Influence of Intra-Molecular Conformational Transitions and some Physico-Chemical Quantities of Liquids on their Thermal Conductivity

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INFLUENCE OF INTRA-MOLECULAR CONFORMATIONAL TRANSITIONS AND SOME PHYSICO-CHEMICAL QUANTITIES OF LIQUIDS ON THEIR THERMAL CONDUCTIVITY

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It is shown that the thermal conductivity of various liquids can be described adequately by taking into account the influence of intra-molecular conformational transitions on the number of bimolecular collisions in the liquid phase. The proposed equations allow the calculation of this transport property at different temperatures.

1. INTRODUCTION

The thermal conductivity λ of liquids is an important physico-chemical characteristic of the liquid phase. The numerical value of λ is equal to the heat transfer across unit area per unit time. This transfer is being realized in the direction which is normal to the above unit area. The temperature gradient of the investigated liquid phase must be unit in this direction.

Basing on the assumption that the velocity of heat transfer equals to the sound velocity – c in the liquid phase of different chemical compounds, Bridgman [1] has proposed the following equation:

$$\lambda = 2kc/L^2 \tag{1}$$

Here k is Boltzmann constant and L is some average distance between the centres of neighbouring molecules, taking part in the process of heat transfer.

The dependence of λ on c was also found in [2]. It has the following form:

$$\lambda = A(dc)^{1/3}, \tag{2}$$

where d is density of a liquid and A is some constant for different liquids (when their absolute temperature T is constant).

The equation given below was proposed by Osida (see [3]):

$$\lambda = B(T_f/M)^{1/2} V^{-2/3}. \tag{3}$$

In Eq. (3) B is some constant for various liquids, M is molecular mass of a liquid, V is its molar volume, and T_f is its freezing point.

Here it is to be noted that the relative calculational errors of Eqs. (1)–(3) may reach as much as 50% [4]. Such errors occur in the case of associated liquids and some organic liquids with conformationally flexible molecules. Different semiempirical methods were worked out in order to avoid the above-mentioned errors. As a rule these methods are based on the use of various empirical addenda which describe the influence of molecular functional groups or numbers of atoms on the quantity λ (see for instance [5,6]). The relative calculational errors of these methods are within 3–10% [7].

However, the above methods do not take into account properly possible intermolecular interactions which exist among molecules, belonging to one of the liquid layers, whose plane is normal to the direction of heat transfer, and also the influence of intra-molecular conformational transitions on the process of heat transfer. The aim of the present work is to find an equation which describes the thermal conductivity of liquids on the basis of the above-mentioned circumstances.

2. THEORY

In the present work we shall consider all the molecules of the investigated liquid phase as spherical particles due to their fast mutual

reorientations. The value of T is supposed to be high enough for such a consideration to be valid. These particles have their effective molecular radius r and may vibrate around their equilibrium centres as some three-dimensional oscillators. Further, let us consider two parallel neighbouring molecular layers of unit area. The temperature gradient of the liquid phase is supposed to be normal to their planes. Let the temperature of the first layer be higher than that of the second one. We shall consider that the process of the heat transfer which exists between molecules of these layers is being realized by means of such bimolecular collisions which are responsible for the transfer of surplus kinetic energy from the first layer to the second one. Let the number of these collisions (per unit time) be equal to n. Each collision may be characterized by some average quantity ε of the surplus molecular kinetic energy which is passed from one molecule of the first layer to one molecule of the second one, when temperature gradient is unit. Hereafter we suppose that ε is constant for different liquids, when their temperatures (and also their pressures) are the same. Further, let the velocity of the considered heat transfer be equal to the sound velocity – c in the investigated liquid phase. In this case we may write the following equation for the quantity λ:

$$\lambda = \varepsilon n c. \tag{4}$$

Here it is to be noted that we suppose that the process of redistribution of the above surplus kinetic energy among the molecules of the first layer is essentially faster than that of heat transfer between the molecules of the considered layers. On this condition the above redistribution may be characterized as a quasi-equilibrium process. As we consider only such bimolecular collisions which pass the surplus kinetic energy from the molecules of the first layer to the molecules of the second one (see above) so we must take into account only the active "hot" molecules of the first layer. In its turn, it means that the number n in Eq. (4) will be equal to:

$$n = \chi N_a, \tag{5}$$

where N_a is the number of these active molecules per unit area and χ is some coefficient of proportionality which is supposed to be constant for different liquids, when their temperatures and pressures (P) are the same. Hereafter we shall suppose that the energy of these active

molecules is greater than or equal to some critical value E. The amplitude of their vibrations is sufficient in order to pass their surplus kinetic energy to the neighbouring molecules of the second layer. The number of N_a of the active molecules, whose energies are $\geq E$ may be easily found by means of Boltzmann statistics. In the two-dimensional case considered this gives (see [8]) the following equation:

$$N_a = N_s \exp(-E/kT), \tag{6}$$

where T is temperature of a liquid, and N_s is the total number of the molecules which are situated on each of the above-mentioned planes of unit area.

It has been shown in [9] that the quantity E may be expressed in the form

$$E = f\pi r^2 \sigma, \tag{7}$$

where σ is the surface tension of the liquid and f is some coefficient of proportionality which is constant for various liquids. Bearing in mind that the number N_s is equal to $1/\pi r^2$ and combining Eqs. (4)–(7), we have for the quantity λ:

$$\lambda = \varepsilon\chi c(\pi r^2)^{-1} \exp(-f\pi r^2\sigma/kT). \tag{8}$$

Equation (8) holds for liquids with conformationally rigid molecules. If each molecule of the investigated liquid has a certain number N of its energetically degenerate (or quasi-degenerate) conformational states, then the intra-molecular conformational transitions which occur among these states will lead to the corresponding increase in the number of its bimolecular collisions with neighbouring molecules. It has been shown in [10,11] that this increase may be described by means of the function $G(N)$ given below:

$$G(N) = (1 - \theta\ln N)^{-1}, \tag{9}$$

where the dimensionless constant θ does not depend on temperature and is equal to 0.05681.

Further, let Q_s be some physico-chemical quantity of the liquid phase which depends on the number of intermolecular interactions

(collisions) therein. As was also shown in [10,11] the following equation holds for this quantity:

$$Q_s = G(N)Q_r, \tag{10}$$

where Q_r is its value calculated for the hypothetical case in which there are not any intra-molecular conformational transitions among the above-mentioned conformational states of the molecules under consideration. Thus, the quantity Q_r must be calculated as if all the investigated molecules were conformationally rigid in the liquid phase.

Passing to liquids whose molecules are capable of such conformational transitions, and bearing in mind the above-mentioned interpretation of the function $G(N)$, we can write Eq. (8) in the form:

$$\lambda = \varepsilon \chi c (\pi r^2)^{-1} G(N) \exp(-f \pi r^2 \sigma / kT). \tag{11}$$

The quantity r is proportional to $V^{1/3}$, where V is molar volume of a liquid. Using this result and combining all the constants of Eq. (11), we obtain for λ the following equation:

$$\lambda = \tau c V^{-2/3} G(N) \exp(-\delta \sigma V^{2/3}/T), \tag{12}$$

where τ and δ are constant quantities for different liquids, when their temperatures (and pressures) are the same.

3. RESULTS AND DISCUSSION

The results of the use of Eq. (12) (at $T = 293.15\,\text{K}$ and $P = 0.1\,\text{MPa}$) are given in Table I. The values of c, σ and V needed for the calculation of the quantity λ were taken from [2,11–17]. For any investigated molecule its number N in Eqs. (9) and (12) is supposed (see [11]) to be equal to the total number of local minima on the surface of its full internal potential energy which arise on this surface under all possible internal rotations, changing the conformation of its non-hydrogen skeleton. Its non-hydrogen atoms are considered hereafter as nonequivalent; so that the conformations similar (for instance) to the two conformations of *n*-butane with its non-planar carbon skeleton are different.

TABLE I   The values of λ calculated by means of Eq. (12)

No.	Compound	N	$V \times 10^6$ $(m^3 mol^{-1})$	$\sigma \times 10^3$ $(N m^{-1})$	c $(m s^{-1})$	λ ($W m^{-1} K^{-1}$)	
						Calc.	Exper.
1	2	3	4	5	6	7	8
1	Acetone	1	73.4	24.02	1192	0.1598	0.1611
2	Carbon tetrachloride	1	96.4	27.04	958	0.1034	0.1029
3	Tetrachloroethylene	1	102.4	32.33	1066	0.1069	0.1097
4	Trichloroethylene	1	89.7	29.50	1049	0.1181	0.1161
5	1,2-Dichloroethane	3	78.7	32.57	1034	0.1353	0.1347
6	Diiodomethane	1	80.5	66.98	977	0.1010	0.0991
7	Bromoform	1	87.5	45.52	928	0.0987	0.1000
8	1-Bromopentane	3^3	124.0	27.41	981	0.1072	0.1082
9	2-Methylbutane	3	116.9	15.00	1035	0.1102	0.1116
10	n-Pentane	3^2	115.2	16.01	1008	0.1155	0.1158
11	n-Hexane	3^3	130.7	18.40	1098	0.1217	0.1217
12	n-Heptane	3^4	146.6	20.14	1162	0.1266	0.1277
13	n-Octane	3^5	162.7	21.76	1197	0.1299	0.1299
14	Acetic anhydride	2^2	93.9	32.65	1384	0.1609	0.1654
15	Methyl formate	2	61.6	25.15	1175	0.1856	0.1881
16	Ethyl acetate	2×3	97.8	24.30	1217	0.1466	0.1451
17	Pyridine	1	80.6	37.21	1445	0.1704	0.1695
18	Benzene	1	88.9	28.88	1326	0.1508	0.1477
19	Aniline	1	91.1	42.66	1656	0.1728	0.1733
20	Toluene	1	106.3	28.52	1328	0.1320	0.1341
21	Ethylbenzene	6	122.4	29.29	1338	0.1321	0.1321
22	Acetophenone	4	116.9	38.21	1496	0.1419	0.1458
23	Benzaldehyde	4	101.6	38.54	1479	0.1568	0.1536
24	Nitrobenzene	4	102.0	44.03	1473	0.1512	0.1516
25	Chlorobenzene	1	101.7	33.59	1287	0.1289	0.1284
26	Bromobenzene	1	105.1	35.82	1170	0.1128	0.1128
27	Iodobenzene	1	111.4	39.27	1113	0.1005	0.1007

Internal rotation of the end groups (such as methyl ones) does not cause an increase in N. Bearing in mind the above-mentioned arguments one can easily find that N is equal to 3 for 2-methylbutane, to 3^2 for n-pentane, to 3^3 for n-hexane and to 3^{n-3} for every n-alkane (n-C_nH_{2n+2}).

In the case of compounds with carboxyl groups: acetic anhydride, methyl formate and ethyl acetate (see Table I) the internal rotation around each of their chemical C–O bonds, belonging to their carboxyl groups, may be characterized by the presence of the two local minima of their internal molecular potential energy [18]. Thus, the numbers N of these compounds (see Table I) contain the multiplier 2^k, where k is the number of their carboxyl C–O bonds per one molecule.

For acetophenone, benzaldehyde and nitrobenzene the number of the minima which characterize the internal rotation of their plane groups: $-COCH_3$, $-COH$ and $-NO_2$ is equal to four [18]. Therefore, their numbers N are also equal to four. However, in the case of ethylbenzene the internal rotation around its $C_{sp}2$–$C_{sp}3$ bond leads to N which is equal to six [18].

The numbers N presented in Table I were used for the calculation of the quantity λ (together with the known experimental values of c, σ, and V). The comparison of the values of λ calculated by means of Eq. (12) and the corresponding experimental ones taken from [4,7,13,19–22] shows that, when the constants τ and δ are equal to 2.60×10^{-7} ($J\,K^{-1}\,mol^{-2/3}$) and 7.03×10^5 ($J^{-1}\,K\,mol^{2/3}$) respectively, Eq. (12) describes the quantity λ adequately. For the liquids presented in Table I the average absolute value (module) of its calculational error is equal to 1.0%.

The chemical compounds represented in Table II were investigated in order to establish the temperature dependence of the quantity τ (at $P = 0.1$ MPa). As τ is proportional to ε which, in its turn, is some

TABLE II The use of Eqs. (12) and (13) for the calculation of λ at different temperatures

No.	Compound	N	T (K)	$V \times 10^6$ $(m^3\,mol^{-1})$	$\sigma \times 10^3$ $(N\,m^{-1})$	c $(m\,s^{-1})$	λ $(W\,m^{-1}\,K^{-1})$ Calc.	Exper.
1	Helium	1	3.50	29.5	0.177	208	0.0244	0.0238
2	Argon	1	87.15	28.7	11.00	837	0.1294	0.1256
3	Oxygen	1	90.15	28.0	13.20	911	0.1428	0.1470
4	Carbon tetrachloride	1	253.15	92.0	31.94	1086	0.1066	0.1100
			273.15	94.2	29.49	1019	0.1050	0.1058
			333.15	101.4	22.15	842	0.0978	0.0965
5	Trichlorofluoro-methane	1	263.15	88.0	22.14	863	0.0950	0.0967
6	Chlorobenzene	1	273.15	99.8	35.97	1404	0.1335	0.1324
			333.15	105.8	28.82	1130	0.1232	0.1204
7	Bromobenzene	1	263.15	102.2	39.30	1311	0.1167	0.1168
8	Toluene	1	353.15	114.4	21.39	1094	0.1215	0.1209
			373.15	117.6	19.01	1015	0.1161	0.1163
9	Hexane	3^3	253.15	124.0	22.48	1321	0.1342	0.1354
			273.15	127.3	20.44	1231	0.1308	0.1320
			333.15	138.5	14.31	973	0.1153	0.1140
10	Propyl acetate	2×3^2	333.15	120.8	19.88	1079	0.1333	0.1324
			353.15	124.1	17.64	994	0.1268	0.1284

quantity of molecular kinetic energy passed by bimolecular collisions (see above), so one can expect that τ is some linear function of T:

$$\tau = aT + b, \tag{13}$$

where a and b are some constants which do not depend on the nature of the liquid phase.

The comparison of the values of λ calculated by means of Eqs. (12) and (13) and the corresponding experimental ones taken from [2,7,13,19,20] shows that, when the constants a and b are equal to 4.961×10^{-10} ($J\,K^{-2}\,mol^{-2/3}$) and 1.142×10^{-7} ($J\,K^{-1}\,mol^{-2/3}$) respectively, these equations describe the quantity λ at different temperatures adequately (see Table II). The values of V, σ and c needed for the use of Eq. (12) were taken from [2,12–15,20,22].

Here it is to be noted that for any liquid there is a lower temperature limit of the use of Eq. (12). It follows from the fact that the above-mentioned redistribution of the surplus kinetic energy does not take place in the liquid phase considered at low temperatures which are near to its freezing point. From the physical point of view it means that at such temperatures the velocity of the transfer of the surplus kinetic energy from the first layer to the second one is near (or equal) to the velocity of its redistribution among the molecules of the first layer. Therefore, Eqs. (6) and (12) do not hold at such temperatures.

Let us consider an example. Chlorobenzene has its freezing point at $227.95\,K$ [20]. Its low-temperature liquid phase considered at $T = 229.15\,K$ has the following values of σ, V and c: 41.21×10^{-3} ($N\,m^{-1}$), 95.7×10^{-6} ($m^3\,mol^{-1}$) and 1586 ($m\,s^{-1}$), respectively [14,15]. The value of λ calculated by means of Eqs. (12) and (13) is equal to 0.1326 ($W\,m^{-1}\,K^{-1}$). This value is less than the corresponding experimental one which equals 0.1404 ($W\,m^{-1}\,K^{-1}$) [19]. At the same time, when $T = 273.15\,K$, Eqs. (12) and (13) describe the thermal conductivity of chlorobenzene adequately (see Table II).

4. CONCLUSION

The following conclusions may be drawn. The intra-molecular conformational transitions, existing among degenerate (or quasi-degenerate)

molecular conformational states, influence on the thermal conductivity of liquids with conformationally labile molecules. Their action may be properly described on the basis of the function $G(N)$ (see Eq. (9)). If the liquid phase under investigation does not contain strong intermolecular hydrogen bonds (such as in water, glycerol etc.), Eqs. (12) and (13) allow one to calculate the quantity λ adequately and indeed more precisely than other equations proposed earlier.

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