VARIATION IN THERMAL CONDUCTIVITY OF ORGANIC SUBSTANCES IN MELTING PHASE CHANGES

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The thermal conductivity of 15 organic compounds near the melting phase change temperature is studied experimentally. An evaluation of the variation in thermal conductivity accompanying these phase changes is conducted.

During phase changes the kinetic coefficients of a substance, among them the thermal conductivity, change simultaneously with the variation in its structural parameters. A comparison of the thermal conductivity of the same substance in the liquid and solid states near the melting temperature is of definite interest. For this reason measurements of the thermal-conductivity coefficients of 15 organic substances were conducted in the regions of the melting temperatures and the phase change temperatures. The method of the measurements is described in [1]. The results of the experiment are presented in Table 1 and are partially published in [1-4]. Also in Table 1 data obtained by Filippov [5] are presented (marked by an asterisk). An increase in the thermal conductivity took place during crystallization in all cases. Near the transition points the thermal conductivity of the low-temperature modifications of the compounds studied was higher than that of the high-temperature phases. In a number of substances, such as acetone and n-hexane, the thermal conductivity in the solid state near the melting temperature depended considerably on the rate of freezing of the melt. Rapid freezing produced a phase having a higher thermal conductivity than slow freezing. An analogous effect was noted in stearic acid [5]. Evidently, in acetone the melt has a complicated structure, as indicated by an anomalous hump on the curve of the temperature dependence of

TABLE 1. Jumps in Thermal Conductivity during Melting Phase Changes

Substance	T_m, °K	T_{tr}, °K	Δ_m	Δ_{tr}	$p_m^{1/3}$	$^+p_{tr}^{1/3}$	$p_{tr}^{1/3}$
Tetrachloromethane	250,2	225,8	1,2	1,1	1,2	2	2,2
Benzene	278,5	—	1,6	—	2,7	—	—
Cyclohexane	279,5	186,1	1,07	1,6	1,4	2,2	3,3
Cyclohexanol	298,3	244,6	1,03	1,2	1,2	2,8	3,3
Toluene	178	—	1,4	—	3,0	—	—
o-Xylene	247	—	1,6	—	4,6	—	—
m-Xylene	219	—	1,6	—	4,6	—	—
n-Xylene	286	—	1,3	—	7,2	—	—
Mesitelene	228	—	1,45	—	3,7	—	—
n-Hexane	177,8	—	1,7 (2,1)	—	12(9,5)	—	—
n-Butyric acid	263	—	1,55	—	3,3	—	—
1,2-Dichloroethane	237	—	1,15	—	4	—	—
1,2-Dibromoethane	283	—	1,5	—	3	—	—
Thiophene	235	—	1,15	—	2	—	—
Acetone	176,5	—	1,1 (1,35)	—	3,4 (2,7)	—	—
Stearic acid*	342	—	1,35 (1,85)	—	545 (400)	—	—
n-Dibromobenzene*	359	—	1,6	—	6,8	—	—
Phenol*	314	—	1,02	—	4,2	—	—

Note: $\Delta_m \equiv (\lambda_s/\lambda_l)_{T_m}$; $\Delta_{tr} \equiv (\lambda^I/\lambda^{II})_{T_{tr}}$. The factor $+p_{tr}^{1/3}$ is calculated from Eq. (2); $p_{tr}^{1/3}$ is calculated from Eq. (3).

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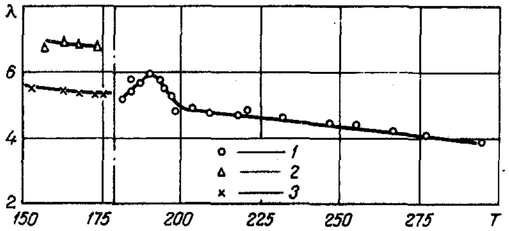

Fig. 1. Temperature dependence of thermal conductivity of acetone: dot-dash line: melting temperature; 1) liquid phase; 2) phase obtained by rapid crystallization of the melt; 3) slow crystallization of the melt. λ, (cal · cm · sec/deg) · 10^{-4}; T, °K.

the thermal conductivity of this compound shown in Fig. 1. The thermal conductivity of liquid acetone from melting to room temperature is shown in Fig. 1 for clarity. The thermal conductivity maximum in the region of 190°K corresponds to a minimum on the $C_p(T)$ curve and, according to [6], is explained by the quasicrystallinity of the structure of the liquid near T_m. It can be assumed that rapid cooling of the melt led to a freezing of this structure, as a consequence of which the solid phase obtained in this way has a higher thermal conductivity than that which is formed as a result of slow crystallization. In Table 1 the data in parentheses refers to the phase obtained by rapid crystallization. One should also point out the dependence of the thermal conductivity of the solid and liquid phases on the purity of the starting material in the region immediately adjoining the melting temperature, because of the formation of a double layer of the solid and liquid phases. The circumstance mentioned can lead to the appearance of a false thermal conductivity minimum [7, 8]. Therefore we are inclined to treat as anomalous the thermal resistance (negative thermal conductivity values) near T_m noted earlier in 1,2-dichloroethane [3].

The quasilattice model of the melt adopted in [9] will be used for an analysis of the magnitude of the jumps in thermal conductivity during melting phase changes. For solid bodies, when all the oscillatory modes are excited, $\lambda_s \sim C_{V_s} v_s l_s$, while in the case of liquids $\lambda_l \sim C_{V_l} v l_l$. Uncomplicated analyses, based for solid bodies on the Leibfried–Schleman equation and Lindeman's rule [10], and for liquids on the equation presented in [9], lead to a relation between the lengths l_s and l_l, depending only on the anharmonic nature of the solid phase and valid near the melting temperature:

$$\left[\frac{l_s}{l_l}\right]_{T_m} = \frac{10}{\gamma^2}. \tag{1}$$

Equation (1) signifies the upper limit of the ratio of l_s and l_l, since the Leibfried–Schleman equation refers to completely pure monoatomic bodies, while the highest numerical constant, equal to 120, obtained experimentally for face-centered metal lattices [11] was applied in using the Lindeman rule. In other words, the ratio (1) refers to the highest of the experimentally determined evaluations of the path length l_s at T_m. As for the lower limit of the ratio l_s/l_l, it is evident that it cannot be less than one. In molecular solid bodies, in addition to three-phonon processes, one should also consider anharmonism of a higher order and scattering caused by rotation of molecules or molecular radicals [1]. All these factors further decrease the path length, which near T_m is close to the intermolecular distance. It can therefore be considered that the jump in thermal conductivity at the melting point is mainly connected with a change in the effective rate of propagation of oscillations, since at T_m, $C_{V_l} \approx C_{V_s}$ [11]. As a result, $(\lambda_s/\lambda_l)_{T_m}$ is proportional to the ratio of the corresponding limiting frequencies $\omega_s \sim v_s/V^{1/3}$ and $\omega_l \sim v_l/V_{0l}^{1/3}$, and not to the ratio of the cubes of these frequencies, as given in Keyes' article [12]. Equating the free energies of the solid body and the liquid at the melting point, we have

$$\left(\frac{\lambda_s}{\lambda_l}\right)_{T_m} \approx \left(\frac{\omega_s}{\omega_l}\right)_{T_m} \approx \frac{1}{p^{1/3}} \exp\frac{S_m}{3K_B}. \tag{2}$$

Here $p^{1/3}$ is introduced in order to allow for the difference in the degree of ordering of the two phases, since the entropy of melting of molecular substances has not only an oscillatory but also a large configurational component: $S_{con} = K_B \ln p$. The latter in the simplest case of monoatomic bodies has the meaning of the so-called "collective entropy" [13].

It can be considered that the relation (2) it also applicable to the case of mechanical melting (according to Ubellode's terminology [11]), i.e., to conversion in the solid state from the crystalline phase I to the strongly amorphic plastic phase II, if it is assumed that $l^{I} \sim l^{II}$ at the melting point. On the other hand, if this assumption is not satisfied and the path length of the oscillations of the crystal $l^{I} \sim T^{-1}$ becomes close to that in the melt only at the temperature of the final breakdown of long-range order (true melting), then $(l^{I}/l^{II})_{T_{tr}} \simeq T_m/T_{tr}$. Therefore the ratio of the corresponding coefficients of thermal conductivity λ^{I} and λ^{II} at the temperature of the phase transition

$$\left(\frac{\lambda^{I}}{\lambda^{II}}\right)_{T_{tr}} \approx \frac{1}{p^{1/3}} \cdot \frac{T_m}{T_{tr}} \exp\left(\frac{S_{tr}}{3K_B}\right). \tag{3}$$

Evidently Keyes' approximation is valid only for the transition from the one crystalline phase I to the other true crystalline phase II. In this case, taking into account that the limiting frequency is $\omega_s \sim H_{sb}^{1/2}$ [14],

$$\left(\frac{\lambda^{I}}{\lambda^{II}}\right)_{T_{tr}} \approx \left(\frac{H_{sb}}{H_{sb}-H_{tr}}\right)^{3/2}. \tag{4}$$

The functions (2) and (3) are used in the present article to evaluate p, the degree of configurational changes during melting phase transitions, drawing on the results of the experiment on the relative jumps $(\lambda_s/\lambda_l)_{T_m}$ and $(\lambda^I/\lambda^{II})_{T_{tr}}$, as well as data on the entropies of melting and transitions [13]. It must be pointed out that Eq. (2) gives a lower estimate of the parameters p in accordance with the assumption, in place of (1), that l_s and l_l are close in value. It is seen from Table 1 that there is a correlation between the magnitude of the parameter p and the number of possible conformational changes during melting, i. e., the complexity of the structure and the number of free components of the molecule. For substances composed of globular molecules, such as tetrachloromethane, cyclohexane, and cyclohexanol, the values of p obtained are close to the theoretical values, if the rule of "collective entropy" is taken into account, i. e., if one sets p = e. In transitions connected with orientation melting for tetrahedric molecules, according to [13], p = 10, which is close to the value calculated from the experimental data by Eq. (2). As should be expected, the factor p increases in the case of crystals composed of monoatomic molecules, in which a considerable part of the heat of melting is expended in conformational changes.

NOTATION

λ_s, λ_l	are the coefficients of thermal conductivity of the solid and liquid phases;
λ^I, λ^{II}	are the coefficients of thermal conductivity of low-temperature and high-temperature crystalline modifications, respectively.
T_m	is the melting temperature;
T_{tr}	is the temperature of phase transition;
S_m	is the entropy of melting;
S_{tr}	is the entropy of phase transition;
ω_s, ω_l	are the limiting oscillation frequencies of molecules in solid and liquid phases, respectively;
H_{sb}	is the heat of sublimation;
H_{tr}	is the heat of transition;
p	is the ordering factor;
C_{V_s}, C_{V_l}	are the heat capacity at constant volume for solid and liquid states;
$C_p(T)$	is the temperature dependence of the heat capacity at constant pressure;
v_s, v_l	are the propagation rates of oscillations in solid and liquid states;
l_s, l_l	are the free path lengths of oscillations for solid and liquid states;
l^I, l^{II}	are the free path lengths of oscillations for low-temperature and high-temperature crystalline modifications, respectively;
V_{0l}, V_0	are the molar volumes in liquid and solid states;
γ	is the Gruneizen constant;
K_B	is the Boltzman constant.

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