TEMPERATURE DEPENDENCE OF THE TRANSFER COEFFICIENTS OF LIQUID HOMOLOGS AND THEIR MIXTURES

V. Z. Geller and S. F. Gorykin

UDC 536.2:532.133

A generalized method is proposed for the calculation of the thermal conductivity and viscosity of liquid hydrocarbons and their mixtures belonging to the same homologous series; its use requires no initial information other than the molecular mass.

In solving many problems of chemical technology, reliable data on the viscosity and thermal conductivity of liquid hydrocarbons and their mixtures are required. A series of methods for calculating λ and η are known [1], but most require the use of at least limited experimental information. In the present work, a generalized method is proposed for calculating the temperature dependence of the transfer coefficients of liquid homologs and their mixtures, without the need for any such initial information.

Thermal Conductivity. In [2], a generalized dependence was obtained for calculating the thermal conductivity of liquids in a state of saturation in the case of some hydrocarbons and petroleum fractions, on the basis of a single-parameter law of homologous states

$$\lambda_s = \sum_i \sum_j a_{ij} \tau^{-i} A^j. \tag{1}$$

However, data on the curve of saturated vapor pressure is required to determine A. In addition, the correlation in Eq. (1) is not intended for the calculation of λ for mixtures.

Analysis shows that, for hydrocarbons and their derivatives, within the limits of the homologous series, A and the critical parameters are unique functions of the molecular mass. In Fig. 1, as an example, such curves are shown for normal paraffins and olefins forming a unified system of curves with an error no greater than the error of the corresponding tabular data (the only exception is P_c for 1-pentane). It is evident from Fig. 1 that A decreases with increase in molecular mass in normal liquids, qualitatively repeating the trend of the dependence $P_c(M)$. Analogous curves are obtained for cyclic aromatic hydrocarbons, cyclopentanes, cyclohexanes, perfluoroparaffins, and other homologous groups.

The existence of a unique function A(M) within the framework of the homologous series offers the possibility of eliminating A from Eq. (1) and obtaining the correlation of the temperature dependence of the thermal conductivity with the molecular mass. For some homologous series of hydrocarbons, an analogous form of this dependence common to all of the series of hydrocarbons investigated is obtained using the experimental data of [3-5]

$$\lambda = \sum_i \sum_j a_{ij} (M/100)^{-i} \tau^j. \tag{2}$$

The coefficients of Eq. (2), the maximum error in the description of the experimental data, and the representative intervals of some homologs are shown in Table 1, from which it follows that the maximum discrepancy between the theoretical and experimental thermal conductivities is in the range 1.6-3.9%; this is within the limits of experimental error.

In some materials (n-hexane, n-tridecane, n-octadecane), systematic underestimation of the theoretical values of λ relative to the experimental data by 1.5-3% is noted.

In developing this method, data on the thermal conductivity undistorted by radiant heat transfer are used. Radiant corrections to the effective thermal conductivity in the reference literature and original studies are introduced by the method of [10] for results obtained by the plane-layer method and by the method of [11] for a cylindrical layer. Note, however, that data on the thermal conductivity of liquids at temperatures no higher than 473 K are used in the calculation, and therefore, in accordance with [11], where the influence of radiation on the effective thermal

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M. V. Lomonosov Odessa Technological Institute of the Food Industry. Translated from Inzhenerno-Fizicheskii Zhurnal, Vol. 58, No. 3, pp. 456-461, March, 1990. Original article submitted October 13, 1988.

0022-0841/90/5803-0335$12.50

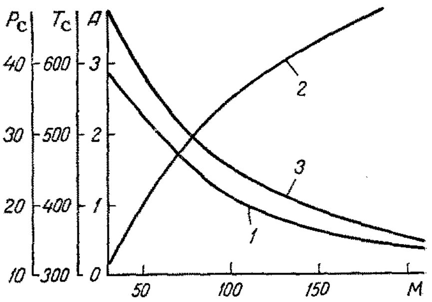

Fig. 1. Dependence of the critical parameters and Filippov number on the molecular mass for n-paraffins and n-olefins: 1) critical pressure, 10^5 Pa; 2) critical temperature, K; 3) Filippov number A.

TABLE 1. Coefficients of Eqs. (2) and (3)

Index	n-Paraffins (C_4—C_{20})		n-Olefins (C_2—C_{20})		Alkylbenzenes (C_7—C_{14})	
	a_{ij}	b_{ij}	a_{ij}	b_{ij}	a_{ij}	b_{ij}
00	—0,017	595,4	2,206	2647,3	8,224	—374215,1
01	1,398	347,8	—10,983	—96,6	—42,728	68569,1
02	—3,297	—27,7	19,600	—28,6	84,192	—1748,1
03	2,310	1,26	—11,647	3,34	—56,658	—78,4
10	0,848	—946,2	—7,866	—10414,3	—31,319	851577,6
11	—5,706	284,2	42,428	1098,8	165,975	—163710,1
12	11,958	53,8	—76,618	250,9	—322,962	5792,7
13	—8,235	—4,78	45,550	—21,3	213,679	92,0
20	—0,735	101,7	8,365	7685,5	38,709	—635740,8
21	4,965	222,3	—45,158	1645,8	—205,087	129882,1
22	—10,451	—68,1	81,391	—694,8	394,611	—5882,0
23	7,218	7,29	—48,339	43,55	—257,917	6,2
30	0,173	26,9	—1,765	—861,8	—15,348	155809,4
31	—1,148	—70,5	9,548	—1561,9	81,369	—33680,4
32	2,418	17,2	—17,204	390,9	—155,282	1825,6
33	—1,680	—1,64	10,214	—20,97	100,569	—19,4
Number of experimental points	249	104	128	39	121	39
Maximum relative error, %	3,9	4,4	1,6	5,6	3,4	6,4

conductivity of toluene was investigated in detail, the contribution of the radiant component of the heat flux is no more than 5-6% with a working-layer thickness of the liquid of 0.4-0.5 mm, and the error on taking it into account in determining the thermal conductivity is 0.5%.

Dynamic Viscosity. Using the above approach and the experimental data of [3, 6], equations of similar form are obtained for calculating the temperature dependence of the viscosity of n-paraffins, n-olefins, and aromatic hydrocarbons

$$\eta = \sum_i \sum_j b_{ij} (M/100)^i \tau^{-3j}. \tag{3}$$

The coefficients of the equations, the maximum errors of the description, and the representative intervals of the hydrocarbons are also shown in Table 1, from which it is evident that the maximum deviation of the theoretical dynamic viscosity from the experimental values is 4.4-6.4%. An error of more than 5% is noted at only 11 points.

The temperature interval of the experimental data used to obtain the coefficients of Eqs. (2) and (3) is $0.38 \leq \tau \leq 0.625$. However, for some hydrocarbons which have been more completely experimentally investigated, it is somewhat broader: $0.33 \leq \tau \leq 0.8$.

Transfer Coefficients of Hydrocarbon Mixtures. Note that no additional information other than the critical temperature and the structure of the liquid (in order to assign it to a definite homologous series and calculate its molecular mass) is required for the calculation of the temperature dependence of the thermal conductivity and dynamic viscosity according to Eqs. (2) and (3). This offers good prospects for using the proposed method to calculate the temperature dependence of the thermal conductivity and viscosity of liquid mixtures whose components belong to the

TABLE 2. Thermal Conductivity and Viscosity of n-Paraffin Mixtures

Coefficient	Interval of mixture components	Number of experimental points	Literature source	Maximum relative error, %
Thermal conductivity	$C_5—C_{16}$	158	[5,7]	4,6
Viscosity	$C_7—C_{16}$	114	[8,9]	3,9

TABLE 3. Comparison of Thermal Conductivity of n-Paraffins with Data on Their Mixtures of the Same Molecular Mass

n-Paraffin	T	λ	Mixture composition (*mole fraction)	λ_{mi}	$\frac{\lambda-\lambda_{mi}}{\lambda}\cdot 100$ %
n-Heptane	293,6	0,129	$0,5C_6$*	0,1289	0,1
	313,2	0,123	$0,5C_8$	0,1239	—0,73
	333,2	0,118		0,1187	—0,68
n-Octane	298	0,130	$0,25C_{11}$	0,1271	2,2
	314	0,125	$0,75C_7$	0,1240	0,8
n-Decane	334	0,120		0,1192	0,07
	293,8	0,135	$0,333C_7$	0,1342	0,6
	303,5	0,132	$0,333C_{11}$	0,1317	0,22
	313,4	0,131	$0,333C_{16}$	0,1302	0,6
	324,2	0,128		0,1275	0,2
	332,4	0,126		0,1258	0,2
n-Dodecane	294,6	0,141	$0,25C_{16}$	0,1367	3,0
	314,1	0,137	$0,75C_{11}$	0,1326	3,2
	333,9	0,133		0,1300	2,3
n-Tridecane	296,6	0,143	$0,1C_7$*	0,1390	2,8
	315,2	0,139	$0,299C_{11}$	0,1352	2,7
	333,4	0,136	$0,601C_{16}$	0,1311	3,6
n-Tridecane	259,9	0,143	$0,5C_{11}$	0,1390	2,8
	313,3	0,136	$0,5C_{16}$	0,1369	—0,7
	334,1	0,135		0,1325	1,9

same homologous series if the mixture is identified with some hydrocarbon of the same series with molecular mass M_{mi} and critical temperature $T_{cr.mi}$.

In the present work, Eqs. (2) and (3) are verified for a series of mixtures of liquid n-paraffins whose thermal conductivity was measured in [5, 7] and viscosity in [8, 9]. The molecular mass of the mixtures is determined here from the additive component of the composition, and the critical temperature from Eq. (4), written for the dependence $T_c(M)$ in the form

$$T_c = \sum_i a_i (100/M)^i, \tag{4}$$

where $a_0 = 931.1$; $a_1 = -569.9$; $a_2 = 204.6$; $a_3 = -26.93$.

The calculation results and comparison with experimental data may be seen in Table 2, from which it follows that the maximum discrepancy between the theoretical and experimental values is commensurate with the analogous indices for pure hydrocarbons.

Thus, the method here proposed may be used to calculate the temperature dependence of the thermal conductivity and viscosity of both individual homologs and their mixtures. This conclusion provides the basis for the assumption that, within the framework of homologous series, data on the transfer coefficients of an individual homolog may be interpreted as the corresponding properties of some mixture of the same molecular mass consisting of terms of the same series.

The known experimental results on the thermal conductivity and viscosity of the hydrocarbons and their mixtures permit the testing of this hypothesis. From the whole set of experimental data on λ and η for n-paraffin mixtures, points for mixtures with molecular mass coinciding, within limits of 1.5%, with the molecular mass of some n-paraffin are chosen. According to the above hypothesis, coincidence of the corresponding numerical values of the properties would be expected, and this is in fact seen. Tables 3 and 4 give some results of such comparisons. It follows from Table 3, for example, that the temperature dependence of the thermal conductivity of n-tridecane is identical to that of the binary mixture $C_{11} + C_{16}$ and the ternary mixture $C_7 + C_{11} + C_{16}$, and λ of n-octane is identical to that of the mixture $C_7 + C_{11}$. The maximum discrepancy observed is no more than 3.6%. This indicates that, within the framework of context of a homologous series, the experimental results on the thermal conductivity of liquid homologs may be interpreted as data on λ of mixtures of the same molecular mass whose components are also terms of the same

TABLE 4. Results of Comparing the Viscosity of n-Paraffins with Data on Mixtures of the Same Molecular Mass

n-Paraffin	T	η	Mixture composition (*mole fraction)	η_{mi}	$\frac{\eta-\eta_{mi}}{\eta}\cdot 100$ %
n-Decane	303	8366	$0{,}3C_7$*	8190	—2,1
	313	6960	$0{,}65C_{11}$	7129	—2,4
	333	5601	$0{,}05C_{16}$	5520	1,4
	353	4410		4462	—1,2
	363	4125		4045	1,8
	373	3630		3657	—0,7
n-Undecane	313	8710	$0{,}75C_{10}$	9000	—3,3
	333	6710	$0{,}25C_{16}$	6840	—1,9
	353	5370		5500	—2,8
n-Undecane	313	8710	$0{,}05C_7$*	8612	1,1
	333	6710	$0{,}9C_{11}$	6638	1,1
	353	5350	$0{,}05C_{16}$	5228	2,2
	373	4370		4244	2,9
n-Tetradecane	313	16000	$0{,}25C_{10}$	16000	0
	333	11500	$0{,}75C_{16}$	11700	—1,7
	353	8780		8900	—1,4
n-Pentadecane	303	22930	$0{,}05C_7$*	23320	—1,7
	313	19500	$0{,}05C_{11}$	19013	2,5
	333	13774	$0{,}9C_{16}$	13422	2,4
	353	10200		9989	3,0
	363	8888		8740	1,6
	373	7850		7740	1,4

homologous series. In the general case, solving the inverse problem of calculating the molecular mass of the mixture from the known composition of the mixture and M of the components, each homolog may be regarded as corresponding to an infinite set of mixtures, equivalent in their properties, with components which are also homologs of the same series.

Analogously, from the experimental data of [8, 9], mixture analogs of n-decane, n-undecane, and n-pentadecane (mixtures $C_7 + C_{11} + C_{16}$) and also n-undecane and n-tetradecane (mixtures $C_{10} + C_{16}$) are isolated in terms of the dynamic viscosity. A comparison of the corresponding data is shown in Table 4, from which it is evident that the discrepancy is nowhere more than 3.0%.

The given approach permits considerable expansion of the available information on the transfer coefficients of liquid mixtures and, in many cases, eliminates the need for laborious and expensive experiments.

NOTATION

λ, thermal conductivity of liquid at atmospheric pressure, W/m·K; η, dynamic viscosity of liquid at atmospheric pressure, $10^7\cdot(\mathrm{N\cdot sec/m^2})$; $\tau = T/T_c$, reduced temperature; T_c, critical temperature; $\pi = P/P_c$, reduced pressure; P_c, critical pressure; M, molecular mass; $A = 100\pi$ (at $\tau = 0.625$), Filippov number.

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THEORY OF HEAT AND MASS TRANSFER IN DISPERSE MEDIA

A. I. Moshinskii

UDC 536.242:532.546

The equations of heat and mass transfer in heterogeneous media obtained in [1] are generalized to the case of disperse-phase particles of arbitrary form.

In describing a series of processes in nature and engineering associated with heat or mass propagation in granular layers, the model of two coexisting continua is widely used, in the form

$$\varepsilon d_1 c_1 \left(\frac{\partial}{\partial \tau} + \mathbf{u}\cdot\nabla\right) T_1 = \lambda_* \Delta T_1 + \sigma (T_2 - T_1), \tag{1}$$

$$(1-\varepsilon) d_2 c_2 \frac{\partial T_2}{\partial \tau} = \sigma (T_1 - T_2),$$

which has been repeatedly derived by different methods [2-5]. It is written here for the case of heat transfer. The quasi-steady approximation, in which the coefficients λ_* and σ may be regarded as constants, has become the most popular in practical calculations. However, even in this simplest formulation, the solution of problems is obtained in a form that is cumbersome and difficult to interpret [3, 6, 7]. In addition, the coefficients λ_*, σ are by no means always constant [1, 5]. Therefore, there is a pressing need both for the investigation of different approximate methods of solving Eq. (1) [8, 9] and for theoretical understanding of the given system and the possibility of replacing it by simpler equations [1, 10].

As is known [1], two relaxational processes occur in a heterogeneous disperse system: inside the particles and in the intergranular channels. Depending on the relations between the corresponding relaxation times and the characteristic time of the problem specified from additional conditions, particular limiting models may be constructed. In [1], under the condition $\tau_1 \ll \tau_2$, approximate equations of the problem are formulated in the region of large and small times for a monodisperse system with spherical particles, and possible applications of the given scheme to practical problems including only one (in the terminology of [8], "equivalent") equation are discussed. Comparison with the experimental data in [11] shows a definite improvement in the agreement between theory and experiment in comparison with other models [1].

The basic advantage of describing the heterogeneous system under the condition that $\tau_1 \ll \tau_2$ reduces to the possibility of constructing closing relations for exchange heat (mass) fluxes by a relatively simple method: requiring that the surface temperature of the particle be equal to the corresponding temperature value in the carrier phase (in the macroscale L), while in the microscale ℓ ($\ell \ll$ L), this temperature may be assumed to depend only on the time. This markedly simplifies the calculations in comparison with the various traditional [5, 12] versions of cell models with an isolated particle.

1. General formulas for the heat-transfer characteristics of the particle—disperse-medium system are now obtained with the above-noted relaxational relations, with a negligibly small role of contact resistance to heat transfer. The problem in the region inside the particle is formulated as follows

$$\Delta T = \partial T / \partial t, \quad t = \lambda_2 \tau / d_2 c_2 l^2, \tag{2}$$

$$T|_{t=0} = T_0(x, y, z), \qquad T|_s = T_1(t), \tag{3}$$

where $\ell = \mathrm{V}^{1/3}$; V is the particle volume; s is its surface. Laplace transformation with respect to the time is now applied to Eq. (2) and the boundary condition in Eq. (3)

$$\Delta T^* = pT^* - T_0, \quad T^*|_s = T_1^*(p), \tag{4}$$

State-Institute-of-Applied-Chemistry Scientific and Productive Combine, Leningrad. Translated from Inzhenerno-Fizicheskii Zhurnal, Vol. 58, No. 3, pp. 461-470, March, 1990. Original article submitted October 4, 1988.