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RESEARCH NOTES

AN APPARATUS FOR MEASURING THERMAL CONDUCTIVITY OF LIQUIDS UNDER HIGH PRESSURE

Wang Congyu(王琮玉)*and **Yang Menglin**(杨孟林)
Thermochemistry Institute, Northwestern University, Xian 710069, China

Wang Jicheng(王季澄) and **He Yin**(贺寅)
Research Institute of Petroleum Exploration Development, Beijing 100083, China

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We have reported a method for measuring the thermal conductivity of liquids under high pressure previously [1, 2]. Such data are necessary for improving the technologies such like processing as acidity, pressure cracking, thermal exploitation of petroleum, *etc.*

An apparatus has thus been constructed, as shown schematically in Fig. 1, to measure the thermal conductivity of liquids under pressure up to 25 MPa and temperature ranging from 150 to 250 ℃. The thermal conductivity cell is cylindrical in form, 35mm in length and 25mm in inner diameter. The sample is poured into the cell through the sample transmission tube. The vacuum pump is used to clear the cell.

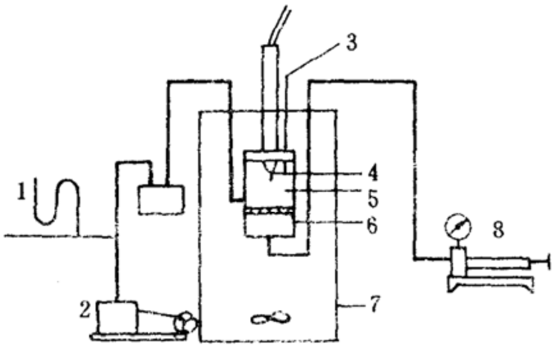

Figure 1 Experimental apparatus

1－vacuum gauge; 2－vacuum pump;
3－sample transmission tube;
4－thermistor; 5－thermal conductivity cell;
6－isolator; 7－oil thermostat;
8－pressure gauge

As the crude oils contain water and electrolytes, they are electro-conductive, and hence, the conventional "hot-wire" method is not applicable. A specially-made small bead-in-glass thermistor is used as the heating element. It is immersed in the liquid to be investigated. An unbalance thermistor bridge has been designed as shown in Fig.2.

when a steady current passed through the thermistor, the rate of dynamic temperature rise dT/dt ($S_i = dV/dt = dV/dT \cdot dT/dt$) has been found to be related to the

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* To whom correspondence should be addressed.

thermal conductivity, λ, of the liquid to be tested as [1].

$$\lambda = A - B \cdot S_i \tag{1}$$

where A and B are instrument constants determined by reference liquids, while S_i can be measured with the circuit shown in Fig. 3. The time duration for measuring S_i is 1 second.

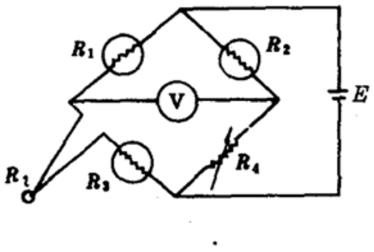

Figure 2 Thermistor bridge

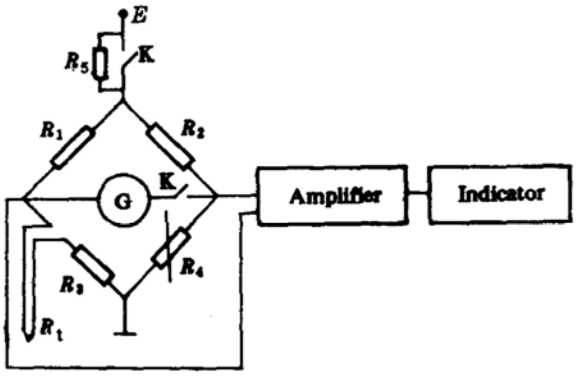

Figure 3 Circuit for measuring S_i

Eight liquids, *i. e.* ethanol, *n*-propanol, *n*-butanol, propanol-2, *n*-octane, *n*-heptane, octene-1 and *n*-hexane were used as the reference liquids, of which the thermal conductivities are known, to calibrate the experimental apparatus. Fig.4 shows the typical plot of λ vs. S_i. Treating the corresponding data by least square, we have obtained the equation:

$$\lambda = 413.70 - 0.177 S_i \tag{2}$$

Hence, λ can be calculated simply from the measured S_i. Table 1 shows the comparisons between the predicted values by Eq.(2) and the corresponding literature values. The average deviation is within 2%.

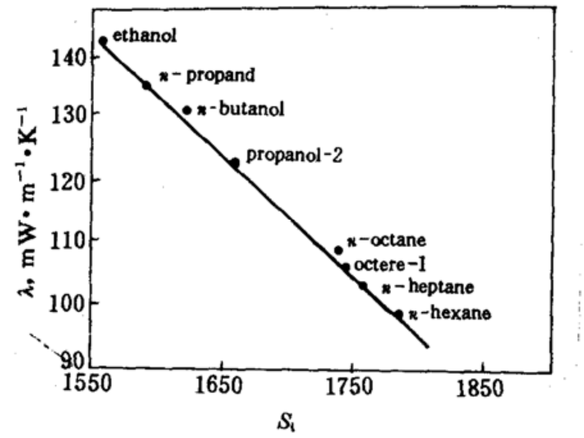

Figure 4 The plot of λ versus S_i (250 ℃ , 25MPa)

Table 1 Comparisons between the experimental and the literature values of λ (250 ℃, 25MPa)

Sample	S_i	λ, mW · m^{-1} · K^{-1}		dev., %
		exp.	lit.	
n-hexane	1784.8	97.8	98.0 [3]	0.3
n-heptane	1758.0	102.5	101.7 [4]	0.8
n-octane	1738.9	105.9	109.3 [5]	3
propanol-2	1645.2	122.5	122.1 [6]	0
n-butanol	1607.6	129.2	130.7 [7]	1
n-propanol	1571.3	135.6	134.1 [8]	1
ethanol	1537.8	141.5	142.3 [9]	0.5
octene-1	1754.0	103.4	101.8 [10]	2

The measuring results and working equations at various temperatures and pressures are summarized in Table 2.

Table 2 Measuring results and working equations at various temperatures and pressures

	5MPa, 150 ℃				5MPa, 175 ℃				5MPa, 200℃			
	S_i	λ,mW · m^{-1} · K^{-1}		dev.	S_i	λ,mW · m^{-1} · K^{-1}		dev.	S_i	λ,mW · m^{-1} · K^{-1}		dev.
		lit.	exp.	%		lit.	exp.	%		lit.	exp.	%
n-hexane	3683.2	97.0	97.0	0	4050.8	92.8	93.6	1	2628.8	87.0	87.0	0
n-heptane	3603.8	102.0	101.5	0.5	3978.1	98.9	97.7	1	2578.6	91.2	92.3	1
n-octane	3553.2	105.5	104.4	1	3910.2	101.8	101.6	0	2538.2	98.0	96.5	2
propanol-2	3137.8	122.0	128.2	5	3556.0	118.4	121.5	3	2333.5	114.2	118.0	3
n-butanol					3478.4	130.1	125.9	4	2275.3	125.6	124.0	1
n-propanol	3020.2	135.2	134.9	0	3406.8	131.0	129.9	1	2235.0	127.8	128.3	1
ethanol	2929.5	144.1	140.6	3	3337.1	135.5	133.8	2	2167.9	136.6	135.3	1
octene-1					3938.3	99.5	100.0	0	2560.8	95.2	94.2	1
Working equation	$\lambda = 307.63 - 0.0572S_i$				$\lambda = 321.73 - 0.0573S_i$				$\lambda = 362.30 - 0.105S_i$			

	5MPa, 225 ℃				5MPa, 250 ℃				15MPa, 150 ℃			
	S_i	λ,mW · m^{-1} · K^{-1}		dev.	S_i	λ,mW · m^{-1} · K^{-1}		dev.	S_i	λ,mW · m^{-1} · K^{-1}		dev.
		lit.	exp.	%		lit.	exp.	%		lit.	exp.	%
n-hexane	1545.6	81.5	84.3	3	1875.3	73.0	76.5	4	3598.3	103.5	102.6	1
n-heptane	1509.6	90.5	90.4	0	1856.0	81.8	80.1	1	3530.8	109.0	106.8	2
n-octane	1487.2	94.3	94.2	0	1818.9	90.5	87.0	4	3487.7	117.6	109.4	3
propanol-2									3086.0	127.8	134.1	5
n-butanol	1346.6	120.5	117.8	2	1666.4	115.0	115.4	0.3				
n-propanol	1319.3	124.5	122.2	2					2974.7	141.0	140.9	0
ethanol	1235.4	132.0	136.4	3					2889.3	150.7	146.2	3
octene-1	1449.2	90.9	92.1	1	1838.2	86.4	83.4	4				
Working equation	$\lambda = 343.97 - 0.168S_i$				$\lambda = 425.35 - 0.186S_i$				$\lambda = 323.79 - 0.0615S_i$			

Table 2 (Continued)

	15MPa, 175℃				15MPa, 220℃				15MPa, 225℃			
	S_i	$\lambda,\mathrm{mW\cdot m^{-1}\cdot K^{-1}}$		dev.	S_i	$\lambda,\mathrm{mW\cdot m^{-1}\cdot K^{-1}}$		dev.	S_i	$\lambda,\mathrm{mW\cdot m^{-1}\cdot K^{-1}}$		dev.
		lit.	exp.	%		lit.	exp.	%		lit.	exp.	%
n-hexane	2957.0	99.5	100.6	1	2572.5	96.0	95.4	1	1497.6	92.0	93.9	2
n-heptane	3904.8	106.1	104.0	2	2525.2	100.1	100.6	0	1474.8	99.6	99.3	0.3
n-octane	3848.0	109.0	107.7	2	2488.3	106.0	104.6	2	1456.0	104.0	102.0	2
propanol-2	3504.6	124.8	129.8	4	2301.7	121.8	124.9	3	1364.0	118.4	119.7	1
n-butanol	3435.2	136.0	134.2	2	2240.0	132.2	131.6	1	1328.2	128.2	128.4	1
n-propanol	3362.0	137.6	138.9	1	2221.4	134.3	133.7	0	1296.3	131.3	132.8	1
ethanol	3282.8	146.9	144.0	2	2142.8	143.1	142.2	1	1265.0	139.0	138.8	0
octene-1	3868.2	105.8	106.4	0	2506.6	102.4	102.6	0	1467.0	98.8	99.5	1
Working equation	$\lambda=253.32-0.0644S_i$				$\lambda=375.76-0.109S_i$				$\lambda=382.96-0.193S_i$			

	15MPa, 250℃				25MPa, 150℃				25MPa, 175℃			
	S_i	$\lambda,\mathrm{mW\cdot m^{-1}\cdot K^{-1}}$		dev.	S_i	$\lambda,\mathrm{mW\cdot m^{-1}\cdot K^{-1}}$		dev.	S_i	$\lambda,\mathrm{mW\cdot m^{-1}\cdot K^{-1}}$		dev.
		lit.	exp.	%		lit.	exp.	%		lit.	exp.	%
n-hexane	1828.0	90.0	89.4	1	3529.1	109.8	110.3	1	3884.8	106.6	107.3	1
n-heptane	1798.3	93.5	94.6	1	3474.0	115.1	113.6	2	3832.0	112.5	110.8	2
n-octane	1774.6	100.0	98.7	1	3430.0	123.1	116.2	1	3786.8	115.3	113.7	2
propanol-2	1687.5	114.6	115.3	0.6	3036.2	132.7	139.8	5	3453.8	130.0	135.3	4
n-butanol	1633.7	124.5	123.1	1					3393.0	141.2	139.3	2
n-propanol	1599.0	128.3	129.1	0.5	2932.4	146.0	146.0	0	3318.7	142.8	144.1	1
ethanol	1569.4	134.0	134.2	0	2848.5	156.0	151.1	4	3240.9	152.1	149.2	2
octene-1	1790.0	95.6	96.0	0					3812.2	111.2	110.9	0
Working equation	$\lambda=405.7-0.173S_i$				$\lambda=321.83-0.0599S_i$				$\lambda=359.63-0.069S_i$			

	25MPa, 200℃				25MPa, 225℃			
	S_i	$\lambda,\mathrm{mW\cdot m^{-1}\cdot K^{-1}}$		dev.	S_i	$\lambda,\mathrm{mW\cdot m^{-1}\cdot K^{-1}}$		dev.
		lit.	exp.	%		lit.	exp.	%
n-hexane	2507.1	102.5	104.3	2	1467.7	100.0	100.5	0.5
n-heptane	2482.8	107.5	107.0	0.4	1444.4	106.8	106.0	0.5
n-octane	2454.9	113.0	110.0	3	1430.0	110.2	108.2	2
propanol-2	2260.2	127.4	131.2	3	1333.3	124.9	127.2	2
n-butanol	2208.3	137.8	136.8	0.5	1305.5	134.3	132.8	1
n-propanol	2184.2	139.7	139.5	0	1274.3	136.9	139.0	2
ethanol	2104.4	148.8	147.7	1	1244.0	146.9	145.0	1
octene-1	2473.6	107.8	108.0	0	1434.0	104.8	107.2	2
Working equation	$\lambda=377.42-0.109S_i$				$\lambda=392.57-0.199S_i$			

The measured results for toluene have also been compared with literature values [11] in Table 3. The maximum deviation is 4%.

Table 3 Comparisons between the experimental and literature values of λ of toluene (20MPa)

T, ℃	λ, $mW \cdot m^{-1} \cdot K^{-1}$		dev., %
	exp.	lit. [11]	
150	112.5	112.4	0.1
175	110.2	107.8	2
200	106.2	103.6	2
225	104.0	100.2	4
250	100.5	97.2	3

Since this is a comparative method, the accuracy will depend on the uncertainty of the thermal conductivity value of reference liquid. As the measuring time duration is only 1 sec, and the temperature rise is 0.3−0.5℃, the influence of radiation and convection would be negligible.

The stability of the thermistor is not very well, and the change in resistance is estimated as 0.1% a year. If obvious change in thermistor resistance was appeared the apparatus should be calibrated again.

NOMENCLATURE

A	instrument constant
B	instrument constant in Eq.(1)
B_T	isothermal compression coefficient
m	molecular mass
p	pressure, MPa
R	resistance
S_t	change rate of bridge voltage, dV/dt transformed into frequency number
T	temperature, K
t	time, s
λ	thermal conductivity, $mW \cdot m^{-1} \cdot K^{-1}$
$\lambda_{exp.}$	experimental values of thermal conductivity, $mW \cdot m^{-1} \cdot K^{-1}$
$\lambda_{lit.}$	literature values of thermal conductivity, $mW \cdot m^{-1} \cdot K^{-1}$

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