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THE EFFECT OF POLYMORPHISM ON THERMAL CONDUCTIVITY

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The change in thermal conductivity as a result of phase transformations in the solid state, associated with various forms of polymorphism (reversible and irreversible transitions of modifications), is of considerable scientific and applied interest from the standpoint of molecular physics. The first observations in this area, carried out with inorganic substances, in particular with sulfur (⌒1), showed the presence of a substantial difference in the numerical value of the thermal conductivity of different polymorphic phases. A different temperature dependence of thermal conductivity was also established for different modifications. We are almost unaware of studies on thermal conductivity during phase transitions in solid organic substances, as well as during changes in the aggregate state of these substances (melting, crystallization). This is apparently connected with the considerable methodological difficulties that arise in setting up such experiments.

To clarify the effect of polymorphism on thermal conductivity, we used an apparatus developed by us that made it possible to carry out measurements with sufficient accuracy (the experimental error did not exceed 2%). As the object of investigation, *n*-dichlorobenzene was chosen. As is known from the literature, this substance has clearly pronounced polymorphism, and in particular a reversible transition at ~32°. The number of phases, according to different authors, varies from two to three (⌒2-5).

Measurements of the thermal conductivity of $n\text{-}C_6H_4Cl_2$ were carried out under stationary conditions by a relative method on an apparatus of the type of two coaxial cylinders, which was designed so as to make it possible to measure the thermal conductivity of the substance in both the solid and liquid states.

The apparatus (Fig. 1) was made of glass and consisted of a working cylinder *1* (inner diameter 3-4 mm), passing at the top into a funnel *2* for loading the substance. Along the axis of the working cylinder *1*, by means of a Teflon bushing *3*, a four-channel glass capillary *4* (outer diameter 1.5-2.0 mm) was centered, inside which were placed a copper-constantan thermocouple *5* (diameter 0.10 mm) and a nichrome heater *6* (diameter 0.10 mm). The length of capillary *4* was 8-10 cm less than the length of the working cylinder *1*, and thus the funnel formed during crystallization of the substance in the cylinder did not reach the

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upper end of the capillary by 2-5 cm. The working cylinder was enclosed in two jackets *7* and *8*, into which thermostated liquid from a Vöber thermostat was supplied. The temperature of the liquid in the apparatus was measured by means of thermocouple *9*, enclosed in capillary *10*. From above, the apparatus was hermetically closed by a spherical cap *11*, having outlet *12*, which through valve *13* was connected to a vacuum pump.

Thermocouples *5* and *9* were connected so that it was possible to measure both the temperatures on the walls of capillary *4* and working cylinder *1*, and the difference between these temperatures. The emf of the thermocouples was measured on a PPTN-1 potentiometer.

If a constant temperature is maintained on the walls of the working cylinder, and in the capillary the same amount of heat is released per unit time, which is achieved by maintaining a constant current supplied to heater 6, then under steady-state conditions the temperature difference between capillary 4 and the wall of the cylinder will depend only on the thermal conductivity of the substance placed between them (6):

$$t_1 - t_2 = \frac{Q \ln\left(\frac{d_2}{d_1}\right)}{\lambda l 2\pi}$$

(when

$$\frac{Q \ln\left(\frac{d_2}{d_1}\right)}{l 2\pi} = \text{const},$$

then $t_1 - t_2 = f(\lambda)$), where Q is the amount of heat released per unit time in the heater, l is the length of capillary 4, t_1 is the temperature on the surface of capillary 4, t_2 is the temperature on the surface of working cylinder 1, d_2 is the diameter of working cylinder 1, and d_1 is the diameter of capillary 4.

Fig. 1. Apparatus for measuring the thermal conductivity of substances in the solid and liquid states

Placing substances with different, previously known thermal conductivity into working cylinder 1, we find the dependence of Δt on λ for various temperatures. We then construct a graph of the dependence $\Delta t, \lambda$ in the form of isotherms, from which, subsequently, by measuring Δt for substances with unknown λ, we find the thermal-conductivity coefficient of the substance under investigation for the given temperature.

Fig. 2. Thermal conductivity of paradichlorobenzene

Figure 2: Fig. 2. Thermal conductivity of paradichlorobenzene

As calibration substances we selected substances over a wide range of thermal conductivity, such as water, glycerin, toluene, and air.

These substances have been investigated by various authors over a wide temperature interval, and the results of the investigations agree well with one another.

For those calibration substances whose thermal conductivity had been studied over an insufficiently wide temperature interval, we extrapolated the value of the thermal-conductivity coefficient to higher or lower temperatures, after first making sure that in the extrapolated temperature interval the calibration substance undergoes no phase transformations and, consequently, that the temperature coefficient of thermal conductivity remains constant.

For our investigation we took a very pure sample of n-dichlorobenzene. The measurements, whose results are presented in Fig. 2, were carried out on apparatuses of two variants (glass and metal) at temperatures from $+98$ to -40°C, i.e., the thermal conductivity of the substance was investigated in the liquid and solid states ($t_{\text{m.p.}} = 53^\circ$). Before the experiment the substance was placed in the working cylinder, where it was melted, and the thermal conductivity of the melt was measured; then rapid or slow crystallization was carried out and the thermal conductivity of the different solid phases was measured. Considering the thermal conductivity of liquid n-$C_6H_4Cl_2$, one may note a rather considerable increase in the thermal-conductivity coefficient with increasing temperature, which is characteristic of few substances (glycerin, etc.). Up to 98°

the thermal-conductivity curve undergoes no breaks. Depending on the methods of crystallization of the melt, the holding time at definite temperatures, etc., different modifications of n-$C_6H_4Cl_2$ are obtained, having different thermal conductivities.

In the solid state, we have found two stable modifications of n-$C_6H_4Cl_2$: the low-temperature α modification (Fig. 2, IV), possessing low thermal conductivity (29–$35 \cdot 10^{-5}$ cal/cm · sec · deg), and the high-temperature β modification (Fig. 2, III), possessing a higher thermal conductivity (37–$40 \cdot 10^{-5}$ cal/cm · sec · deg). The enantiotropic transition between these two modifications $\alpha \rightleftarrows \beta$, according to our measurements, corresponds to $\sim 32^\circ$. With rapid heating, the α modification could sometimes be superheated to 40° without causing a transition; the β modification can be supercooled to 30°.

Fig. 2. Thermal conductivity of paradichlorobenzene

The temperature of the $\alpha \rightleftarrows \beta$ transition can be determined accurately only with prolonged thermostating.

Besides the stable modifications, in n-$C_6H_4Cl_2$ we found the presence of metastable forms. On rapid cooling of the melt, the first metastable modification β' is formed (Fig. 2, II), existing in the temperature interval $+32 \div +53°$, which possesses a thermal conductivity of $63–70 \cdot 10^{-5}$ cal/cm · sec · deg. It was possible to trace the thermal conductivity of this modification down to +20°.

In the temperature interval $+32 \div +53°$, the β' modification passes, over 4-5 days, into the stable β form. This transition apparently proceeds through a number of metastable forms with a short lifetime, since it is sometimes possible to obtain thermal-conductivity curves which, in their value, lie between the curves of the β' and β modifications.

The transition from β to α proceeds through the metastable form α', possessing a thermal conductivity of $35–39 \cdot 10^{-5}$ cal/cm · sec · deg.

Thus, we were able to record clearly, in the temperature interval $-40 \div +53°$, two stable and two metastable modifications. At the same time, for different polymorphic forms not only does the magnitude of the coefficient of thermal conductivity change, but also the value of the temperature coefficient of thermal conductivity.

This may be of interest both for a deeper interpretation of the nature of transformations and for various thermophysical problems connected with the passage of heat through solid organic substances.

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