag{8}$$

The area of the doubled segment when α < 50° is estimated in approximate terms by the well known formula, which when we take into account the association between a, h, σ and l, leads to the form

$$f_3 = \frac{4}{3} ah = \frac{8}{3} \sqrt{\left(\sigma - \frac{l}{2}\right)^2 \left(\sigma + \frac{l}{2}\right)} \tag{9}$$

Several particles surround each particle for which the collision cross section is considered. Figure 1, d shows the pattern of the tetrahedral structure, from which it is clear that, for example, in the plane of the figure the particle under study (dash line) is surrounded by six others. In the plane passing through the dash line and two upper (cross-hatched) particles there are four spheres, etc. Therefore, in an approximate fashion we assume that on an average five segmental cross sections of ternary collisions fit into the collision cross section of the molecule under consideration, if we consider the plane of collision cross sections averaged over directions.

As a result, for the total cross section F_3 we get the formula

$$F_3 \cong 13.3 \sqrt{\left(\sigma - \frac{l}{2}\right)^3 \left(\sigma + \frac{l}{2}\right)} \tag{10}$$

In a similar way, we can also estimate the cross section of quaternary interactions (Figure 1, b) which is proportional to the area of the curvilinear triangle. We replace this triangle, in approximate fashion, by the circumference described in it having the radius

$$R = \sigma - \frac{l}{2 \cdot \cos 30^\circ} \tag{11}$$

and then F_4 is estimated from the function

$$F_4 \cong 5\pi(\sigma - 0{,}65\,\ell)^2 \tag{12}$$

Hence, taking account of ternary and quaternary interactions leads to the following correctional multiplier in the kinetic formula (3)

$$\nu = \left[1 + \frac{13{,}3}{\pi\sigma^2}\sqrt{\left(\sigma - \frac{\ell}{2}\right)^3\left(\sigma + \frac{\ell}{2}\right)} + \frac{5}{\sigma^2}\left(\sigma - 0{,}65\ell\right)^2\right]^{-1} \tag{13}$$

We now pass on directly to calculation of thermal conductivity of liquids. For this we use the customary gas-kinetic model schematically represented in Figure 1c, and to a line of thought similar to that given in [9], but containing a number of refinements compared with [9].

The following energy flux is transported through an area with temperature T (flat internal problem)

$$q = \frac{A}{6}\,n\,W\,\frac{i}{2}\,k\left[\left(T + \frac{dT}{dx}x\right) - \left(T - \frac{dT}{dx}\right)\right] \tag{14}$$

The quantity of the transport rate with cognizance taken of transport by collisions (through the molecules themselves) can be represented in the following form [9]

$$W = \frac{\Lambda + \sigma\cos\varphi}{\frac{\Lambda}{C} + \frac{\sigma\cos\varphi}{C_M}} = C\left(1 + \frac{\sigma}{\Lambda}\cos\varphi\right) \tag{15}$$

if we take into account that $C \ll C_M$ [4, 5]. It is clear from Figure 1c, that

$$x = \Lambda + \sigma\cos\varphi = \Lambda\left(1 + \frac{\sigma}{\Lambda}\cos\varphi\right) \tag{16}$$

and therefore thermal conductivity caused by collisions at an angle φ

from zero to $\pi/2$ amounts to the following, with consideration of (14)-(16)

$$\lambda = \frac{A}{3} n \dot{W} x \frac{i}{2} \kappa = \lambda_o \left(1 + \frac{\sigma}{\Lambda} \cos\varphi\right)^2 \tag{17}$$

Molecules can collide at any angle ϕ, and further the probability of collisions at angles in the range from ϕ to $\phi + d\phi$ is written in the form [9]

$$p = \sin 2\varphi \cdot d\varphi \tag{18}$$

Thus, the correctional multiplier in formula (17) averaged over angles turns out to be expressed as

$$\xi = \int_0^{\pi/2} \left(1 + \frac{\sigma}{\Lambda} \cos\varphi\right)^2 \sin 2\varphi \, d\varphi = 1 + \frac{4}{3} \frac{\sigma}{\Lambda} + \frac{1}{2} \left(\frac{\sigma}{\Lambda}\right)^2 \tag{19}$$

Based on the formulas (16)-(19), assuming $A \neq (p)$, we get the following function for the thermal conductivity of a compressed liquid

$$\lambda = \lambda_o \left[1 + \frac{4\sigma}{3\Lambda_o \nu} + \frac{1}{2} \left(\frac{\sigma}{\Lambda_o \nu}\right)^2\right] \tag{20}$$

in which the parameter σ/Λ_o can be replaced by the relationship [9]

$$\frac{\sigma}{\Lambda_o} = \sigma \cdot \sqrt{2} \pi n \sigma^2 = \frac{\sqrt{2} \pi N \sigma^3}{V} = \beta \frac{\sigma^3}{V} \tag{21}$$

For convenience in discussing the results obtained and in making quantitative calculations, we make explicit the significance of the main variables in formula (20) by using the expressions (8), (13) and (19),

$$\frac{\lambda}{\lambda_o}=1+\frac{4}{3}\frac{\beta\sigma^3}{V}\Bigg[1+\frac{4{,}23}{\sigma^2}\sqrt{\left(\sigma-0{,}57\sqrt[3]{\frac{V}{N}}\right)^3\left(\sigma+0{,}57\sqrt[3]{\frac{V}{N}}\right)}+$$

$$+\frac{5}{\sigma^2}\left(\sigma-0{,}65\sqrt{\frac{V}{N}}\right)^2\Bigg]+\frac{1}{2}\left(\frac{\beta\sigma^3}{V}\right)^2\Bigg[1+ \qquad (22)$$

$$+\frac{4{,}23}{\sigma^2}\sqrt{\left(\sigma-0{,}57\sqrt[3]{\frac{V}{N}}\right)^3\left(\sigma+0{,}57\sqrt[3]{\frac{V}{N}}\right)}+\frac{5}{\sigma^2}\left(\sigma-0{,}65\sqrt[3]{\frac{V}{N}}\right)^2\Bigg]^2$$

It is clear from function (22) that the thermal conductivity as a function of pressure is not difficult to calculate if we know the relationship between the molar volume and the pressure, since $\sigma \neq f(p)$ and $\lambda_o \neq f(p)$ is on the thermal conductivity isotherm.

Generally speaking, the quantities V, λ_o and σ can be estimated in approximate terms by various methods of calculation [2-6], which however can give sizeable errors. Therefore, for quantitative verification of formula (22), we use experimental data for $V = f(p)$, and we find the quantity σ from two support experimental points -- λ_o and λ_1, corresponding to the thermal conductivity of an ideal gas ($p < p$) [sic] and the thermal conductivity of the liquid (at atmospheric pressure p_1). We make all calculations for the thermal conductivity isotherms.

Analysis of Bridgmen's experimental results [1] and recent generalizations of experimentation [10] shows that in verifying formula (22) unfortunately the available necessary data are extremely limited and embrace only alcohols, pentane and water. It is precisely for these compounds that experimental support points λ_o and λ_1 and the function $V = f(p)$ do exist.

Figure 2a, shows experimental points for methanol, pentane and water, the vertical dashes in which correspond to experimental error [1]. Here however the lines 1-3 indicate the corresponding calculated isotherms obtained from formula (22). Values of σ for the calculated curves were found by graphic solution from (22) based on experimental data for λ_0, λ_1 and V_1 [1, 10].

A comparison of experimental and calculated data makes is clear that the deviation between them lies within the limits of error of experimental determination of thermal conductivity, that is, is about 3-4 percent.

So satisfactory an agreement between calculation and experiment for the region of ultrahigh pressures where the thermal conductivity of liquid consisting of complex multiatomic molecules is under consideration is unexpected, since the basis of analysis was taken to be the simple model of spherically symmetric particles. A similar result was noted also in [6] where, for example, the following is related: although this is hard to prove and appears strange, the spherically symmetrical model leads to good results in analysis of viscosity and of the second virial coefficient of compressed gases, even for such complex molecules as benzene, alcohol and hexane.

Taking the result obtained for thermal conductivity into account, let us try to calculate also the viscosity of a compressed liquid based on similar considerations.

It is well known [2-8] that mechanisms of thermal conductivity and of viscosity in a liquid, in spite of some common ground they share, do have key differences. This, for example, is evident from a comparison of Figure 2a and Figure 2b, where, under otherwise equal conditions, an incomparably greater effect of pressure on viscosity compared to that on thermal conductivity is noticeable. Therefore, use of the ideas advanced above requires some additional correction when we analyze viscosity.

In elucidating the differences between λ and η noted, it is convenient to represent viscosity in the kinetic form similar to relationship (17)

$$\eta = 0{,}499\, n m W x \tag{23}$$

and first analyzed in [9].

In heat transport, all n molecules participate in transport of energy via thermal movement of particles, that is, their micromovement. Viscosity in fact combines both micromovement as well as macromovement of neighboring layers of liquid with ordered velocities C*. The transport of macrovelocity C* from one layer to another will be possible if the particle is able to overcome the intermolecular potential of attraction in the layer where it is initially present.

In determining the fraction of particles which can pass from one layer to another, we assume that thermal distribution of velocities is governed by the Maxwell distribution, and $C \gg C^*$. We estimate in approximate terms the intermolecular potential of attraction from the component of the Lennard-Jones potential or the Stockmeyer potential for two particles [4, 6], neglecting the components of repulsion and dipole interaction

$$U \approx -4\varepsilon\left(\frac{r_0}{l}\right)^6 \qquad (24)$$

In reality, the particle under consideration lies in the potential field of many of its surrounding neighboring particles. But, given the symmetric arrangement of particles in the structure of the short-order range within the bulk of the liquid, the passage of the particle under consideration into the "vacancy" of the neighboring layer can be simply viewed as a one-dimensional passage relative to the two mutually colliding molecules. The effect of the other particles, whose interaction potentials with the molecule under consideration are uniformly distributed over directions, is mutually compensated.

Of the total number of n molecules the potential of attraction can be overcome by those particles whose kinetic (thermal) energy E exceeds U, $E > U$. The number of such particles n_U can be found from the Maxwellian distribution over energies [8]

$$n_u \approx n\frac{2}{\sqrt{\pi}}\int_{\frac{U}{kT}}^{\infty} \exp\left(-\frac{U}{kT}\right)\sqrt{\frac{U}{kT}}\cdot d\left(\frac{U}{kT}\right) \qquad (25)$$

Calculation of the quantities l, U and kT relevantly for the Bridgmen experimental data [1] for η and V using the corresponding constants r_o and ε for the interaction potentials in [2-4, 6] show that $U \approx kT$, and therefore the integral (25), with account taken of formulas (8) and (24), leads to the form [8]

$$n_U \approx n \cdot \exp\left(-\frac{U}{kT}\right) \approx n \cdot \exp\Bigl[-\left(-\frac{4\varepsilon r_0^6 N^2}{2kTV^2}\right) \sim \exp\left(\frac{2\varepsilon r_0^6 N^2}{kTV^2}\right) \tag{26}$$

Consequently, the formula for the viscosity of a compressed liquid in contrast to the function for thermal conductivity contains an additional correctional comultiplier in the form of the exponential (26).

These considerations, if an attempt is made to describe viscosity based on formulas (23) and the relationships (15), (16) and (26), leads to the equation

$$\frac{\eta}{\eta_0} = \exp\left(\frac{2\varepsilon r_0^6 N^2}{k} \cdot \frac{1}{TV^2}\right) \cdot \left[1 + \frac{4}{3}\frac{\sigma}{\Lambda_0 \nu} + \frac{1}{2}\left(\frac{\sigma}{\Lambda_0 \nu}\right)^2\right] \tag{27}$$

Quantitative verification of the latter function was made on the basis of the viscosity isotherms for water, methanol and n-pentane, similar to the already considered viscosity isotherms for the same compounds. This selection of experimental data [1] for verification of formula (27) stemmed from an effort to compare values of σ obtained from experiments on viscosity and thermal conductivity. As in the calculation of thermal conductivity, the value of σ was found from the support points η_0, η_1 and V_1. For methanol and n-pentane, the constants r_0 and ε were taken from the data for the Lennard-Jones potential, and for water -- from the Stockmeyer potential [2-4, 6].

Results of comparing calculated curves and experimental data are shown in Figure 2b. Analysis of this figure leads to the conclusion that in this case as well, also beyond expectation, the deviation of calculation curves relative to experimental points is close to the experimental error (about 8-10 percent) and can be random in nature (not systematic).

In the table below a comparison is made of the diameters of interaction of ideal gas molecules found by the method set forth here for thermal conductivity and the viscosity of a compressed liquid. These values were compared with values of σ^* (in Angstroms) which are found from the

Lennard-Jones potential (methanol and n-pentane) and the Stockmeyer potential (water), if we equate the repulsion branch of the indicated potentials with the kinetic energy of the molecules.

Table

Compound	$\sigma(\lambda)$	$\sigma(\eta)$	σ^*
Methanol	3,14	3,06	3,41
N-pantane	4,08	3,84	5,60
Water	2,65	2,44	2,70

From fundamental considerations [5, 11], numerical values of the collision diameters for various processes must have small systematic differences, which is also confirmed by the table given above.

In conclusion we note that qualitative verification of formulas of the form (20) and (27) when various transformations are used with precision up to numerical coefficients makes possible derivation of a series of well known theoretical and empirical functions found earlier by Predvoditelev, Vargaftik, Osid, Rama Rao, **Bridgmen,** Bachinskiy and Stolyrov. In the future **statistical** treatment of calculated errors which need to be found by comparison with all known experimental data for λ and η for liquids at ultrahigh pressures is necessary.

Symbols

p, V and T = pressure, molar volume and absolute temperature; p_1 and t = normal pressure (1 atm, 10^5 n/m^2) and temperature (°C); λ and η = thermal conductivity and viscosity of gas at p; λ_1 and η_1 = as above, for p_1; λ_o and η_o = as above, in the ideal-gas state $p_o \ll p_1$; k and N = Boltzmann constant and Avogadro's number; U and E = potential of intermolecular interaction and thermal energy of molecules; r_o and ε = constants of the interaction potential; m, c, Λ, σ and n = mass, mean arithmetic velocity of thermal movement, mean free path, gas-kinetic diameter, and number of particles per unit volume; i and A = number of degrees of molecular freedom and correctional multiplier (when i = 3, A ≈ 2.5, when i = 5, A ≈ 1.9, and when i = 6, A ≈ 1.7); x = mean distance between center of molecule and plane through which transport is considered; l = distance between molecules of the liquid averaged over time and space; v = volume of elementary tetrahedral cell; Z_2, Z_3, and Z_4 = number of collisions for a single particle per unit time for binary, ternary and quaternary interactions; S_2, S_3, S_4 are the total number of collisions per unit time with binary, ternary and quaternary interactions; F_2, F_3 and F_4 = cross sectiors of binary, ternary and quaternary interaction; f = function taking into account multiple interaction; ϕ = angle between direction of movement and line of centers of colliding particles; P = probability of interaction at angle ϕ; c_M and C* = rate of transport by collisions (through molecules) and relative velocity of neighboring layers of liquid; n* = number of molecules whose thermal energy exceeds the potential of intermolecular interaction; q = specific thermal flux; Λ_0 = mean free path of particles in the ideal-gas state; σ^* = diameter of particles found from E and U.

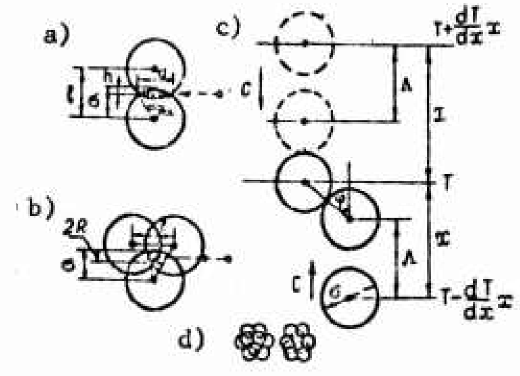

Figure 1. Calculated diagrams used in taking account of multiple collisions and transport by collisions: a, Overlapping of interaction fields having radius σ in ternary interactions; b, As above, for quaternary interactions; c, Diagram of transport for spherical molecules of diameter σ; d, Diagram for estimating the coordination number of molecules in a plane averaged over directions.

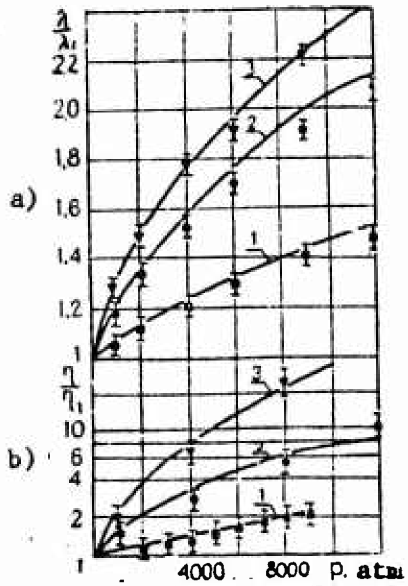

Figure 2. Isotherms of relative thermal conductivity (a) and viscosity (b) of a compressed liquid: 1, Water, t = 75°C; 2, Methanol, t = 30°C; 3, n-pentane, t = 30°C.

References

1. Bridgmen, P. V., *Fizika Vysokikh Davleniy, (High Pressure Physics)*, ONTI Press, 1935.

2. Reid, R. and T. Sherwood, *Svoystva Gasov i Zhidkostey, (Properties of Gases and Liquids)*, Gostoptekhizdat Press, Moscow, 1964.

3. Bretshnayder, S., *Svoystva Gasov i Zhidkostey, (Properties of Gases and Liquids)*, Khimiya Press, Moscow, 1966.

4. Hirschfelder, J. Curtis, C.; Byrd, R. , *Molekulyarnaya Teoriya i Zhidkostey, (Molecular Theory of Gases and Liquids)*, IL Press, Moscow, 1961.

5. Chapman, S. and T. Cowling, *Matematicheskaya Teoriya Neodnorodnykh Gazov, (Mathematical Theory of Nonhomogeneous Gases)*, IL Press, Moscow, 1960.

6. Ch'ien Hsueh-sen, *Fizicheskaya Mekhanika, (Physical Mechanics)*, Mir Press, Moscow, 1965.

7. Geyntse, V., *Vvedeniye v Vakuumnuyu Tekhniku, (Introduction to Vacuum Techniques)*, Gosenergoizdat Press, Moscow, 1960.

8. Telesnin, R. V., *Molekulyarnaya Fizika, (Molecular Physics)*, Vysshaya Shkola Press, Moscow, 1965.

9. Prasolov, R. S., *Masso- i Teploperenos v Topochnykh Ustroystvakh, (Mass and Heat Transfer in Furnace Installations)*, Energiya Press, Moscow-Lenigrad, 1964.

10. Vargaftik, N. B., *Spravochnik po Teplofizicheskim Svoystvam Gasov i Zhidkostey, (Handbook on Thermophysical Properties of Gases and Liquids)*, Fismatgiz Press, Moscow, 1963.

11. Kogan, M. N., *Dinamika Razrezhennogo Gaza, (Dynamics of Rarefied Gases)*, Nauka Press, Moscow, 1967.

CALCULATION OF POTENTIAL PARAMETERS OF INTERACTION FROM EXPERIMENTAL DATA ON VISCOSITY AND COMPRESSIBILITY OF GASES

P. Ye. Suyetin, B. A. Ivakin and B. A. Kalinin

In solving many physical and technological gas kinetics problems, we need to have reliable information on kinetic coefficients governing the rate of change of any particular macroscopic parameters with time. The fullest and most reliable information has been secured experimentally for the viscosity coefficients of gases. The enormous range of application of these coefficients and the relative simplicity of experimental arrangement helped bring about this state of affairs.

Less reliable data, and in a narrower range of change of experimental parameters were obtained for coefficients of thermal conductivity, diffusion and thermal diffusion both by virtue of experimental complexity, and also owing to stubborn side effects complicating treatment of experimental results.

The lack of information on these kinetic coefficients can be made up for by certain empirical formulas that fairly well describe available experimental data. However, reliability of extrapolation of these formulas has always remained doubtful.

To solve this problem use of formulas of rigorous theory [1] is more warranted from the physical point of view.

Kinetic theory allows us to calculate all kinetic coefficients if we know the potentials of interaction between gas molecules. At present, calculations of kinetic coefficients based on these formulas does not present any problem, since most laborious calculations have been tabulated for different potential models and are given in [2].

The common ground of the approach to calculating kinetic coefficients that is afforded us by kinetic theory is preferable also in the respect that it allows us to calculate some coefficients if we have experimental data for others. Additionally, when we have potential parameters calculated from kinetic properties of a compound, we can calculate the equilibrium properties of a gas, and vice versa. The potential parameters obtained also allow us to estimate critical properties of the compound and properties of crystals at low temperatures. Thusly, potential parameters allow us not only to calculate kinetic coefficients, but also to determine a great many physical properties of a compound.

However, for practical purposes we need to have quantitative estimates of the applicability of kinetic formulas in calculating particular properties.

The aim of this study is quantitative estimation of the applicability of potential parameters derived from viscosity and compressibility of gases in calculating other kinetic properties of gases.

We must select the potential model of interaction among gas particles to determine parameters. At the present time the two-parametric Lennard-Jones (6-12) model is fairly well physically validated and is the most often used. Three-parametric models greatly complicating calculations are little refined in practical terms owing to the great indeterminacy in calculation of parameters.

A large number of different parameters of the (6-12) model calculated by different methods for different ranges of change in experimental parameters is set forth in [2]. We must state that existing methods (the method of intersections, the method of relationships, etc.) are not well enough validated, which introduces elements of arbitrariness into calculations of parameters.

Apparently, the two-parametric least-squares model with preliminary analytical graph treatment of experimental data, precluding their random scatter, is the most valid procedure in calculating the parameters of the model (6-12).

Let us look at this model by the example of calculation of parameters from experimental data on viscosity of pure gases as a function of temperature.

The viscosity coefficient in the first approximation is calculated from the formula in [2]:

$$\eta \cdot 10^7 = 266{,}93 \frac{\sqrt{MT}}{\sigma^2 \Omega^{(2,2)}(T^*)} \cdot \tag{1}$$

We bring [1] into linear form with respect to σ^2 and ε/k. Further, we will assume that we know σ_0^2 and $(\varepsilon/k)_0$ from other sources (for example, from equilibrium or critical properties of the gas):

$$\eta = \eta_0 + x\left(\frac{\partial \eta}{\partial \sigma^2}\right)_0 + y\left(\frac{\partial \eta}{\partial (\varepsilon/\kappa)}\right)_0 , \tag{2}$$

where x and y = small corrections to σ_0^2 and $(\varepsilon/k)_0$. Substituting (1) in (2), we get:

$$\eta = \eta_0 - x\frac{\eta_0}{\sigma_0^2} + y\frac{\eta_0}{(\varepsilon/\kappa)_0}\frac{d\ln\Omega^{(2,2)}}{d\ln T^*} . \tag{3}$$

Using the recurrent formula (2), we have:

$$\frac{d\ln\Omega^{(2,2)}}{d\ln T^*} \approx -4\left(1-\frac{\Omega^{(2,3)}}{\Omega^{(2,2)}}\right) \approx -\alpha . \tag{4}$$

Following the least-squares method, we obtain:

$$\sum_i\left[x\frac{\eta_{0i}}{\sigma_0^2} + y\frac{\eta_{0i}}{(\varepsilon/\kappa)_0}\alpha_i - (\eta_{0i}-\eta_i^*)\right]^2 = \min \tag{5}$$

The approximation to zero of the partial derivatives with respect to x and y is a necessary condition of the minimum (5). Making the necessary calculations, we obtain the system of equations for finding the corrections.

$$x\left(\frac{\varepsilon}{k}\right)_0 \sum_i \eta_{0i}^2 + y\sigma_0^2 \sum_i \eta_{0i}^2 \alpha_i = \sigma_0^2 \left(\frac{\varepsilon}{k}\right)_0 \sum_i \eta_{0i}(\eta_{0i} - \eta_i^*)$$

$$x\left(\frac{\varepsilon}{k}\right)_0 \sum_i \eta_{0i}^2 \alpha_i + y\sigma_0^2 \sum_i (\eta_{0i}\alpha_i)^2 = \sigma_0^2 \left(\frac{\varepsilon}{k}\right)_0 \sum_i \eta_{0i}\alpha_i(\eta_{0i} - \eta_i^*) \qquad (6)$$

After determination of x and y from (6), we find the corrected values of σ^2 and ε/k. Adopting them as the new initial parameters, the process of refinement can go on. As a rule, one or two iterations are enough.

In spite of the apparent cumbersomeness of the method, it gives a unique value for the parameters σ^2 and ε/k, best describing experimental data within the limits of the functional relationship (1) of rigorous kinetic theory.

Table 1 presents potential parameters of the (6-12) model calculated from experimental data on viscosity of 18 gases [3]. The table sets forth inert, polyatomic, and polar gases. As we can see from Table 1, the viscosity of all inert gases, except for helium, given correct calculation of potential parameters can be described by the theoretical formula (1) with precision approximating the precision of experimental data. Column 5 of Table 1 sets forth the main deviation from experimental quantities in the entire temperature range indicated in column 2. Moreover, it proves to be possible both for polyatomic and polar gases to select potential parameters with a precision adequate for technical purposes that describe the viscosity of pure gases as a function of temperature. The greater deviation for hydrogen and helium is accounted for, evidently, by the necessity of quantum mechanical calculations and for chlorine -- by the low reliability of experimental data.

Coefficients of mutual diffusion for 14 pairs of gases in the range of temperature change 273-1000°K were calculated by using the derived potential parameters and combining rules. The experimental values proved to be 4-10 percent above the theoretical, which either indicates the incorrectness of the combining rules or points to some systematic errors in measurement of the diffusion coefficients.

We made an attempt at direct calculation of the parameters of interaction among dissimilar molecules from experimental data on the viscosity of gas mixtures. The above-described procedure was used in the calculations.

Table 2 sets forth the calculation results for five mixtures. The calculation was carried out for three different concentrations, however, as it turned out, calculation results did not depend on concentration within the limits of precision of the experimental data.

Table 1

Gas	Temperature range, °K	ε/k, °K	$\sigma \cdot 10^{10}$, M	$\frac{\Delta\eta}{\eta}$ Experimental %
I	2	3	4	5
He	273 ÷[1] I273	I0,I6	2,543	I,24
Ne	273 ÷ 873	27,I4	2,845	0,20
Ar	273 ÷ I273	II4,3	3,450	0,54
Kr	273 ÷ 873	I78,6	3,645	0,I5
Xe	273 ÷ 873	230,0	4,054	0,I3
N_2	200 ÷ I000	8I,I	3,722	0,67
O_2	200 ÷ I000	I08,8	3,446	0,44
Air	273 ÷ I273	70,2	3,727	0,8I
CO_2	273 ÷ I273	208,6	3,893	0,48
SF_6	470 ÷ 974	248,7	5,040	0,69
C_2H_4	273 ÷ 773	217,9	4,I7I	0,20
H_2	73 ÷ I273	39,8	2,889	I,II
Cl_2	273 ÷ 873	426,2	3,918	I,I8
CO	273 ÷ I273	I22,7	3,569	0,35
NO	273 ÷ I273	64,9	3,703	0,64
SO_2	273 ÷ I273	3I9,2	4,I3I	0,93
NO_2	273 ÷ 773	259,2	3,747	0,36
NH_3	273 ÷ I273	446,5	3,057	0,66

It is clear from Table 2 that potential parameters obtained from the viscosity of mixtures and from combining rules agree very well. This result that appears to us unexpected is accounted for most likely by the specifics of the formula for the viscosity of mixtures than by the reliability of the combining rules.

---

[1] See p. 198

Similar calculations were made with the aid of the second approximation of the theory for the viscosity coefficient of pure gases. Here it turned out that use of the second approximation does not improve the description of experimental results, and in some cases even somewhat deteriorates the outcome. Potential parameters obtained in this case and considerably complicating all calculations differ little from parameters obtained to the first approximation of theory, and introduce no improvement into the description of kinetic properties of gases.

The above-described method was used to obtain potential parameters of pure gases from experimental data on their compressibility [4]. First of all, the least-squares method was used to calculate the second virial coefficients for ten gases in the range of change of temperature and pressure shown in columns 2 and 3 of Table 3. Then, the potential parameters were calculated from the temperature dependence of the second virial coefficient. Table 3 gives us the results of the calculation, from which it is clear that the potential parameters derived from experiments on compressibility differ considerably from parameters obtained from viscosity. This fact has already been noted by almost all researchers. We present here only some quantitative results.

The viscosity of gases, set forth in Table 3, was calculated by using potential parameters obtained from equilibrium properties. Comparison of the derived viscosity values with experimental data shows a deviation of 6-14 percent, and further this deviation is as one-sided as in the case of diffusion.

In conclusion, we must note that viscosity of gases given the corresponding selection of potential parameters is well described by the theoretical formula (1) (with a precision of up to one percent). Potential parameters given in Table 1 can be recommended for calculation of other kinetic coefficients. In the absence of experimental data on diffusion coefficients, they can be calculated with a precision of up to 10 percent using the theoretical formula (1) with the employment of potential parameters from viscosity and the combining rules. Data on potential parameters obtained from compressibility of gases are poorly suited for calculating kinetic properties.

Table 2

Gases	Temperature range, °K	From viscosity of mixtures		From combining rules	
		$(\varepsilon/\kappa)_{12}$, °K	$\sigma_{12}\cdot 10^{10}$, м	$(\varepsilon/\kappa)_{12}$, °K	$\sigma_{12}\cdot 10^{10}$, м
I	2	3	4	5	6
He - Ar	293÷623	57,8	3,I50	55,7	3,I47
He - He	293÷473	I7,8	2,687	16,6	2,694
H_2 - CO_2	300÷550	I00,2	3,370	9I,I	3,39I
H_2 - Ne	300÷550	30,9	2,9I0	32,9	2,867
N_2 - O_2	293÷623	94,0	3,584	93,9	3,584

Table 3

Gases	Pressure range × × 10^{-5}, n/m2	Temperature range, °K	ε/κ, °K	$\sigma\cdot 10^{10}$, м
I	2	3	4	5
H_2	0,I ÷ I00	I50 ÷ 600	3I,50	2,940
Ar	0,I ÷ I00	I00 ÷I000	II8,7	3,420
O_2	0,I ÷ 70	200 ÷3000	II5,4	3,526
Cl_2	0,07 ÷ I,4	244 ÷ 550	3I6,9	4,259
N_2	0,I ÷ I00	220 ÷I000	94,48	3,686
He	0,I ÷ 70	200 ÷3000	I00,2	3,837
CO	I ÷ 90	273 ÷II73	4,732	2,568
CO_2	0,I ÷ I00	250 ÷I500	209,8	4,I28
H_2O	0,I ÷ I20	373 ÷I273	385,9	4,259
D_2O	0,I ÷ 80	373 ÷ 823	396,0	2,67I

Symbols

η_i and η_i^* = theoretical and experimental viscosity coefficients; T and T* = absolute and reduced temperatures; M = molecular weight; K = Boltzmann constant; $\Omega^{(2.2)}$ and $\Omega^{(2.3)}$ = reduced collision integrals; ε and σ = corrections on potential parameters; x and y = potential parameters of the (6-12) model.

Footnotes

1. To p. 195 The sign ÷ is the Russian counterpart for the hyphen in Western usage -- Tr.

References

1. Chapman, S., and T. Cowling, *Matematicheskaya teoriya neodnorodnykh gazov, (Mathematical Theory of Nonhomogeneous Gases)*, IL Press, Moscow, 1960.
2. Hirschfelder, J.; Curtis, C. Byrd, R. *Molekulyarnaya Teoriya Gazov i Zhidkostey, (Molecular Theory of Gases and Liquids)*, IL Press, Moscow, 1961.
3. Golubev, I. F., *Vyazkost' Gazov i Gazovykh Smesey, (Viscosity of Gases and Gas Mixtures)*, GIFML Press, Moscow, 1959.
4. Vargaftik, N. B., *Spravochnik po Teplofizicheskim Svoustvam 'Gazovi Zhidkostrey, (Handbook on Thermophysical Properties of Gases and Liquids)*, Fizmatgiz Press, Moscow, 1963.

CALCULATION OF THE VISCOSITY OF A STOICHIOMETRIC MIXTURE OF NITROGEN TETROXIDE AND ITS DECOMPOSITION PRODUCTS

A. G. Tabachnikov and S. M. Mezheritskiy

Experimental data on the viscosity of the system under study[1] in the vapor phase, published thus far, are mainly limited to atmospheric pressure. The only study [1] embraces the pressure range 0.5-5 atm (at temperatures of 298°-443°K). Data in [1] is the most recent and the most reliable.

The experimental study [2] in the temperature range 277.6°-410.9°K up to 300 kg/cm^2 (on the 310.9°K isotherm the data is obtained up to 431.8 kg/cm^2) is known on the viscosity of the system in the liquid phase.

A calculation of the coefficient of dynamic viscosity of the system in the vapor phase is carried out in the present study in the pressure range 1-500 kg/cm^2 and the temperature range 300°-2000°K. The calculation results agreed with experimental results in the liquid phase which had previously undergone critical analysis.

Calculation of the Viscosity of the System in the Gas Phase

We know that reaction effects only slightly influence the viscosity of an equilibrium reacting system [3-4]. This allows us the opportunity when calculating viscosity to view this system in each state as a mixture constant in composition and corresponding to the equilibrium composition.

Thusly, for each state it is necessary to determine the value of the viscosity which would occur at $p = 1$ atm for a mixture of the given real composition, and then to calculate the value of the excess viscosity corresponding to the given density.

The method in [5] employing a well known expression in [3] for the viscosity of clean gases at low pressures has been adopted in the present

---

[1] See p. 209

study for calculating viscosity at 1 atm:

$$\eta^{*}_{cm} = 26,69\sqrt{TM_{cm}}/\sigma^{2}_{cm}\cdot\Omega^{(2,2)*}_{cm}, \tag{1}$$

with the substitution in this formula of combinations of the potential parameters

$$\sigma_{cm} = \sum_{i=1}^{n} x_i\sigma_i\,; \quad (\varepsilon/\kappa)_{cm} = \Big[\sum_{i=1}^{n} x_i(\varepsilon/\kappa)_i\sigma_i^{3}\Big]/\sigma^{3}_{cm}.$$

The reliability of this method has been verified by the authors [5] for a large number of mixtures in a wide temperature range.

A generalized function [6] for multicomponent mixtures has been employed in calculating excess viscosity:

$$(\eta-\eta^{*})\xi = 1,058\left[\exp 1,439\omega - \exp(-1,111\omega^{1,858})\right] \tag{2}$$

Further, pseudocritical parameters were calculated from the following expressions:

$$T_{Kcm} = \sum_i x_i T_{Ki}\,; \quad V_{Kcm} = \sum_i x_i V_{Ki}\,; \quad Z_{Kcm} = \sum_i x_i Z_{Ki}\,;$$
$$p_{Kcm} = Z_{Kcm}\cdot R\cdot T_{Kcm}/V_{Kcm}.$$

It is shown in [6] with a wealth of experimental material that calculation of viscosity for various mixtures relying on the equation in [2] for a wide range of densities (up to $\omega \approx 2$) gives a mean error of 3.7 percent and a maximum error up to 6 percent.

The force constants of the Lennard-Jones potentials of the components adopted in the calculations are listed in Table 1.

Potential parameters for N_2O_4 and NO_2 were derived from the condition of the best approximation of experimental data [1] to the corresponding equation for calculation of viscosity [3] based on the kinetic theory of gas mixtures. Further, they find good agreement with the values recommended in [7].

Table 1

	N_2O_4	NO_2	NO	O_2
σ, Å	4,58	3,71	3,47	3,433
ε/k, °K	347	230	119	113

The values of σ and ε/k for NO and O_2 were taken from [3].

The values of the critical parameters used for the components are given in Table 2.

Table 2

	N_2O_4	NO_2	NO	O_2
$T_к$, °K	450	300	180,2	154,8
$P_к$, kg/cm^2	70	80	66,7	51,8
$\rho_к$, kmole/m^3	6,16	10,22	17,3	12,81

The values of the critical parameters adopted for N_2O_4 and NO_2 were derived in [8] from the condition of the best agreement of compressibility coefficients for the mixture N_2O_4–NO_2 calculated from experimental data on the density of the mixture [9] and from the equation for mixtures in [10]. Additionally, the compressibility coefficient for the components were determined by relying on generalized functions in [14].

For NO and O_2, the critical constants were borrowed from [11].

Densities of the system were adopted in accordance with experimental data [9] and from the results of the calculation made in [8].

Compositions of the system in each of the states is calculated with the aid of the following equations:

$$K_{P_1} = \frac{4\alpha_1^2}{1-\alpha_1^2} P, \tag{3}$$

$$K_{P_2} = \frac{\alpha_2^3}{(2+\alpha_2)(1-\alpha_2)^2} P, \tag{4}$$

in which

$$K_{p_1} = K_{p01}/K_{\gamma_1}, \quad K_{\gamma_1} = \gamma^2_{NO_2}/\gamma_{N_2O_4},$$
$$K_{p_2} = K_{p02}/K_{\gamma_2}, \quad K_{\gamma_2} = \gamma^2_{NO}\cdot\gamma_{O_2}/\gamma^2_{NO_2}$$

The fugacity coefficients of components γ_i were taken according to the generalized functions in [14].

Equations (3) and (4) are written on the assumption that reactions I and II occur successively.

This presupposition, though fundamentally not rigorous enough, does much to simplify the calculation without introducing substantial errors. Possible errors in determination of the mole fraction here, as analysis has shown, do not exceed 0.001-0.002.

The main errors in determining system compositions stem from imprecise values of K_{γ_1} and k_{γ_2}, which at high pressures and low temperatures can have errors up to 15 percent (owing to imprecision of critical parameters of N_2O_4 and NO_2, and also on account of the use of generalized functions for calculating γ_i). We must however note that, as analysis has shown, possible errors when real mole fractions of components are dtermined, proved all the same to be considerably less than their difference from mole fractions of an ideal system.

The calculation made for the vapor phase has shown that viscosity drops only slightly up to ~ 20 kg/cm^2 with rise in pressure on isotherms, and then slowly rises. This is brought about by the fact that with the pressure build-up equilibrium shifts toward the side of increased content of the less viscous N_2O_4 and therefore in the region of low pressures where the value $(\eta-\eta^*)$ is negligibly small, viscosity of the system decreases.

With further pressure build-up the influence of nonideality, responsible for a rise in viscosity, begins to play a dominant role.

Analysis of Data on the Viscosity of the System in the Liquid Phase

As has been noted above, experimental determination of the viscosity of N_2O_4 has been made by Richter, Reamer and Sage [2], who used the rolling sphere method to determine the value of the viscosity on five isotherms, and then graphically extrapolated them to saturation pressures for the purpose of determining the values of η' on the left boundary curve.

The values of η^* obtained in [2] at high temperatures raised doubts based on the following considerations. Extrapolation of the saturation curve, and also the critical isobar from the liquid side to the critical temperature $T_k = 431.4°K$ gives a viscosity value at the critical state equal to ~ 150 micropoises. This value proved to be appreciably less than the value of the viscosity at $p = 1$ atm on the critical isotherm not only for the system itself ($\eta^* = 228$ micropoises), but also for clean N_2O_4 ($\eta^* = 174$ micropoises), the latter value was obtained via calculation.

Still, we know that the following relationship [15] exists for particular compounds as between viscosity at the critical state $\eta_{Tk,Pk}$ and at 1 atm on the critical isotherm η^*_{Tk}:

$$\eta_{T_k,P_k} \approx (1{,}7 \div 2{,}5)\,\eta^*_{T_k} \qquad (5)$$

If we further consider that at the critical state the system, in addition to N_2O_4, contains a considerable amount (> 50 percent) of the more viscous NO_2, doubt over the reliability of the value of $\eta_{Tk,Pk} = 150$ micropoises becomes clear.

Accordingly, an agreement was made between the lower boundary curve and the results of calculation of viscosity of dry saturated vapor, and the nature of the 377.6° and 410.9°K isotherms was somewhat modified. And a saturation curve was obtained on the side of the liquid, which gave a more acceptable value of $\eta_{Tk,Pk} = 385$ micropoises and did not contradict, in principle, the experimental results [2], since, by raising sections of these isotherms near the saturation curve somewhat higher than was done in [2], some experimental points had to be shifted from within limits of scatter, and others better fitted. In the process of reconciling the data, the isotherms were graphically extrapolated to 500 kg/cm^2.

In the temperature range 410°-460°K for pressures $P > 100\ kg/cm^2$, viscosity values were obtained as a result of merging experimental liquid-phase isobars with vapor-phase calculated isobars; the regularity of the resulting curves were checked by the appearance of the isotherms. The results of calculations and the agreement are given in Table 3(η in micropoises).

Appraisal of Precision

In appraising the precision of the viscosity values obtained, errors in evaluating critical parameters, calculation of actual compositions, system densities, and also the intrinsic error of equation (2) the error when calculating values of η^* were taken into account. The maximum error can be ~ 15 percent in the 480°K region, where the error with respect to densities was evaluated at up to 6 percent for the general case. Here we also adopted the maximum error of equation (2), though it should have been expected close to $\omega \approx 2$, while in this region the maximum reduced density is only ~ 1.5. Thus, the actually indicated maximum error must be lower.

At temperatures > 520°K, the error drops to 5-3 percent. We must bear in mind that the values in the near-critical region have to be viewed as approximate, since experimental data here is not reliable enough. Data in the liquid phase, in accordance with the scatter of experimental points in [2], have a precision of ~ 7 percent.

Discussion of Results

In [16], the authors used for (η-η^*) the generalized function in [17] obtained via treatment of experimental data for individual gases in calculating the viscosity of the system N_2O_4-NO_2-NO-O_2 in the temperature range 300°-1500°K and the pressure range 1-150 atm. Here, the authors [16] viewed the system under study as some pure compound of variable molecular weight with wholly determinate critical state, whose parameters they used in forming the reduced coordinates.

Table 3

T, °K \ P, kg/cm²	I	4	I0	20	50	I00	I50	200	250	300	400	500
290	4330	4335	4350	4370	4432	4620	4628	4720	4820	4920	5II0	5300
320	I5I,0	3059	3068	3080	3I25	3I95	3250	3306	3350	3394	3490	3595
350	I79,3	I66	2II9	2I37	2I88	2255	2309	2360	2403	2440	25I5	2555
400	2I3,0	208	203	I98	873	II32	I265	I335	I390	I435	I500	I550
450	236	235	234	233	239	275	350	460	575	685	830	930
500	259	258	258	258	267	280	3I0	340	390	445	530	645
600	305	303	303	303	308	3I9	332	347	366	378	428	472
700	35I	35I	35I	35I	35I	356	363	373	384	395	422	452
800	390	389	387	388	389	393	40I	409	4I7	425	440	455
I000	46I	459	458	458	458	459	462	467	472	476	486	496
I200	522	52I	520	520	520	52I	524	527	53I	534	540	547
I400	576	576	576	576	576	578	580	582	584	587	59I	597
I600	628	628	628	628	628	630	632	634	636	638	642	646
I800	678	678	678	678	678	680	682	684	685	686	690	693
2000	726	726	726	726	727	728	730	73I	732	733	736	739

Actually, a chemically equilibrated reacting mixture, like a single-component system (according to Gibbs), is very analogous to pure compounds and, in particular, has a wholly determinate critical point which reflects the limiting state of existence of the phases. However, it does not at all follow from this fact that this system can be thermodynamically similar to clean gases, and the critical point reflects all of its specific features. Critical parameters used in this case do not characterize the properties of the reacting system in a wide range of parameters, which corresponds to the totality of states of mixtures of different compositions, while at the same time the critical state refers to mixtures of wholly determinate composition. These considerations make use of the function in [17] theoretically poorly validated.

Meanwhile, it turns out that when calculating the viscosity of the reacting system under investigation, fairly reliable results can be secured by using the method in [17] if the variable molecular weight is properly taken account of.

The calculation made according to the method in [17] with the use of true critical parameters of the system N_2O_4-NO_2-NO-O_2 and molecular weights corresponding to actual compositions, gave good agreement with the results of the above-described determination of viscosity according to [6].

This is accounted for by the following circumstances. First of all, as shown by comparison with the experimental data of a number of mixtures, the method in [17] is applicable when calculating their viscosity if into the calculation expression pseudocritical parameters combined according to the method in [6] are substituted. Secondly, though the relationships of pseudocritical parameters T_{k-mix}/p_{k-mix} for different states of the system deviate appreciably from T_k/p_k (true critical parameters), this fact does not have a substantial effect on the values of $(\eta-\eta^*)$ determined according to [17].

Thus, the method in [17] used in [16] to determine $(\eta-\eta^*)$, though unsubstantiated from the standpoint of first principles, nonetheless can give an acceptable result. Doubts arise however over the reliability of the calculation made in [16]. A result of this calculation was a decrease in the viscosity of the system on isotherms not only in the low-pressure region (about which we have remarked above), but as far as 150 atm. This function cannot be derived if the compositions of the system in each of the states are determined reliably enough. We note that it is precisely this aspect of the question in [16] that has received very little attention, and the lack of numerical values for η does not allow us to make the needed analysis.

Symbols

η = coefficient of dynamic viscosity of a mixture at given p [kg/cm^2] and T [°K] of a mixture, micropoises; η^* = viscosity at temperature T and p = 1 atm; $\omega = V_{k_{mix}}/V_{mix}$ = reduced volume; $V_{k_{mix}}$ = pseudocritical molal volume of the mixture, m^3/kmole; $\xi = T^{1/6}_{k\text{-}mix}/[\Sigma(x_i M_i)]^{1/2} \cdot p^{2/3}_{k\text{-}mix}$ = coefficient in equation (2); $(\varepsilon/k)_i$ and σ_i = force constants of the (Lennard-Jones (6-12) potential for the component; x_i = mole fractions of component; α_1 = degree of dissociation of N_2O_4; α_2 = number of moles of O_2 formed as a result of decomposition of NO_2 and referred to a single mole of starting N_2O_4; K_{p01} and K_{p02} -- ideal-gas equilibrium constants of the decomposition reactions of N_2O_4 (reaction I) and NO_2(reaction II) adopted from [12] and [13], respectively.

Footnotes

1. To p. 200 The system is formed as a result of the dissociation of N_2O_4 and NO_2 in accordance with the reactions $N_2O_4 \rightleftarrows 2NO_2 \rightleftarrows 2NO + O_2$.

References

1. Petker, J. and D. Mason, *Ind. Chem. Eng. Data,* Vol. 9, No. 2, p. 280, 1964.

2. Richter, G. N., H. H. Reamer, and B. H. Sage, *Ind. Eng. Chem.,* Vol. 45, p. 2117, 1953.

3. Hirschfelder, J., Curtis, C., and Byrd, R. *Molekulyarnaya Teoriya Gazov i Zhidkostey, (Molecular Theory of Gases and Liquids),* IL Press, Moscow, 1961.

4. Barua, A. K. amd T. K. R. Dastidar, *J. Chem. Phys.,* Vol. 43, No. 1, p. 4140, 1965.

5. Strunk, M. R. and G. D. Fensenfeld, *Am. Inst. Ch. Eng. J.,* Vol. 11, No. 3, p. 389, 1965.

6. Dean, D. E. and L. Steil, *Am. Inst. Ch. Eng. J.,* Vol. 11, p. 526, 1965.

7. Brokaw, R. S. and R. A. Svehla, *J. Chem. Phys.,*Vol. 44, No. 12, p. 4643, 1966.

8. Tabachnikov, A. G. and S. M. Mezheritskiy, *Tezisy Dolkada na Vsesouuznoy Konferentsii po Teplofizicheskim Svoystvam Veshchestv pri Vysokikh Temperaturakh, (Abstracts of Reports Presented at the All-Union Conference on Thermophysical Properties of Compounds at High Temperatures),* Novosibirsk, Moscow, 1966.

9. Schlinger, W. G., and B. H. Sage, *Ind. Eng. Chem.,* Vol. 42, p. 2158, 1950.

10. Tabachnikov, A. G., *IZV. VUZ, Neft' i Gaz,* No. 12, 1966.

11. Vargaftik, N. B., *Spravochnik po Teplofizicheskim Svoystvam Gazov i Zhidkostey, (Handbook on Thermophysical Properties of Gases and Liquids),* Fizmatgiz Press, Moscow, 1963.

12. Giaque, W. F. and J. D. Kemp, *J. Chem. Phys.,* Vol. 6, p. 40, 1938.

13. Gurvich, L. V., et al., *Termodinamisheskiye Svoystva Individual'nykh Veshchestv, (Thermodynamic Properties of Individual Compounds),* Academy of Sciences USSR Press, 1962.

14. Hougen, O. A., K. M. Watson and R. S. Ragatz, *Chemical Process Principles,* Vol, 11, New York, 1959.

15. Golubev, I. F., *Vyazkost' Gazov i Gazovykh Smesey, (Viscosity of Gases and Gas Mixtures),* Fizmatgiz Press, Moscow, 1959.

16. Maksimov, B. G., L. V. Mishina, and B. D. Timofeyev, *Izv.* AN SSSR, Ser. Fiz-Tekhn, n., No. 1, p. 19, 1966.

17. Filippova, G. P. and I. P. Ishkin, *IFZh,* Vol. 10, no. 9, 1961.

METHOD OF CALCULATED DETERMINATION OF THERMOPHYSICAL CHARACTERISTICS OF REAL GASES FROM MOLECULAR DATA

A. L. Tsykalo

The rapid growth of heat power engineering, chemical technology and other branches of the national economy that require detailed knowledge of thermophysical characteristics of a wide range of compounds has led to intensive study of properties of real gases, liquids, and mixtures. However, experimental data unfortunately is available at present only for a relatively small number of compounds and, as a rule, for fairly narrow ranges of change in external parameters. Consequently, it is quite understandable that there is mounting interest in developing calculation methods of determining properties of compounds that are of interest.

Some successes in solving this problem were achieved only by solving the problem of determining thermophysical properties of rarefied gases. Efforts at taking into account interactions of three and more molecules in most cases do not lead to satisfactory agreement with experiment. By way of example we can note calculations based on the Enskog theory [1], the theory of Snider and Curtis [2, 3], the theory of Hoffman and Curtis [4], the theory of Flynn and Ross [5], and the theory of Stogryn and Hirschfelder [6] for the second virial coefficient of viscosity and thermal conductivity. Relatively fair results came from using the theories of Stogryn and Hirschfelder [6] for calculating the second virial coefficient of thermal conductivity and Kim, Flynn and Ross [5] -- for calculating the second virial coefficient of viscosity. However, even in these cases appreciable deviations of experimental and calculated values were observed for some gases.

In particular, appreciable deviations occurred for xenon (viscosity and thermal conductivity), nitrogen (thermal conductivity), etc. Unfortunately, rigorous solution of the problem encountered both fundamental and calculational difficulties, so that simplifying assumptions were used in the above-mentioned theories.

Methods of determining transport properties based on use of the principle of corresponding states have enjoyed relatively wide acceptance. However, this approach has two substantial shortcomings that reduce the importance of this method and greatly limit its application. These shortcomings include the need to know thermophysical properties at the points of reduction (for example, at the critical point), and in addition, allowing for existing differences between the compounds investigated and those used as standards is hampering, and these differences can sometimes lead to considerable deviations from the law of corresponding states.

In light of the foregoing, it appeared useful, in addition to using the results of theory, to resort to considering experimental data for well studied compounds. Comparing numerical results of theoretical calculations of thermophysical properties with the corresponding experimental data, we can, by analyzing the corresponding deviations, account for molecular characteristics of the compound under study and the assumptions made, and thereby judge the shortcomings of theory in each particular case.

Consider the case of viscosity and thermal conductivity of a moderately compressed gas for which it is necessary to take into account, in addition to pairwise, also ternary interactions. In this case the coefficients of viscosity and thermal conductivity can be represented in the form:

$$\eta = \eta_0 + b\rho,$$
$$\lambda = \lambda_0 + \beta\rho.$$

Comparison of experimental values of the reduced virial coefficients b* and β* with the values calculated with the aid of various theories [1-6] is given in Tables 2 and 3. This comparison makes clear that when the theories in [5, 6] are used for certain gases, agreement is satisfactory. However, in some cases (Xe) the deviations are very great.

A common assumption in the theories used [1-6] was the customary assumption of the additivity of the potential energy of interaction of particles. Careful analysis, however, allows us to conclude that in calculating b* and β*, we must also take into account the nonadditive component of the potential energy of interaction of three particles, the need for taking this into account when calculating the third virial coefficient of the equation of state was demonstrated in [7, 8]. It is quite natural that allowing for the nonadditive component is highly important also when calculating transport properties that are highly sensitive to the function of potential energy of interaction of the system's particles.

We know that the potential energy of a system of three particles depends in a complex way on distances between particles and on the angles of the triangle formed by the interacting particles [7, 8]. Calculating the second virial coefficient of transport properties with the aid of ordinary relationships in this case imposes great difficulties, even if simplifying assumptions are adopted. Accordingly, in the present study an approximational method of allowing for the nonadditive component of the potential energy of interaction is proposed, founded on use of the conventional effective Lennard-Jones potential function, corrected with account taken of the fact of nonadditivity of the interaction of a three-particle system. In principle an approximation, this method insures acceptable precision; an advantage of the method is the possibility of its employment for the case of interacting particles when their number is greater than three, in which case precision calculations become practically impossible.

This method is based on using the results of calculating the third virial coefficient of the equation of state made by Sherwood and Prausniz [7], Sherwood, de Rocco and Mason [8] allowing for the nonadditive component of the potential energy of interaction of three particles for several model potentials. The results of these authors, including two expansion members in the expression for the reduced third virial coefficient of the equation of state can be written in the form

$$C^{*} = C^{*}_{0,12} + \alpha^{*} \Delta C^{*} + \varepsilon^{*1/2} \delta C^{*},$$

The functions log C* = f(log T*), plotted for various values of α^* and $\varepsilon^{*1/2}$ (Table 1), can, by the well known Lennard-Jones method by a parallel transport relative to the coordinate axes, be combined with the function $\log C^*_{add} = \phi(\log T^*)$. Here, it is easy to find the values of the corrections $\Delta \log \varepsilon$ and $\Delta \log \sigma$ allowing us to determine the force constants of the new effective function of pairwise interaction ε' and σ', corrected with allowance for the fact of nonadditivity of the potential function of interaction. This new potential function can be used in calculating the second virial coefficients of transport properties by the aid of the theories in [5, 6].

Table 1 presents the values of σ, ε, σ' and ε' for Ne, Ar, Kr and Xe, and also the values of α^* and $\varepsilon^{*1/2}$. Results of calculating the reduced second virial coefficients of viscosity and thermal conductivity in Tables 2 and 3 are compared with experimental values and with values calculated on the customary assumption of additivity of the potential energy of interaction of particles.

The comparisons made demonstrate that in the case of Xe, Ar and Kr when the nonadditive component is allowed for, it is possible only to slightly improve the results of calculation, which for these gases find satisfactory agreement with experimental values. In the case of Xe an appreciable improvement in agreement between calculation and experimental values of b^* and β^* is observed. This doubtless is accounted for by the considerably greater contribution of the nonadditive component of the potential energy of interaction in the case of Xe than in the case of the first three substances.

It must be noted that, as shown by calculations of the third virial coefficient, the contribution of the nonadditive component to the first approximation is proportional to the quantity $k^* = (2.8\alpha^* - \varepsilon^{*1/2})$. This is manifested in particular in the fact that the values of $\Delta \log (\varepsilon/k)$ and $\Delta \log \sigma$, determined as noted above by the Lennard-Jones method and allowing us to advance on to the effective function of pairwise interaction, are similar for substances characterized by similar values of k^* (cf. Ar and Kr in Table 1).

Analysis of experimental data and the results of theoretical claculation of b^* and β^* with the aid of theories in [5, 6] shows that when $T^* = 0.8$-2.0, the following approximational relationships hold:

$$b^* = 0,3877T^{*1/2} + 0,50$$

$$\beta^* = 2.8700T^{*1/2} + 1.65.$$

Table 1. Interaction Potential Constants and α^*, $\varepsilon^{*1/2}$ and k^*

и α^*, $\varepsilon^{*1/2}$, κ^*

Substance	Without allowing for nonadditive component		Allowing for nonadditive component		α^*	$\varepsilon^{*1/2}$	k^*
	σ, Å	ε/k, °K	σ', Å	ε'/k, °K			
	2,79	35,7	2,75	36,7	0,0I8	0,025	0,025
	3,42	I24	3,26	I38	0,038	0,050	0,060
	3,6I	I90	3,44	2I4	0,044	0,06I	0,059
	4,06	229	3,78	254	0,058	0,074	0,086

Table 2[1]. Comparison of Calculated and Experimental Values of b*

Substance	t, °C	T^*	b^*						
			Experiment [5]	Author's calculation	From [1]	From [4]	From [2,3]	From [6]	From [5]
	20	7,98	0,76 ± 0,I2	0,62	I,I0	0,44	-	I,I5	0,6I
	25	2,I6	I,0I ± 0,07	I,04	0,57	0,65	I,32	0,65	I,05
	20	I,37	0,97 ± 0,03	0,96	0,46	-0,I2	0,32	0,49	0,95
	25	I.I7	0,77 ± 0,05	0,84	0,42	-0,50	-0,06	0,42	0,93

Table 3[1]. Comparison of Calculated and Experimental Values of β^*

Substance	t, °C	T^*	β^*						
			Experiment [5]	Author's calculation	From [1]	From [4]	From [2,3]	From [6]	From [5]
	60	9,I0	3,98	3,60	4,00	3,I8	6,I2	3,49	2,I2
	25	2,I6	3,38	3,36	I,88	3,42	3,95	3,I8	4,76
	20	I,I5	4,07	4,00	I,4I	2,88	3,29	3,88	5,76

---

[1] See p. 218

These expressions can be directly used in calculating b and β if first the values of the force constants σ' and ε' are determined by the above-described method.

Symbols

ρ = density; η_o and λ_o = values of the coefficients of viscosity and thermal conductivity, respectively; C^*_{add} = reduced third virial coefficient of the equation of state calculated in the usual assumption of additivity of the potential energy of interaction; $\alpha^* = \alpha/\sigma^3$, $\varepsilon^* = \varepsilon\sigma/e^2$, α = polarizability; ε and σ = force constants of the paired potential; ΔC^* and δC^* = corrections associated with nonadditivity of dispersional and repulsive forces, respectively, and tabulated in [7, 8].

Footnotes

1. To p. 216 The values of T* (column 3) and of b* and β* of the experiment and the calculations (columns 4 and 5) were obtained by reduction with the aid of force constants σ' and ε'. The remaining values of b* and β* were obtained by using the force constants σ and ε.

References

1. Enskog, D. Kgl. Svenska Vetenskapskad . Handl, Vol. 63, p. 4, 1922.
2. Snider, R. F. and C. F. Curtiss, *Physics Fluids*, Vol. 1, p. 122, 1958.
3. Curtiss, C, F., *J. Eng. Sci.*, Vol. 3, p. 269, 1965.
4. Hoffman, D. K. and C. F. Curtiss, *Phys. Fluids*, Vol. 8, p. 8990, 1965.
5. Kim, S. K., G. P. Flynn, and J. Ross, *J. Chem. Phys.*, Vol. 43, p. 11, 1965.
6. Stogryn D. E. and J. O. Hirschfelder, *J. Chem. Phys.*, Vol. 31, pp. 1531, 1545, 1959; Vol. 33, p. 942, 1960.
7. Sherwood, A. E., and J. Prausig, *J. Chem. Phys.*, Vol. 41, p. 2, 1964.
8. Sherwood, A. E., De Rocco, and A. J. Mason, *J. Chem. Phys.*, Vol. 44, p. 8, 1966.

THERMOPHYSICAL PROPERTIES OF TWO- AND THREE-COMPONENT SEMICONDUCTOR ALLOYS

A. F. Chudnovskiy

The formal similarity in structure of differential equations describing the behavior of mechanical, thermal, electrical and magnetic phenomena is well known and has been used in describing an extensive class of processes of generalized conductivity. These procedures have proven especially productive for purposes of analyzing heterogeneous multiphase and in general complex systems. There are numerous studies in which various aspects of the method of generalized conductivity are developed and which are extended for an ever broader range of materials and an ever increasing list of their properties. As we know, two kinds of objects are usually distinguished -- a statistical mixture and matrical systems. For the former, for which dispersional powdered, granular and fibrous masses can be calculated, the equivalents of all miscible phases of the system is characteristic: the main phase (index 1) and the inclusion phase (index 2), such that interchanging of indices is not reflected in the final value of the generalized conductivity for the system. For the latter, such as porcelain, ceramics, asbestos, plastics, cable insulation and the vast majority of metal alloys, the existence of a single main phase is characteristic -- the matrix in which the second phase is included in the form of minute particles, grains and other elements, and for which interchanging of phase indi-ces (1) and (2) leads to a substantial change in the overall conductivity of the system.

Denoting by the generalized conductivity Λ and of the quantities entering into the analogy list -- coefficient of thermal conductivity, diffusion, dielectric permeability, Young modulus, the Poisson modulus, etc., the listed characteristics of each of the two kinds of materials can be written in the form:

$$F(\Lambda_1, \Lambda_2, V_1, V_2) = F(\Lambda_2, \Lambda_1, V_2, V_1)$$
$$F(\Lambda_1, \Lambda_2, V_1, V_2) \neq F(\Lambda_2, \Lambda_1, V_2, V_1) \qquad (1)$$

V_1 and V_2 = bulk concentrations of the main and secondary phases in the system. We will not dwell on a survey of the numerous studies in which: 1) a number of formulas of generalized conductivity have been established or proposed [1, 8-13]; 2) the practical use is proposed in various fields of dielectrics and metals [2-5, 14]; 3) the generalizations derived for electrophysical parameters are extended for thermophysical characteristics of materials [6, 15].

Throughout all this multifaceted range of activity attention has failed to be directed to aspects associated with the specifics of semiconductor compounds, some of which can be placed in the class of statistical mixtures (sintered or pressed briquettes of metal oxides, thermal resistances, ceramic and alumina materials), and others -- and the class of matrical systems (intermetallic alloys and solid solutions). In the case of solidifying alloys both a statistical as well as a matrical system can be obtained. We know only of one or two studies of S. V. Ayrapetyanets [16], who investigated thermoelectric systems viewed as two-phase compositions, for which the formulas of Odelevskiy were applied [7]. Here expressions were obtained for the coefficients of the thermoelectromotive force (α_1 and α_2), electro- (σ_1 and σ_2), and thermal conductivity (λ_1 and λ_2) of both phases (V_1 and V_2).

These formulas have the following form:

-- for the matrical system at low inclusion concentration

$$\alpha = \alpha_1 + \frac{9\sigma_2 \lambda_1 (\sigma_2 - \sigma_1)}{(2\sigma_1 + \sigma_2)(2\lambda_1 + \lambda_2)} V_2 \qquad (2)$$

-- for the matrical system at low concentration of the matrical phase

$$\alpha = \alpha_1 + \frac{\sigma_2 - \sigma_1}{1 + \frac{V_1}{3}\left(2\frac{\sigma_1}{\sigma_2} + \frac{\lambda_2}{\lambda_1}\right)} \quad (3)$$

-- for the matrical system at any concentration of components

$$\sigma = \sigma_1\left(1 + \frac{V_2}{\frac{1-V_2}{3} \quad \frac{\sigma_1}{\sigma_2 - \sigma_1}}\right) \quad (4)$$

$$\lambda = \lambda_1\left(1 + \frac{V_2}{\frac{1-V_2}{3} + \frac{\lambda_1}{\lambda_2 - \lambda_1}}\right) \quad (5)$$

-- for the statistical mixture at any concentration of components

$$\alpha = \frac{\alpha_1 \sigma_1 \gamma_1 + \alpha_2 \sigma_2 \gamma_2}{1 - 2\sigma(\gamma_1 + \gamma_2)} \quad (6)$$

$$\gamma_1 = \frac{3\lambda V_1}{(2\sigma + \sigma_1)(2\lambda + \lambda_1)} \quad (7)$$

$$\gamma_2 = \frac{3\lambda V_2}{(2\sigma + \sigma_2)(2\lambda + \lambda_2)} \quad (7a)$$

$$\sigma = a_1 + \sqrt{a_1^2 + \frac{\sigma_1 \sigma_2}{2}} \quad (7b)$$

where

$$a_1 = \frac{(3V_1 - 1)\sigma_1 + (3V_2 - 1)\sigma_2}{4} \quad (8)$$

$$\lambda = a_2 + \sqrt{a_2^2 + \frac{\lambda_1 \lambda_2}{4}} \tag{8a}$$

where

$$a_2 = \frac{(3V_1 - 1)\lambda_1 + (3V_2 - 1)\lambda_2}{4} \tag{8b}$$

The interesting work of S. V. Ayrapetyants can be expanded and developed in various directions.

1. There is the possibility of supplementing the earlier obtained conclusions by finding a complex quantity $Z = \alpha^2\sigma/\lambda$, effectiveness of thermoelectric materials.

2. It appears possible to find, by using the expression for α, σ and λ, that concentration at which conditions for obtaining the maximum value of the thermoelectric parameter arise. These conditions evidently are determined from the relationship:

$$\frac{dz}{dV_1} = \frac{d\left(\frac{\alpha_1^2\sigma_1}{\lambda_1}\right)}{dV_1} \quad \text{or} \quad \frac{d\left(\frac{\alpha_2^2\sigma_2}{\lambda_2}\right)}{dV_2}$$

Here, the prerequisites on the smallness of one of the faces are retained.

3. An avenue is opened up for the use of those variants of the formulas which are applicable for the relative equivalents of both phases, when the value of V_1 does not differ much from V_2. Here we are referring to methods of obtaining thermoelectric compounds by other than the widely accepted approaches.

Above all we have in mind powder metallurgy methods, where the compound of interest to us can be obtained not by alloying, but by pressing the original powders. For such mixtures, formulas of the type (4-8) with allowance for the conditions $V_1 \approx V_2$ are wholly applicable.

A graphic example of this kind of object are thermistors, studied only from one point of view, namely as semiconductor thermal resistances, and have not at all been considered from the aspect of their thermoelectric properties. Still, there can be no doubt that for these materials which are subjected either to pressing or sintering, calculations of generalized conductivity are wholly applicable and that by this approach their thermoelectric characteristics can be discovered, which can find use for measurement purposes. Here also methods of obtaining thermoelectric materials by reversible pressing at elevated temperatures [17] are of interest.

As has been established by the authors of this method, as a result of pressing and sintering without fusion, it is possible to produce material with good thermoelectric parameters.

Thus, use of the generalized conductivity formulas is wholly possible under this method. Here we must bear in mind only the following. Increasing the effectiveness of the value of Z involves searching for materials and conditions for their use that satisfy requirements corresponding to the highest values of Z and σ and the smallest possible values of λ. We need to underscore that such requirements must necessarily be corrected allowing for the requirements of practical expediency, economy and technological simplicity. In taking up the question from this point of view, it must be stated that it is not obligatory under all conditions to obtain only large values of the parameter Z. A whole series of tasks can be formulated that are most expeditiously solved when there are not sufficiently high absolute values of Z. The only important thing is that depending on concrete scientific-production conditions the values be either reduced, but optimal out of all possible values.

How then can such situations be formed? Let us cite a number of examples.

1. We were interested in obtaining for hot and cold junctions thermal elements of moderate, but not of maximum possible temperature drop.

2. We were limited to semiconductor material in short supply and were interested in economizing it. Then, when $V_1 \approx V_2$, owing to the reduction in

in the overall Z, we can use one of the component elements customarily discarded as rejects, adding it to another element with a high Z parameter.

3. At high temperatures we were limited in selection of a heat-resistant semiconductor material; then we could use even metal or metal-like arms with low values of α, and consequently, of Z. Additionally, as shown in [18], substitution of the semiconductors with metal promises a whole series of other advantages.

Let us now turn to a brief exposition of the essentials of the problem formulated.

Beginning with formulas (2-5), we obtain expressions for the thermoelectric parameter $Z = \alpha^{2\sigma}/\lambda$ of the matrical system for the case of low concentrations of inclusions ($V_2 \ll 1$) and for the case of low matrical phase concentrations ($V_1 \ll 1$), and we also calculate for each of these cases optimal component concentrations at which the value of C reaches an extremum.

To calculate the variable, dZ/dV is conveniently expressed in the form $\alpha^2\sigma/\lambda$; then after transformation we obtain the condition of extremum in the form

$$\alpha\lambda\sigma' - \alpha\sigma\lambda' + 2\lambda\sigma\alpha' = 0 \qquad (9)$$

The values of α, σ and λ were obtained by simplifying the original formulas, in which it was taken into account that when $V_2 \ll 1$, $V_2^2 \approx 0$, and when $V_1 \ll 1$, $V_1^2 \approx 0$. The values of α', σ' and λ' were obtained by differentiation of the starting formulas, where members containing V_2 were dropped in the results. Thus, we have the following.

1. For the matrical system at low inclusion concentrations

$$\alpha = \alpha_1 + \frac{9\sigma_2\lambda_1(\alpha_2 - \alpha_1)}{(2\sigma_1 + \sigma_2)(2\lambda_1 + \lambda_2)} V_2$$

$$\sigma = \sigma_1 + \frac{3\sigma_1(\sigma_2 - \sigma_1)}{\sigma_2 + 2\sigma_1} V_2$$

$$\lambda = \lambda_1 + \frac{3\lambda_1(\lambda_2 - \lambda_1)}{\lambda_2 + 2\lambda_1} V_2$$

$$\alpha' = \frac{9\sigma_2 \lambda_1(\alpha_2 - \alpha_1)}{(2\sigma_1 + \sigma_2)(2\lambda_1 + \lambda_2)}$$

$$\sigma' = \frac{3\sigma_1(\sigma_2 - \sigma_1)}{\sigma_2 + 2\sigma_1} + \frac{6\sigma_1(\sigma_2 - \sigma_1)^2}{(\sigma_2 + 2\sigma_1)^2} V_2$$

$$\lambda' = \frac{3\lambda_1(\lambda_2 - \lambda_1)}{\lambda_2 + 2\lambda_1} + \frac{6\lambda_1(\lambda_2 - \lambda_1)}{(\lambda_2 + 2\lambda_1)} V$$

2. For the matrical system at low concentrations of the matrical phase ($V_1 \ll 1$):

$$\alpha = \alpha_2 + \frac{(\alpha_1 - \alpha_2)(2\sigma_1\lambda_1 + \sigma_2\lambda_2)}{3\sigma_2\lambda_1} V_1$$

$$\sigma = \sigma_2 + \frac{(\sigma_1 - \sigma_2)(2\sigma_1 + \sigma_2)}{3\sigma_1} V_1$$

$$\lambda = \lambda_2 + \frac{(\lambda_1 - \lambda_2)(2\lambda_1 + \lambda_2)}{3\lambda_1} V_1$$

$$\alpha' = \frac{(\alpha_1 - \alpha_2)(2\sigma_1\lambda_1 + \sigma_2\lambda_2)}{3\sigma_2\lambda_1} -$$

$$- \frac{2(\alpha_1 - \alpha_2)(2\sigma_1\lambda_1 + \sigma_2\lambda_2)}{9\sigma_2^2\lambda_1^2} V_1$$

$$\sigma' = \frac{(\sigma_1 - \sigma_2)(2\sigma_1 + \sigma_2)}{3\sigma_1} + \frac{2(\sigma_1 - \sigma_2)^2(2\sigma_1 + \sigma_2)}{9\sigma_1^2} V_1$$

$$\lambda' = \frac{(\lambda_1 - \lambda_2)(2\lambda_1 + \lambda_2)}{3\lambda_1} + \frac{2(\lambda_1 - \lambda_2)^2(2\lambda_1 + \lambda_2)}{9\lambda_1^2} V_1$$

The reduced expressions were substituted into equation (9). We obtained the following results:

1. For the case ($V_2 \ll 1$)

$$V_2^{opt} = \{(\sigma_2 + 2\sigma_1)(\lambda_2 + 2\lambda_1)[\alpha_1(\lambda_2 - \lambda_1)(\sigma_2 + 2\sigma_1) - \alpha_1(\sigma_2 - \sigma_1)(\lambda_2 + 2\lambda_1) - 6\lambda_1\sigma_2(\alpha_2 - \alpha_1)]\}A \tag{10}$$

$$A = (\lambda_2 - 2\lambda_1)(\sigma_2 - \sigma_1)M - (\lambda_2 - \lambda_1)(\sigma_2 + 2\sigma_1)N + 18\sigma_2\lambda_1(\alpha_2 - \alpha_1)K,$$

$$M = 9\sigma_2\lambda_1(\alpha_2 - \alpha_1) + 3\alpha_1(\lambda_2 - \lambda_1)(\sigma_2 + 2\sigma_1) + 2\alpha_1(\sigma_2 - \sigma_1)(\lambda_2 + 2\lambda_1),$$

$$N = 9\sigma_2\lambda_1(\alpha_2 - \alpha_1) + 3\alpha_1(\sigma_2 - \sigma_1)(\lambda_2 + 2\lambda_1) + 2\alpha_1(\lambda_2 - \lambda_1)(\sigma_2 + 2\sigma),$$

$$K = (\lambda_2 - \lambda_1)(\sigma_2 + 2\sigma_1) + (\sigma_2 - \sigma_1)(\lambda_2 + 2\lambda_1)$$

$$z = \frac{\alpha_1^2\sigma}{\lambda_1} + \frac{9\lambda_1\sigma_1(2\alpha_1\sigma_2\lambda_1 - \alpha_1\sigma_2\lambda_1) - \lambda_1\sigma_1\lambda_2}{\lambda_1(\sigma_2 + 2\sigma_1)(\lambda_2 + 2\lambda_1)} V_2 \tag{11}$$

2. For the case ($V_1 \ll 1$)

$$V_1^{opt} = \{3\sigma_1\sigma_2\lambda_1[\sigma_1\sigma_2\alpha_2(\lambda_1 - \lambda_2)(2\lambda_1 + \lambda_2) - \lambda_1\lambda_2\alpha_2(\sigma_1 - \sigma_2)(2\sigma_1 + \sigma_2) - 2\sigma_1\lambda_1(\alpha_1 - \alpha_2)(2\sigma_1\lambda_1 + \sigma_2\lambda_2)]\} \tag{12}$$

$$B = \lambda_1(\sigma_1 - \sigma_2)(2\sigma_1 + \sigma_2)M_1 - \sigma_1\sigma_2(\lambda_1 - \lambda_2)(2\lambda_1 + \lambda_2)N + 2\sigma(\alpha_1 - \alpha_2)(2\sigma_1\lambda_1 + \sigma_2\lambda_2)K_1$$

$$M_1 = 2\alpha_2\sigma_2\lambda_1\lambda_2(\sigma_1-\sigma_2)+\sigma_1\lambda_1(\alpha_1-\alpha_2)(2\sigma_1\lambda_1+\sigma_2\lambda_2)+$$
$$+\alpha_2\sigma_1\sigma_2(\lambda_1-\lambda_2)(2\lambda_1+2\lambda_2).$$

$$N_1=2\alpha_2\sigma_1\sigma_2(\lambda_1-\lambda_2)+\sigma_1(\alpha_1-\alpha_2)(2\sigma_1\lambda_1+\sigma_2\lambda_2)+$$
$$+\alpha_2\lambda_1(\sigma_1-\sigma_2)(2\sigma_1+\sigma_2)$$

$$K_1=\sigma_1\sigma_2(\lambda_1-\lambda_2)(2\lambda_1+\lambda_2)+\lambda_1\lambda_2(\sigma_1-\sigma_2)(2\sigma_1+\sigma_2)-$$
$$-2\sigma_1\lambda_2(2\sigma_1\lambda_1+\sigma_2\lambda_2)$$

$$z=\frac{\alpha_2\sigma_2^2}{\lambda_2}+\frac{V_1}{3\sigma_1\lambda_1\lambda_2^2}\left[\alpha_2(2\sigma_1\lambda_1+\sigma_2\lambda_2)(2\alpha_1\sigma_1\lambda_2-\right.$$
$$\left.-\alpha_2\sigma_1\lambda_2-\alpha_2\sigma_2\lambda)\right] \qquad (13)$$

Below we give the solution to the problem for the more complex three-component system. As we know, the general expression for the system consisting of any number of phases i is of the form [18]:

$$\sum \frac{\Lambda_i-\Lambda}{\Lambda+2\Lambda}V_i=0 \qquad (14)$$

here Λ_i = generalized conductivity of the component phases of the system, V_i = their bulk (in percentages or fractions of unity, since $V_1 + V_2 + \ldots V_i$ = 100 percent or 1) content in the system, and Λ = generalized conductivity of the system as a whole. We must understand by Λ_i and Λ the coefficients of thermal conductivity and electroconductivity, dielectric permeability, thermoelectromotive force, the Young modulus, shear, etc., for each of the components and for the system as a whole, respectively. We will use formula (14) for the system i = 3. Thus, we are referring to finding a function of the form:

$$\Lambda = F(\Lambda_1, \Lambda_2, \Lambda_3, V_2, V_3) \qquad (15)$$

It is easy to see that the task reduces to solving the equation

$$\frac{\Lambda_1-\Lambda}{\Lambda_1+2\Lambda}V_1+\frac{\Lambda_2-\Lambda}{\Lambda_2+2\Lambda}V_2+\frac{\Lambda_3-\Lambda}{\Lambda_3+2\Lambda}V_3 \qquad (16)$$

Omitting all the intermediate operations, we present the solution of (16) in the finished form; it will reduce to the following equation:

$$\Lambda = \sqrt[3]{-q + \sqrt{q^2 + p^3}} + \sqrt[3]{-q - \sqrt{q^2 + p^3}} - \frac{b}{3\alpha} \tag{17}$$

Here we list the following symbols:

$$q = \frac{b^3}{27\alpha^3} - \frac{bc}{6\alpha^2} + \frac{d}{2\alpha} \tag{18}$$

$$p = \frac{\alpha c - b^2/3}{\alpha^2} \tag{19}$$

$$\alpha = 4 \tag{20}$$

$$b = -(n_1 V_1 + n_2 V_2 + n_3 V_3) \tag{21}$$

$$c = -(m_1 V_1 + m_2 V_2 + m_3 V_3) \tag{22}$$

$$d = -\Lambda_1 \Lambda_2 \Lambda_3 \tag{23}$$

$$m_1 = 2\Lambda_1\Lambda_2 + \Lambda_3(2\Lambda_1 - \Lambda_2) \tag{24}$$

$$m_2 = 2\Lambda_1\Lambda_2 + \Lambda_3(2\Lambda_2 - \Lambda_1) \tag{25}$$

$$m_3 = 2\Lambda_1\Lambda_2 + \Lambda_2(2\Lambda_3 - \Lambda_1) \tag{26}$$

$$n_1 = 2(2\Lambda_1 - \Lambda_2 - \Lambda_3) \tag{27}$$

$$n_2 = 2(2\Lambda_2 - \Lambda_1 - \Lambda_3) \tag{28}$$

$$n_3 = 2(2\Lambda - \Lambda_1 - \Lambda_2) \tag{29}$$

We will give a number of examples in which it is possible to use the formulas (17-29).

The first task in calculating coefficients of electroconductivity σ, thermal conductivity λ, thermoelectromotive force α and thermoelectric efficiency Z of three-component alloys. The values of σ and λ are found from formulas (17-29) by simple substitution of the values Λ and Λ_i, respectively, by σ and σ_i and by λ and λ_i. As far as the value of α is concerned, below we present the results of its calculation

$$\alpha = \frac{\alpha_1\sigma_1\gamma_1 + \alpha_2\sigma_2\gamma_2 + \alpha_3\sigma_3\gamma_3}{1 - 2\sigma(\gamma_1 + \gamma_2 + \gamma_3)} \tag{30}$$

here:

$$\gamma_1 = \frac{3\lambda_1 V_1}{2(\sigma + \sigma_1)(2\lambda + \lambda_1)} \tag{31}$$

$$\gamma_2 = \frac{3\lambda V_2}{(2\sigma + \sigma_2)(2\lambda + \lambda_2)} \tag{32}$$

$$\gamma_3 = \frac{3\lambda V_3}{(2\sigma + \sigma_3)(2\lambda + \lambda_3)} \tag{33}$$

From here it is easy to find the values of the thermoelectric efficiency Z, where λ and σ are found from formulas (17-29) and α from formulas (29-33).

The second task is to find visible parameters of the third phase known from characteristics of two components and from measurements of the effective values of the entire three-component composition. In this case it is possible to formulate three equations: one equation (17) in which λ is measured; a second equation (17) [sic -- Tr.], in which σ is measured and λ_1 and λ_2 are known; a third equation (30), in which α is measured and λ_1, λ_2, σ_1 and σ_2 are known. As a result, the task boils down to calculating three unknown parameters λ_3, σ_3 and α_3 from data of measurements of λ, σ and α and based on the earlier found characteristics λ_1, λ_2, σ_1, σ_2, α_1 and σ_2.

Naturally, this task reduces to making the following functions explicit

$$\left.\begin{matrix}\alpha_3\\ \sigma_3\\ \lambda_3\end{matrix}\right\} = f(\alpha_1, \alpha_2, \sigma_1, \sigma_2; \lambda_1, \lambda_2; \alpha, \sigma, \lambda, V_1; V_2, V_3)$$

and can be solved also in the following two versions:

$$\left.\begin{matrix}\alpha_1\\ \sigma_1\\ \lambda_1\end{matrix}\right\} = f(\alpha_2; \alpha_3; \sigma_2; \sigma_3; \lambda_2; \lambda_3; \alpha, \sigma, \lambda, V_1, V_2, V)$$

and

$$\left.\begin{matrix}\alpha_2\\ \sigma_2\\ \lambda_2\end{matrix}\right\} = f(\alpha_1; \alpha_3; \sigma_1; \sigma_3; \lambda_1; \lambda_3; \alpha, \sigma, \lambda, V_1; V_2; V_3)$$

The third task is determining the percentage content of a given component in the mixture.

In this assignment we are faced with the problem of calculating the bulk fraction of any of the phases in the overall compound based on measurements for earlier set characteristics of the physical parameters both of the entire mixture as well as of its components. It is precisely here that we must find out what the porosity or moisture content of the materials is.

Since we know that $V_1 + V_2 + V_3 = 1$, to solve the formulated task it is necessary to know the following values: α, σ, λ, α_i, σ_i, λ_i, V_{i-1} and V_{i-2}.

Symbols

Λ, Λ_1, Λ_2, ..., Λ_i = general conductivity of the entire system and of its components; λ, λ_1, λ_2, ..., λ_i = as above, for the coefficients of thermal conductivity; σ, σ_1, σ_2, ..., σ_i = as above for the specific electroconductivity; α, α_1, α_2, ..., α_i = as above, for the coefficients of the thermoelectromotive force; Z, Z_1, Z_2, ..., Z_i = as above, for the parameters of thermoelectric efficiency.

References

1. Val'ter, A. F. (editor), *Fizika Dielektrikov, (Physics of Dielectrics)*, Gostekhteorizdat Press, Moscow-Lenigrad, 1932.
2. Ioffe, A. F. and B. M. Vul, *Elektrichestvo*, No. 2, 1931.
3. Skanavi, G. I., *Vestnik Elektropromyshlennosti*, No. 6, 1945.
4. Vul, B. M., *Elektrichestvo*, No. 3, 1946.
5. Smolenskiy, G. A., *ZhTF*, Vol. 15, No. 3, 1945.
6. Chudnovskiy, A. F., *Teploobmen v Dispersnykh Sredakh, (Heat Transfer in Disperse Media)*, Gostekhizdat, Moscow, 1954.
7. Odelevskiy, V. I., *ZhTF*, No. 6, 1951.
8. Maxwell, I. C., *A Treatise on Electricity and Magnetism*, Vol. 1, Oxford, 1904.
9. Rayleigh, I. W., *Phil. Mag.*, Vol. 5, No. 34, p. 481, 1892.
10. Weiner, O., *Abhandl. d. Leipz. Akad.*, Vol. 32, p. 509, 1912.
11. Wagner, K. W., *Arch. f. Elektrot.*, Vol. 2, p. 371, 1914.
12. Leichtenecker, K., *Phys. Zeitschr.*, Vol. 27, p. 115, 1926.
13. Leichtenecker, K. and K. Rother, *Phys. Zeitschr.*. Vol. 32, p. 255, 1931.
14. Berbericht, A., *Bell. Journ. Appl. Phys.*, Vol. 11, p. 681, 1940.
15. Series of Articles, *Journ. of the Am. Ceram. Soc.*, Part 11, Febr. 1954.
16. Ayrapetyants, S. V., *ZhTF*, Vol. 27, No. 3, 1951.
17. Smirnov, V. S., N. N. Pavlov, A. F. Chudnovskiy, and S. A. Semennovich, Tr. Leningradskogo Politekhnicheskogo Instituta im. M. I. Kalinina, No. 222, Mashgiz Press, Leningrad, 1963.
18. Odelevskiy, V. I., *ZhTF*, No. 6, 1951.

PROBLEM OF CALCULATING TRANSPORT COEFFICIENTS FOR GASES

G. F. Shaykhiyev and A. G. Ustanov

Thus far a considerable amount of experimental material has been accumulated on transport coefficients of gases that are comprised of molecules of various forms, symmetries and polarities. However, only a small amount of this material finds agreement with calculations according to the following equations:

$$\mathcal{D} = 26280\frac{\sqrt{T^3/M}}{P\sigma^2\Omega^{(11)*}(T^*)}\cdot 10^{-7}, \qquad (1)$$

$$\eta = 266{,}93\,\frac{\sqrt{TM}}{\sigma^2\Omega^{(22)*}(T^*)}\cdot 10^{-7}, \qquad (2)$$

$$\lambda = 1989{,}1\,\frac{\sqrt{T/M}}{\sigma^2\Omega^{(22)*}(T^*)}\cdot 10^{-7}. \qquad (3)$$

derived on the basis of rigorous kinetic theory of gases [1, 2].

The observed disparities between the results of measurement and calculations are accounted for mainly by the lack of a realistic model of intermolecular interaction necessary in determining collision integrals. The nature of change in collision integrals calculated based on idealized models and according to equations (2) and (3) based on experimental data for the transport coefficients is shown in Figures 1 and 2. These curves have been plotted in the coordinates $\Omega^{(2.2)}(T)$ and T for Ar and CO_2. Here are also presented curves of the potential functions obtained based on viscosity data, and the curves for the Morse and Gugenheim-McGlashan potentials -- from data of crystalline structure and to the second virial coefficient. In most cases agreement between experimental and calculated collision integrals of momentum transport (Figures 1 and 2) is observed. When these are used as the starting point in measurement of thermal conductivity, deviations increase as the molecule becomes more complex, starting with argon and extending to carbon dioxide gas. The latter evidently is accounted for by the increment in the neglected influence of internal degrees of freedom on the process of energy transfer. There is little experimental data on self-diffusion coefficients, therefore it is difficult to make an analogous examination. Experimental values of the collision integrals of momentum transport agree with those calculated from many potential functions for the gases under study at atmospheric pressure. In describing the collision integral of heat transport allowing for the effect of internal degrees of freedom, we did not have available the appropriate potential functions. Selection of interaction potentials is even further complicated with increase in valency, change in polarity and in molecular form. It was of interest to search for ways of reducing the number of variables in calculating collision integrals of mass transport, momentum transport and heat transport.

Earlier [4], starting from statistical considerations, the following criterial equation was obtained:

$$U_{\text{отн}} = \varphi\left(\frac{S-S_1}{R}\right), \qquad (4)$$

which was used in generalizing experimental data on transport coefficients in gases and liquids. Here, only the valency of gases was taken account of as a condition of unambiguity in the first studies, and later the simplex S_t/R, reflecting individual characteristics of molecules participating in the process. The form of the function ϕ in (4) proved to be dependent on the form of transport and the number of atoms in the gas molecule. The function (4) is easily presented in the following form applicable to thermal conductivity:

$$\frac{\lambda_{S-S_1}}{\lambda_{\Delta S}} = \frac{T_1' - T_1}{T - T_1} \varphi\left(\frac{S}{S_1}\right). \qquad (5)$$

Experimental data on transport coefficients have been satisfactorily generalized on the basis of (4). Therefore it was of interest to compare the functional relationship (4) with the expression for the relative value of any transport coefficient obtained on the basis of rigorous kinetic theory. Let us take the thermal conductivity as such a coefficient, because it gives the greatest deviation from experiment and requires introduction of the Euchen correction for polyatomic gases. For temperatures T and T_1, we obtain:

$$\frac{\lambda}{\lambda_1} = \left(\frac{T}{T_1}\right)^{0,5} \frac{\Omega_1^{(22)*}(T_1^*)}{\Omega^{(22)*}(T^*)} \qquad (6)$$

Experience in the application of (4) and (5) shows that they allow us the opportunity to calculate coefficients of thermal conductivity based on generalized functions plotted for a group of gases. From this it follows that $\phi(S/S_1)$ in equation (5) must be equivalent to the multiplier

$$\Omega_1^{(2.2)*}(T_1^*)/\Omega^{(2.2)*}T^*)$$

in equation (6). Therefore it can be anticipated that replacing the reduced collision integrals in (1)-(3) by the entropy function must preserve the possibility of their application in calculating transport coefficients. Starting from these prerequisites in equations (1)-(3), we replace the reduced integrals by the relationship:

$$\Omega_i^*(S) = \left(a\frac{\pi\sigma^2}{S}\right)^n \qquad (7)$$

Then instead of the reduced collision integrals, $\Omega_D^*(S)$, $\Omega_\eta^*(S)$ and $\Omega_\lambda^*(S)$ enter into (1)-(3), respectively,

$$D = 26280\frac{\sqrt{T^3/M}}{P\sigma^2\Omega_D^*(S)}\cdot 10^{-7}, \qquad (8)$$

$$\eta = 266{,}93 \frac{\sqrt{TM}}{\sigma^2 \Omega_\eta^*(S)} \cdot 10^{-7}, \tag{9}$$

$$\lambda = 1989{,}1 \frac{\sqrt{T/M}}{\sigma^2 \Omega_\lambda^*(S)} \cdot 10^{-7}. \tag{10}$$

In order for equations (8)-(10) to be applied in calculations, it is necessary to determine the exponent n in (7). This can be readily done based on available experimental data on transport coefficients. Table 1 presents results obtained. From these results it follows that the value of the exponent depends on the kind of transport and the number of atoms in the molecule (an exception is He and Ar). It is retained constant throughout the entire temperature range investigated. For the case of diffusion and self-diffusion, the exponents n prove to be independent of the properties of the molecules and equal 1.5. We note that in these calculations the interaction diameter σ is taken in each case as constant and equal to such in the Lennard-Jones (6-12) potential. Table 2 presents by way of example numerical values of σ and ε/k for Ar, N_2 and CO_2.

Table 1. Exponent As a Function of Kind of Transport and Valency

Kind of Transport	Exponent based on equation (7)					
	He	Ar	CO, N_2, O_2, H_2	CO_2, SO_2, N_2O	CH_4	C_2H_6
Self-diffusion	I,50	I,50	I,50	I,50	I,50	I,50
Viscosity	I,20	I,35	I,20	I,50	0,50	I,40
Thermal conductivity	I,50	I,65	I.80	3,00	4,00	4,00

Table 2. Force Parameters for the Lennard-Jones (6-12) Potential

Gas	Viscosity		Thermal conductivity		Diffusion	
	σ	ε/k	σ	ε/k	σ	ε/k
Ar	3,48	II6	3,48	II6	3,48	II6
N_2	3,76	78,5	3,60	3I,4	3,63	79,8
CO_2	4,I8	II6	3,85	213	4,00	200

As Table 2 shows, force parameters change when we go from viscosity to thermal conductivity or diffusion. This has been taken note of also in [1, 13, 14]. Reduced collision integrals of heat and momentum $\Omega^*_\lambda(S)$ and $\Omega^*_\eta(S)$ are generalized for valency as a function of temperature by multiplying them by some constant b, which proves to be similar in magnitude to the internuclear distance re [15] (Figure 3). Thus, use of some entropy function instead of model collision integrals gives better agreement with experiment. The validity of the assumptions stated can be demonstrated also by the example of polar gases. Let us take water vapor. Its coefficients of viscosity and thermal conductivity have been investigated for a wide range of temperatures and pressures [6].

Figure 4 presents the results of calculating collision integrals from equation (7) and from the Stockmeyer potential [10]. Table 3 presents the values of σ and n at various pressures. It must be noted that the values of σ drop off with rise in pressure, and that the exponent n approaches unity.

Table 3. Parameters of Water Vapor for Calculation According to Equation (7)

P	n_η	σ_η	n_λ	σ_λ
I	3,0	3,93	5,0	3,88
I00	2,0	3,56	3,0	3,4I
200	I,0	3,39	2,0	3,205
300	I,0	3,33	I,0	2,87
400	I,0	3,28	I,0	2,80
500	I,0	3,23	I,0	2,27

At supercritical pressures, it proved necessary to select data relating only to the vapor phase. The curve of heat capacity maxima was adopted as the provisional boundary between liquid and vapor.

Coefficients of viscosity and thermal conductivity of water vapor were calculated from data in Table 3 and from equations (9) and (10) at pressures 100, 200, 300, 400 and 500 bar and temperatures 700-1000°C, that is, in the range of those parameters for which there are as yet no support data (Table 4).

Table 4. Transport Coefficients of Water Vapor at High Parameters

P / T	Viscosity, g/cm·sec 10^{-6}					Thermal conductivity calorie/cm·sec °K 10^{-5}				
	I00	200	300	400	500	I00	200	300	400	500
I073	386	405	426	444	469	28,3	29,9	32,3	35,I	38,2
II73	420	435	456	478	50I	3I,2	32,7	34,6	37,7	4I,2
I273	45I	460	484	506	535	34,3	35,I	36,9	40,I	43,7

Thus, use of some entropy function in place of model collision integrals makes it possible to employ with no less success equations of rigorous kinetic theory of gases in calculating transport coefficients.

Symbols

D = self-diffusion coefficient (cm^2/sec); η = viscosity coefficient (g/cm·sec); λ = coefficient of thermal conductivity (calorie/cm·sec °K); T = absolute temperature (°K); P = absolute pressure (bar); M = molecular weight; σ = interaction diameter (Å); $\Omega^{(2.5)*}(T^*)$ = reduced collision integrals; $T^* = kT/\varepsilon$ = reduced temperature; ε = depth of potential depression (ergs); k = Boltzmann constant; U_{rel} = relative rate of process, which as applied to thermal conductivity is taken as the ratio of heat fluxes $q_S - S_4$ and mass flux $q_{\Delta S}$ corresponding to change in entropy at the boundaries S and S_1 and $\Delta S = S'_1 - S_1$; $\bar{q}_{s-s_1} = \lambda_{s-s_1}(T-T_1)$; $q_{\Delta s} = \lambda_{\Delta s}(T_1' - T_1)$; λ_{S-S_1} and $\lambda_{\Delta S}$ = mean coefficients of thermal conductivity; T, T_1^1, and T_1 = temperatures corresponding to the entropies S, S_1' and S_1; S = absolute molal entropy of the gas; R = universal gas constant; a = dimensional constant in equation (7), found to be equal to unity; $\Omega_L^*(S)$ = reduced collision integrals with respect to entropy, where L_0 denotes the kind of transport; re = internuclear distance (Å); $\phi(r)$ = potential energy (ergs).

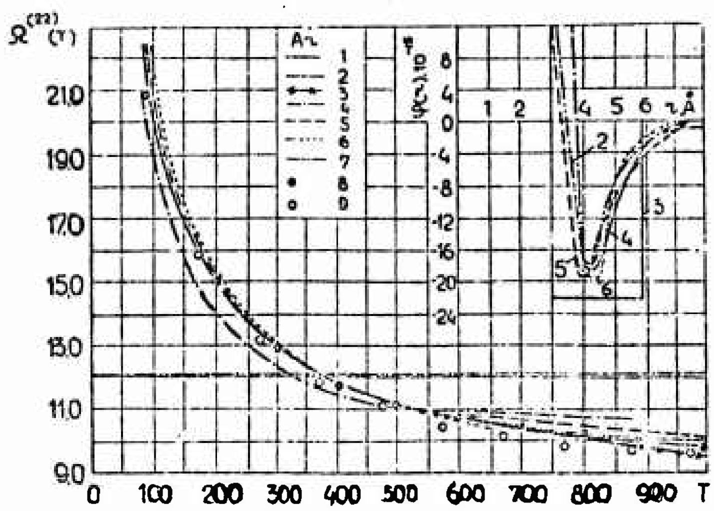

Figure 1. Collision integrals of heat transport and momentum transport $\Omega^{(2.2)}(T)$ of argon as a function of temperature T (°K): 1, Buckingham (epx-6) potential [1]; 2, Lennard-Jones (6-12) potential [1]; 3, Model of potential depression [8, 9]; 4, Gugenheim-McGlashan potential [7, 12]; 5, Kikhara[1] potential [7]; 6, Morse potential [11]; 7, Solid sphere model; 8, Experimental viscosity data [5]; 9, Experimental data on thermal conductivity [5]

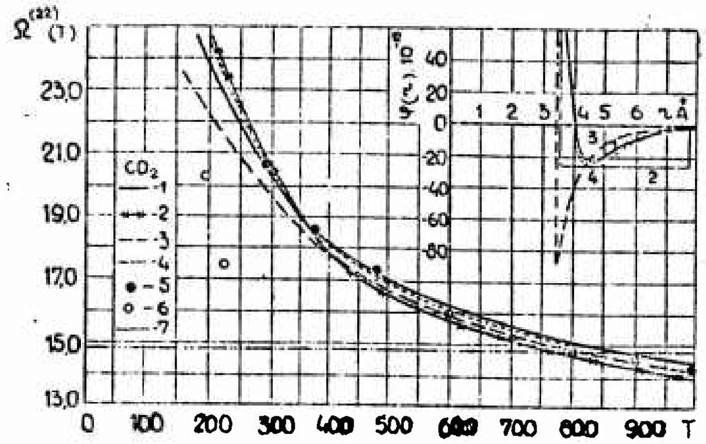

Figure 2. Collision integrals of momentum transport and heat transport $\Omega^{(2.2)}(T)$ of carbon dioxide as a function of temperature T (°K): 1, Lennard-Jones (6-12) potential [1]; 2, Square well model [8, 9]; 3, Sutherland model [1]; 4, Morse potential [11]; 5, Experimental viscosity data [5]; 6, Experimental thermal conductivity data [5]; 7, Solid sphere model.

---

[1] See p. 242

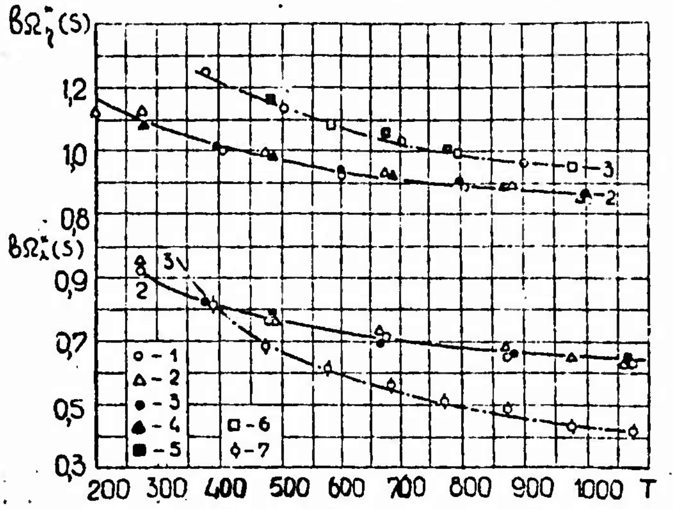

Figure 3. The quantities $b\Omega^*_\eta(S)$ and $b\Omega^*_\lambda(S)$ (cm) as a function of temperature T (°K) for diatomic and triatomic molecules: 1, N_2 (re = 1.094 Å); 2, CO (re = 1.282 Å); 3, O_2 (re = 1.278 Å); 4, H_2 (re = 1.260 Å); 5, N_2O (re = 1.186 Å); 6, SO_2 (re = 1.110 Å); 7, CO_2 (re = 1.162 Å).

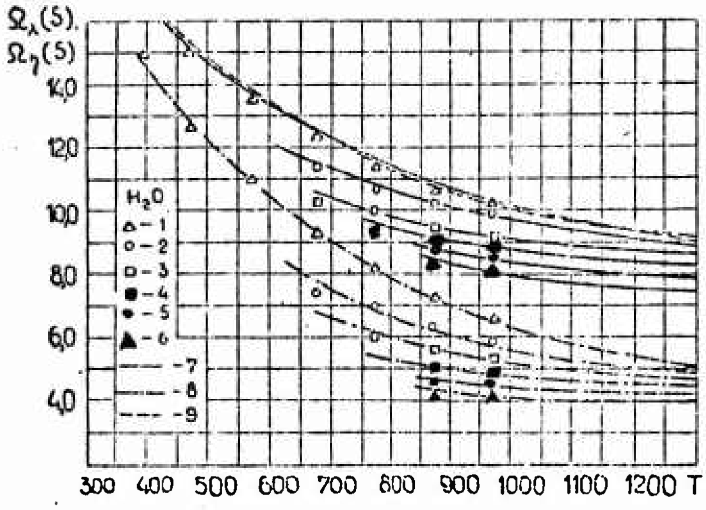

Figure 4. Collision integrals of heat transport $\Omega_\lambda(S)$ and momentum transport $\Omega_\eta(S)$ of water vapor as a function of temperature T (°K) calculated from equation (7) and Table 3. Experimental data in [5, 6]: 1, 1 bar; 2, 100 bar; 3, 200 bar; 4, 300 bar; 5, 400 bar; 6, 500 bar; 7, Collision integrals of momentum transport $\Omega_\eta(S)$; 8, Collision integrals of heat transport $\Omega_\lambda(S)$; 9, Stockmeyer potentials [10].

Footnotes

1. To p.240 Transliterated from the Russian -- Tr.

References

1. Hirschfelder, J.; C. Curtis,, and Byrd,R., *Molekulyarnaya Teoriya Gazov i Zhidkostey, (Molecular Theory of Gases and Liquids),* IL Press, Moscow, 1961.

2. Chapman, S. and T. Cowling, *Matematicheskaya Teoriya Neodnorodnykh Gazov, (Mathematical Theory of Nonhomogeneous Gases),* IL Press, Moscow, 1960.

3. de Bur, Ya., *Vvedeniye v Molekulyarnuyu Fiziky i Termodinamiku, (Introduction to Molecular Physics and Thermodynamics),* IL Press, Moscow, 1962.

4. Usmanov, A. G., *Sb. Teplovoye Modelirovaniye, (Collection: Heat Transfer and Thermal Modeling),* Academy of Sciences USSR Publishing House, 1959.

5. Vargaftik, N. B., *Spravochnik po Teplofizicheskim Svoystvam Gazov i Zhidkostey, (Handbook on Thermophysical Properties of Gases and Liquids),* Fizmatgiz Press, Moscow, 1963.

6. Vargaftik, N. B. and M. P. Vukalovich, *Teploenergetika,* No. 12, 1965.

7. Barker, I. A, W. Fock, and F. Smith, *Phys. Fluids,* Vol. 7, No. 6, 1964.

8. Sherwood , A. E. and J. M. Prausnitz, *J. Chem. Phys.,* Vol. 41, No. 2, 1964.

9. Holleran, E. M and H. M. Hulbert, *J. Chem. Phys.,* Vol. 19, p. 232, 1951.

10. Monchick, L. and E. A. Mason, *J. Chem. Phys.,* Vol. 35, No. 5, 1961.

11. Konowalow, D. D., M. H. Tayler, and J. O. Hirschfelder, *Phys. Fluids,* Vol. 4 p. 622, 1961.

12. Gyggenheim, F. R. Sand, and M. L. Mc Glashan, *Proc. Roy. Soc.,* Vol. 255, p. 1283, 1960.

13. Ivakin, B. A., B. A. Kalinin, and P. Ye. Suyetin, *Atomnaya i Molekulyarnaya Fizika, Trudy UPI, (Atomic and Molecular Physics, Proceeding of the UPI),* Sverdlovsk, 1965.

14. Paul and K. P. Srivastava, *Ind. Phys.,* Vol. 35, p. 465, 1961.

15. *Spravochnik Khimika, (Chemist's Handbook),* GITIKhL Press, Lenigrad-Moscow, Vol. 1, 1963.