Measurement of the Thermal Conductivities of Pentaerythritol, 1,1,1-Tris(hydroxymethyl)ethane, and Their Mixture in the Temperature Range from 20 °C to 200 °C

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The thermal conductivities of pentaerythritol (PE), 1,1,1-tris(hydroxymethyl)ethane (PG), and their mixture (PE + PG, mole ratio 50:50) were measured in the temperature range from 20 °C to 200 °C, by means of a calorimeter equipped with a thermistor. The solid−solid transition and melting temperatures were found to be 87 °C and 197 °C for PG and 135 °C and 190 °C for (PE + PG), and a solid−solid transition temperature of 187 °C was found for PE. The measured thermal conductivities of these substances were fitted in the temperature range from 20 °C to 200 °C to obtain the smoothed best-fit values. The uncertainties of the measured thermal conductivities were evaluated to be ±5.0, ±3.7, and ±5.0% for PE, PG, and (PE + PG), respectively.

Introduction

The thermal parameters of compounds, $CR^1R^2R^3R^4$, where R^s are methyl, methylol, amino, and carboxy, are of significance for the thermal storage of energy. Murrill and Breed[1] reported on the transition parameters of these compounds, by DSC. Zhang and Yang[2−5] measured the heat capacities and transition parameters for a series of polyalcohols each having a solid−solid transition, with an adiabatic calorimeter. Recently, Zhang and Xu[6] reported the thermal conductivities of neopentylglycol (NPG), 1,1,1-trihydroxymethylpropane (TMP), and their mixture (NPG + TMP, mole ratio 50:50) measured with a calorimeter equipped with a thermistor. As a part of the series of measurements of thermal conductivities for the potential substances for the thermal storage of energy, the paper reports the thermal conductivities of PE, PG, and (PE + PG, mole ratio 50:50) from 20 °C to 200 °C. In general, the uncertainty of the thermal conductivity of liquids reported in the literature for industrial design is about ±3−5%. The thermal conductivities measured with an uncertainty of ±5% in this work are satisfactory for the thermal storage of energy.

Experiment

Apparatus. The principles and constructions of the apparatus used in the study were described in a previous work by Zhang and Xu.[6] Basically, the apparatus is composed of a thermal conductivity cell equipped with a specially made small thermistor bead, an electrical bridge circuit, and a thermostated oil bath. In the apparatus, the rate of voltage change of the bridge, dV/dt, an easily measurable quantity, will be a linear function of the thermal conductivity, λ, of the materials. That is

$$\lambda = A - B\,\mathrm{d}V/\mathrm{d}t \qquad (1)$$

where A and B are the constants of the thermal conductivity cell at a certain temperature. By measuring the dV/dt values of reference substances, whose thermal conductivities are known, A and B can be obtained at 10 °C intervals. Thus, the thermal conductivity of the materials under investigation can be determined by the measurement of dV/dt of these materials.

Materials. Samples for this work were prepared in the following manner. PE (No. 1 Reagent Manufactory, Shanghai) was sublimated and recrystallized twice from distilled water. The purity of the PE sample was found to be 99.96% by chemical analysis. PG was used as received from Fluka company. To obtain the sample of (PE + PG), the two purified substances were mixed in a 50:50 mole ratio, heated to produce a clear liquid, and ground into a fine powder after the melted mixture was cooled to room temperature. Chemically pure decanol was purified by evaporating, and two analytically pure unpurified compounds, toluene and 1,1,2,2-tetrachloroethane obtained from No. 1 Reagent Manufactory, Shanghai, were used. Air, one of the reference substances used in the study, was dried.

Calibration. Due to the wide temperature range needed in the study, two thermistors, one 3 $k\Omega$ and the other 30 $k\Omega$ at room temperature, were alternatively used in the apparatus. Thus, two sets of calibration of the conductivity cell were made. One was for the temperature range from 20 °C to 90 °C, and the other was for the temperature range from 90 °C to 200 °C. Air, toluene, and 1,1,2,2-tetrachloroethane were used as reference substances to calibrate the cell from 20 °C to 90 °C, and air, decanol, and 1,1,2,2-tetrachloroethane were used from 90 °C to 200 °C. The thermal conductivities for each of the six reference compounds used in this study have been reported in the literature with an uncertainty of 2−5% measured by the absolute method, for example, that for toluene by Rastorguev and Pugach[7] and Mani and Venart,[8] that for decanol by Ganiev[9] and Jobst,[10] and that for 1,1,2,2-tetrachloroethane by Oshena.[11] The recommended thermal conductivities given by Orcharenko[12] for decanol and given by Vargaftik[13] for air were directly used in this study, while, for the other compounds, we obtained the reference

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Table 1. A ($\times 10^{-3}$ W·m^{-1}·K^{-1}) and B (V^{-1}·s·W·m^{-1}·K^{-1}), Constants of the Cell, and Experimental and Reference Values of λ ($\times 10^{-3}$ W·m^{-1}·K^{-1}) for the Reference Compounds from 20 °C to 90 °C

t	air		toluene		1,1,2,2-tetrachloroethane			
°C	λ_{exp}	λ_{ref}	λ_{exp}	λ_{ref}	λ_{exp}	λ_{ref}	A	B
20	25.50	25.65	134.6	135.3	115.9	114.9	278.8	17.69
30	26.27	26.42	132.2	132.9	113.9	113.1	276.5	17.82
40	27.02	27.15	129.7	130.4	112.1	111.3	274.2	17.94
50	27.82	27.95	127.2	127.9	110.2	109.4	271.6	18.06
60	28.59	28.72	124.9	125.5	108.4	107.6	269.5	18.21
70	29.32	29.45	122.5	123.1	106.6	105.8	267.5	18.38
80	30.12	30.25	119.9	120.6	104.7	103.9	265.2	18.53
90	31.88	31.02	117.5	118.2	102.9	102.1	261.5	18.49
σ	±0.35		±0.72		±0.88			

Table 2. A ($\times 10^{-3}$ W·m^{-1}·K^{-1}) and B (V^{-1}·s·W·m^{-1}·K^{-1}), Constants of the Cell, and Experimental and Reference Values of λ ($\times 10^{-3}$ W·m^{-1}·K^{-1}) for the Reference Compounds from 90 °C to 200 °C

t	air		toluene		1,1,2,2-tetrachloroethane			
°C	λ_{exp}	λ_{ref}	λ_{exp}	λ_{ref}	λ_{exp}	λ_{ref}	A	B
90	30.62	31.02	148.4	148.9	103.1	102.1	311.1	22.16
100	31.42	31.75	145.5	146.0	100.3	100.3	310.5	22.42
110	32.10	32.52	143.3	144.0	99.6	98.5	312.4	22.90
120	32.75	33.25	141.2	142.0	98.0	96.7	314.6	23.42
130	35.63	34.02	138.3	139.0	95.9	94.8	314.8	23.78
140	34.20	34.72	136.3	137.0	94.3	93.0	317.9	24.42
150	35.00	35.42	133.4	134.0	92.2	91.2	319.2	24.90
160	35.82	36.12	130.6	131.0	90.1	89.4	320.9	25.44
170	36.53	36.82	128.1	128.5	88.2	87.5	324.5	26.19
180	37.30	37.52	125.7	126.0	86.2	85.7	329.0	27.03
190	38.09	38.22	123.3	123.5	84.2	83.9	334.5	28.09
200	38.91	38.92	120.8	121.0	82.1	82.1	341.2	29.14
σ	±0.60		±0.56		±0.91			

values from the literature values by the smoothed best-fit method. The relative standard deviations of the individual literature values from the smoothed best-fit values were evaluated to be ±3.0%. The constants of the thermal conductivity cell at 10 °C intervals, A and B, obtained thus from 20 °C to 90 °C and from 90 °C to 200 °C are listed in Tables 1 and 2, respectively. To illustrate the reliability of the apparatus and the calibration, the experimental and reference values of λ for the six reference substances are also listed in Table 1 from 20 °C to 90 °C and in Table 2 from 90 °C to 200 °C. The standard deviations, σ, given in Tables 1 and 2 were evaluated by the formula $\sigma = \pm[(\lambda_{exp} - \lambda_{ref})^2/(n-1)]^{1/2}$, in which n is the number of experimental temperature points.

Thermal Conductivities of PE, PG, and (PE + PG, Mole Ratio 50:50)

The dV/dt values of PE, PG, and (PE + PG, mole ratio 50:50) were measured at 10 °C intervals from 20 °C to 200 °C. On the basis of these measured dV/dt values and the values of A and B, the constants of the cell at 10 °C intervals, the thermal conductivities of PE, PG, and (PE + PG) were determined and illustrated in Figures 1−3. From the figures, it can be seen that the change of the thermal conductivities with temperature over the temperature ranges of transition and melting appears to be curved. The temperatures at dλ/d$T = 0$ were taken as the transition and melting temperatures. Thus, the solid−solid transition and melting temperatures were found to be 87 °C and 197 °C for PG and 135 °C and 190 °C for (PE + PG), and a solid−solid transition temperature of 187 °C was found for PE. The solid−solid transition and melting

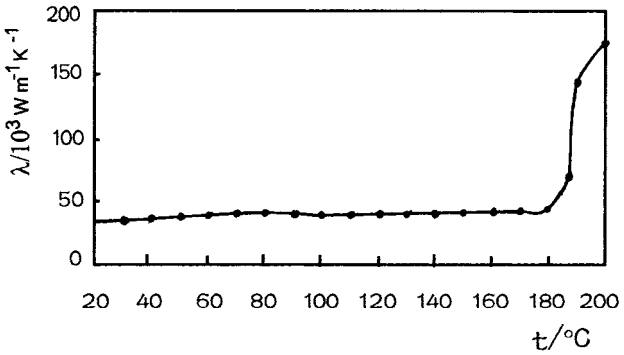

Figure 1. Thermal conductivity of PE from 20 °C to 200 °C.

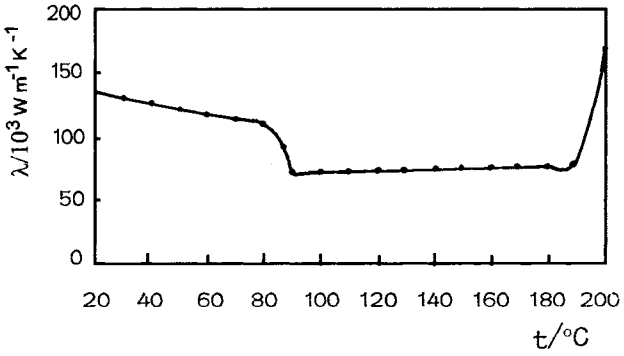

Figure 2. Thermal conductivity of PG from 20 °C to 200 °C.

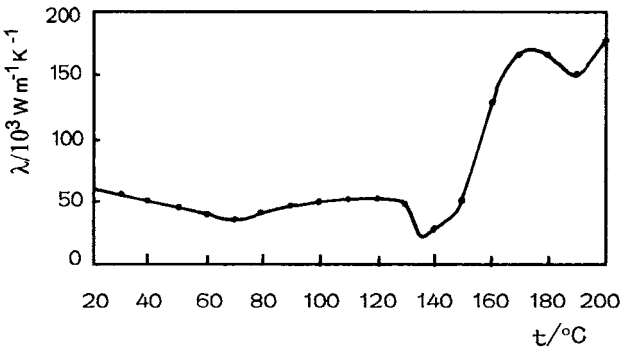

Figure 3. Thermal conductivity of (PE + PG, mole ratio 50:50) from 20 °C to 200 °C.

temperatures, obtained by this study, of PE and PG agreed with the results given by Murrill and Breed[1] from DSC within 2 °C. The experimental thermal conductivities of PE, PG, and (PE + PG) were fitted to a function of temperature to obtain the smoothed best-fit values. The experimental and smoothed λ values of these substances at 10 °C intervals are listed in Table 3. The relative standard deviations of the experimental λ values from the smoothed λ values are ±2.0, ±0.7, and ±2.0% for PE, PG, and (PE + PG), respectively.

Discussion

The experimental method used in this study is a relative method. Basically, the uncertainty of the thermal conductivities measured in the study depends on the accidental change in the experimental conditions and the uncertainty of the thermal conductivities of the reference substances used in the calibration of the apparatus. The former will result in the accidental uncertainty of the measurement, and the latter will bring the systematic uncertainty to the experimental results. The relative standard deviations of the experimental λ values from the smoothed λ values were evaluated to be ±2.0, ±0.7, and ±2.0% for PE, PG, and

Table 3. Thermal Conductivities[a] ($\times 10^{-3}$ W·m^{-1}·K^{-1}) of PE, PG, and (PE + PG, Mole Ratio 50:50)

t	PE		PG		(PE + PG)	
°C	λ_{exp}	λ_{ref}	λ_{exp}	λ_{ref}	λ_{exp}	λ_{ref}
20	34.4	35.4	134.7	134.7	58.6	58.7
30	35.4	35.9	130.7	130.7	53.7	53.6
40	36.3	36.4	126.7	126.7	48.6	48.6
50	37.3	36.9	122.6	122.6	43.6	43.5
60	38.3	37.3	118.6	118.6	38.4	38.4
70	39.2	37.8	114.6	114.6	33.2	33.3
80	40.3	38.2	110.4	110.4	39.6	41.3
87			90.5[a]			
90	39.6	38.7	71.5	71.2	49.3	47.5
100	37.7	39.1	71.8	71.8	51.7	51.3
110	38.3	39.5	72.4	72.4	50.7	52.1
120	38.9	39.9	73.0	73.0	49.6	51.6
130	39.6	40.3	73.5	73.7	48.5	48.1
135					20.2[a]	
140	40.2	40.7	74.2	74.3	28.1	
150	40.9	41.4	74.7	74.9	50.2	50.7
160	41.7	41.1	75.3	75.5	132.6	131.2
170	42.0	41.7	75.6	76.6	169.0	170.5
180	43.0	42.1	76.8	76.8	168.9	168.5
187	65.4[a]					
190	142.7	142.7	77.8	77.4	151.0[b]	
197			130.5[b]			
200	177.1	177.1	168.9		180.5	180.5
σ	±1.0		±0.5		±1.0	

[a] Thermal conductivity at temperatures of transition. [b] Thermal conductivity at melting temperatures.

(PE + PG), respectively. Combining those values of uncertainty with the systematic uncertainty of ±3.0% resulted in the calibration of the apparatus. We evaluated that the uncertainty of the thermal conductivities measured in this study was ±5.0, ±3.7, and ±5.0% for PE, PG, and (PE + PG), respectively.

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