Thermal Conductivity of Some Organic Compounds at Their Melting Points

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The thermal conductivities of o-phenyl phenol, biphenyl, phenyl ether, *n*-octadecyl acetate and 1-octadecanol in the vicinity of their melting points in the solid and liquid phases were investigated. Experimental results reveal two changes in the thermal conductivity at the melting points of these compounds: a sudden drop in the thermal conductivity of the solid, when it is melted, is followed by a change in the relation of thermal conductivity to temperature.

HEAT TRANSFER by conduction involves the transfer of heat energy (molecular and atomic motions) by direct physical contact between molecules, atoms or their parts when they are at different temperatures.

The rate of heat transfer by conduction is proportional to the area perpendicular to the direction of heat flow and temperature gradient. The proportionality factor k is called the thermal conductivity. Its numerical value depends on the chemical composition (size, shape, inner structure of molecules or atoms) and physical state (structure) of the investigated material. Closer contact between molecules, atoms and their parts within the body of uniform chemical composition offers a higher possibility of transfer of molecular and atomic motions among neighboring molecules and results in higher thermal conductivity (*2, 3*).

Melting of a substance is followed by the transformation of a better organized and more compact solid structure into a looser arrangement of molecules or atoms in the liquid state. Accordingly, the thermal conductivity of liquids should be lower than that of respective solids. In general, this is true—bismuth is the only known deviation from this rule.

Most of the data on the thermal conductivity at the melting point are available for metals. This investigation is extended into the field of organic chemistry and involves the determination of conductivity at the melting points of these compounds: *o*-phenyl phenol, biphenyl, phenyl ether, *n*-octadecyl acetate, and 1-octadecanol.

They were acquired from the Eastman Kodak Company in the purest grade available.

The thermal conductivities were determined at several temperatures in the solid and liquid phases in the vicinity of the melting point and then extrapolated to the melting point.

METHODS OF DETERMINATION OF THERMAL CONDUCTIVITIES

The following methods were used to determine the conductivity in the vicinity of the melting point.

Liquid phase. The thermal conductivity in the liquid phase was determined by the hot-wire method as described by Cecil and Munch (*1*).

Solid phase. A modified hot-wire method was employed. An electrically heated element was placed in the center of a long cylindrical shape made of the solid compound whose thermal conductivity was to be determined. To secure even distribution of temperatures in the cylinder it was kept in the constant temperature bath. Thermocouples placed at the midsection of the cylinder at very accurately measured distances from the heating element indicated the distribution of temperatures at various distances from the heating element when thermal equilibrium was established for a given current passing through the element.

EXPERIMENTAL RESULTS

Experimental results for the compounds in question are shown in Table I. In all cases k is expressed in B.t.u./[hr. sq. ft. (° F./ft.)].

To illustrate the behavior of the thermal conductivities of investigated compounds in the vicinity of their melting

Table I. Thermal Conductivities of Compounds at Various Temperatures

Solid		Liquid		Melting Point, ° C.
t, ° C.	k	t, ° C.	k	
		o-Phenyl Phenol		
26.20	0.213	64.0	0.0876	57–58
30.82	0.210	77.0	0.0857	
33.86	0.203	88.8	0.0813	
36.00	0.196	97.5	0.0800	
43.00	0.192	114.2	0.0765	
45.42	0.195			
50.02	0.185			
		Biphenyl		
30.42	0.214	76.4	0.0814	69.5–70.5
32.58	0.205	89.1	0.0847	
36.10	0.194	97.0	0.0867	
44.25	0.190	106.0	0.0881	
49.07	0.185			
52.10	0.175			
58.94	0.175			
59.95	0.164			
61.09	0.168			
		Phenyl Ether		
4.0	0.196	45.0	0.0766	26–27
8.6	0.1895	56.5	0.0796	
11.0	0.186	64.2	0.0816	
12.5	0.176	76.1	0.0840	
14.4	0.178			
		n-Octadecyl Acetate		
3.25	0.227	40.5	0.1011	29–31
4.60	0.232	56.0	0.0975	
5.20	0.223	64.0	0.0954	
8.50	0.222	76.5	0.0942	
13.10	0.2105	89.8	0.0927	
16.50	0.208			
18.20	0.2015			
		1-Octadecanol		
30.85	0.2195	63.9	0.1055	56.5–58
34.31	0.210	76.2	0.1028	
39.21	0.189	84.5	0.1007	
42.01	0.1795	97.1	0.0988	
45.22	0.1685	104.0	0.0998	
49.12	0.1480			

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points, the experimental data for the last compound is represented graphically in Figure 1. The authors believe that the actual change of thermal conductivity at the melting point is represented by a continuous:


-type curve

Unfortunately, experimental data on thermal conductivity in the close vicinity of the melting point are not available, and direct extrapolation of each experimental curve to the melting point tends to reveal a sharp change in *k* at that point.

EVALUATION OF RESULTS

As was expected from theoretical consideration, there is a sudden drop in thermal conductivity for investigated organic compounds at their melting points. This drop amounts to about:

$$0.09 \frac{\text{B.t.u.}}{\text{hr. sq. ft. } \frac{{}^\circ\text{F.}}{\text{ft.}}}$$

for all compounds in question except 1-octadecanol for which it is only about 0.02.

The drop in thermal conductivity of the solid when it is melted is also accompanied by a change in the relation of thermal conductivity to temperature. The thermal conductivity of all compounds in the solid state decreases with temperature. This fact indicates the crystalline structure of the organic compounds in question (2).

The thermal conductivity of the compounds in the liquid state increases or decreases with temperature. So far, there is no appropriate explanation of this phenomenon.

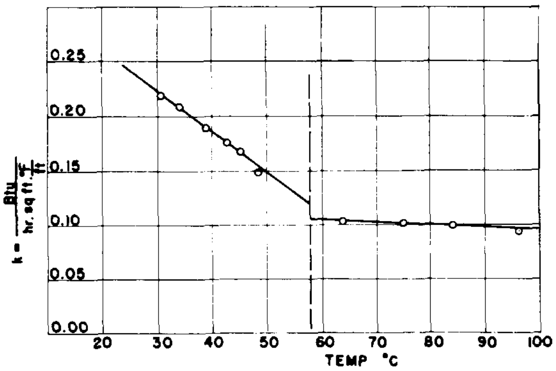

Figure 1. Thermal conductivity of 1-octadecanol in the vicinity of its melting point

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Enthalpy of Combustion and Related Thermodynamic Properties of Triethylenediamine

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The standard enthalpy of combustion of triethylenediamine (1,4-diazabicyclo[2,2,2]-octane) was determined by oxygen bomb calorimetry and found to be −970.8 kcal./mole at 298.15° K. with an r.m.d. of 0.09% and a standard deviation of 1.0 kcal./mole for four determinations. The standard functions of formation ΔH_f° (enthalpy), ΔF_f° (Gibbs free energy), and ΔS_f° (entropy) at 298.15° K. are −3.2 ± 2.2 kcal./mole, 57.4 ± 2.2 kcal./mole, and 203.5 ± 0.3 cal./(mole ° K.), respectively. The measured enthalpy is in good agreement with the enthalpies calculated on the basis of bond energies and the enthalpies of combustion of trimethylamine and triethylamine.

THE THERMODYNAMIC PROPERTIES of globular molecules have been the subject of much investigation and discussion in recent years (*2, 3, 17*). Current widespread interest in this topic derives mainly from the highly disordered solid state in which some of these molecules are capable of existing. For example, triethylenediamine (1,4-diazabicyclo[2,2,2]octane; formula, $N(CH_2CH_2)_3N$), with its highly symmetrical, almost spherical cage-like molecular structure and absence of external barriers to rotation, can readily reorient itself about its lattice site

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