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Experimental determination of the isobaric specific heat capacities of multicomponent vapors up to temperatures of 600 K

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Abstract

A new flow calorimeter has been constructed for the determination of the isobaric specific heat capacities of multicomponent vapors. It can yield reliable values over a wide temperature range with deviations of less than 1.0%. Using this apparatus, the isobaric specific heat capacities of benzene–cyclohexane, benzene–carbon tetrachloride and ethanol–carbon tetrachloride vapor mixtures have been determined under atmospheric pressure and up to 600 K. For polar mixtures, a slightly negative excess heat capacity was found, and this is explained.

INTRODUCTION

Specific heat capacities have mostly been measured for simple substances at low temperatures (often up to 373 K). Only Sinke and Vries [1] and Dong et al. [2] have measured multicomponent vapors at low temperatures, using a glass flow calorimeter. Above 473 K, heat capacities have rarely been measured for mixtures. The aim of the present work was to develop an apparatus for the determination of the specific heat capacities of vapors at high temperatures.

The basis for the experimental determination of the isobaric specific heat capacity C_p is the equation $C_p = (\partial H/\partial T)_p$. Because the differential quotients are not measurable, they are replaced by difference quotients, i.e. $C_p = (\Delta H/\Delta T)_p$. Thus, the isobaric specific heat capacity represents an average heat capacity which, when considered over the temperature difference ΔT, may deviate from the true value.

In the apparatus, the fluid to be investigated is heated isobarically in a virtually adiabatic flow calorimeter. The temperature change of the flowing

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fluid, caused by heating the calorimeter, is determined. From the values of the power input P, the fluid flow rate F, and the temperature change ΔT of the fluid, the isobaric heat capacity C_p can be calculated from eqn. (1)

$$C_p = P/F\Delta T \tag{1}$$

However, heat loss is unavoidable at high temperatures. The effect of this on the accuracy of the measured heat capacities has been discussed by McCullough and Waddington [3], White and Downes [4] and Fortier et al. [5]. For vapor flow calorimeters, measurements can be made at various flow rates, using, for correction, the equation

$$C_p = C_p^* + b/F \tag{2}$$

where C_p is the actual heat capacity to be determined, C_p^* is the apparent heat capacity, F is the vapor flow rate, and b is a correlating factor.

EXPERIMENTAL

Materials

The analytical reagents, benzene, cyclohexane, ethanol and carbon tetrachloride (Shanghai Chemical Corporation), were all purified by fractional distillation using a column 1.5 m long, packed with glass rings. All these purified reagents were stored over 5 Å sieve sorbent. The densities and refractive indices of the reagents agreed well with those reported in the literature [6].

Calorimeter

A new flow calorimeter and flash boiler were designed and constructed; their schematic diagrams are shown in Figs. 1 and 2, respectively. The calorimeter is made from a 3 mm stainless steel tube, with a red copper shell. The joints are all connected by argon arc-welding and silver welding. Therefore, although the calorimeter is operated mainly under atmospheric pressure, it can be used up to 50 MPa. The flash boiler is made of stainless steel. The temperature of the vaporizing chamber can be controlled and maintained precisely. The dish-shaped plate rotates at a high speed that can be regulated.

The calorimeter is placed in an air bath whose temperature can be controlled to ±0.1 K at 600 K over 30 min, and to ±0.5 K over 2 h. The liquid to be investigated is pumped into the flash boiler at a selected flow

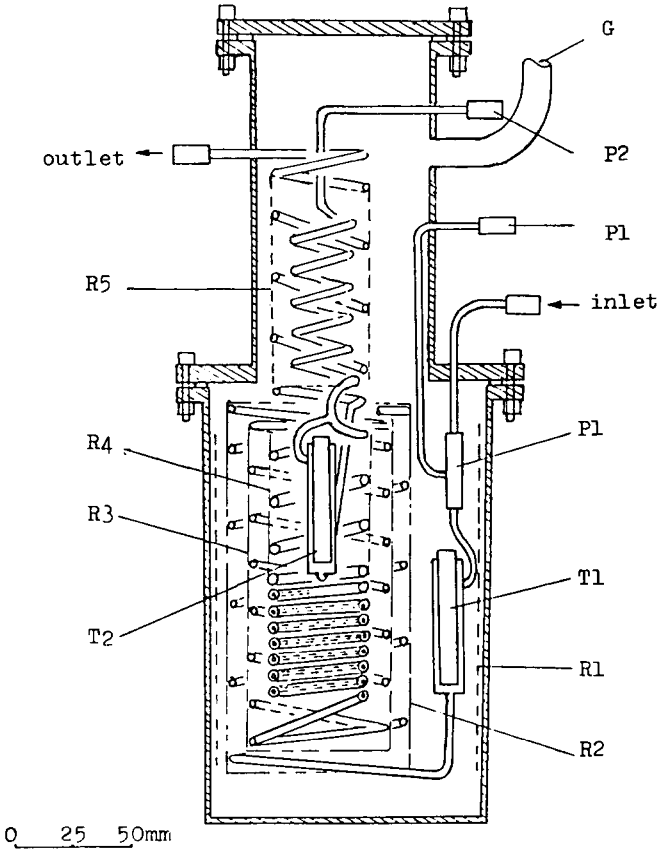

Fig. 1. Calorimeter assembly. P1, inlet pressure tap junction; P2, outlet pressure tap junction; T1, inlet thermometer well; T2, outlet thermometer well; R1, R2, R3, R4, R5, radiation shields; G, vacuum pipe.

rate. In the vaporizing chamber, the fluid is gradually, completely vaporized into a steady stream of vapor. After flowing through the tubular coils in the preheated bath and the calorimeter bath, the vapor flows into the flow calorimeter, and then, through a three-way solenoid valve, into a cooler. The cooled fluid flows to an expansion vessel, from which the liquid returns to the pump. The three-way solenoid valve and the disconnectable weighing vessel are required for the calibration of the flowmeter.

The calibration of the apparatus is monitored using benzene [7] at temperatures between 375 and 600 K, and at pressures of 51.1, 101.3, 309.3, and 495.2 kPa. The results are listed in Table 1. They are in good agreement with data cited in the literature [3, 8, 9], with deviations of less than 1.0%.

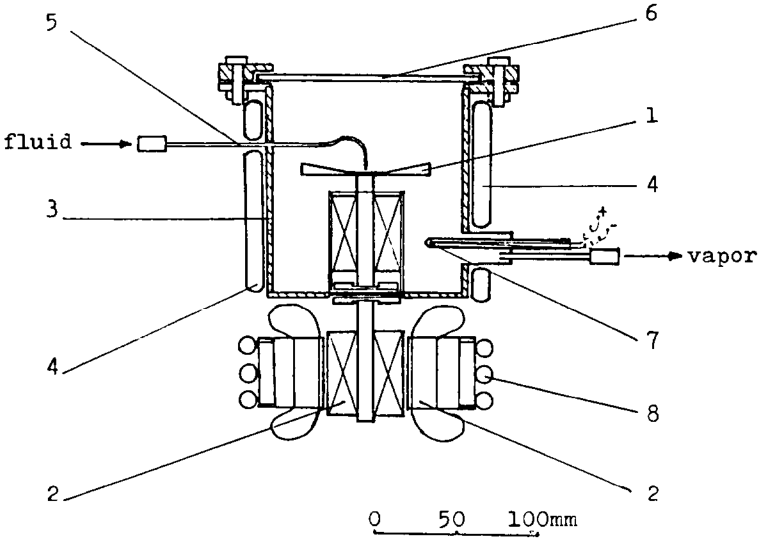

Fig. 2. The flash boiler. 1, stainless steel rotating fan; 2, micro-motor; 3, case shell; 4, heater; 5, capillary tube; 6, glass window; 7, thermocouple; 8, water cooler.

TABLE 1

The heat capacities of benzene in J K^{-1} mol^{-1}

p/(kPa)	T/K							
	378.45	414.78	443.70	473.98	503.57	527.06	585.46	597.86
495.2			129.58	136.02	142.41	147.29	160.75	160.99
309.3		120.57	127.40		141.33	146.41		160.44
101.3	108.50	117.98	125.40	133.05	140.41	146.17	160.19	
51.1	107.70	117.72	124.63	132.25	140.24	145.49	157.45	159.80
$C_p^{\ominus}$	106.89	116.99	124.16	132.02	139.93	145.51	157.30	159.65

RESULTS AND DISCUSSION

The isobaric specific heat capacities have been determined under atmospheric pressure for the binary vapors benzene–cyclohexane, benzene–carbon tetrachloride and ethanol–carbon tetrachloride at various temperatures between 370 and 600 K. The experimental results are summarized in Tables 2 and 3. The results for benzene–cyclohexane vapor at various temperatures T and compositions x are fitted to eqns. (3) and (4), respectively:

$$C_p = -44.750 + 0.5455T - 2.707 \times 10^{-4}T^2 + 9.057 \times 10^{-9}T^3 \quad (3)$$

$$C_p = 160.572 - 41.4815x - 0.6127x^2 + 0.2806x^3 - 3.801 \times 10^{-4}x^4 \quad (4)$$

TABLE 2

The heat capacities of x benzene–$(1-x)$cyclohexane vapors in J K^{-1} mol^{-1}

C_p of 0.55–0.45 vapor				C_p at 421.30 K and 101.3 kPa			
T/K	Exp.	Calc.	Dev. (%)	x	Exp.	Calc.	Dev. (%)
375.03	122.19	123.04	0.70	0.00	160.57	161.26	0.43
410.05	133.97	135.00	0.76	0.23	150.88	152.12	0.82
421.40	137.67	138.73	0.77	0.49	141.88	143.41	1.08
474.95	154.93	156.87	1.25	0.55	137.67	138.86	0.86
523.65	167.87	169.36	0.89	0.74	131.17	133.01	1.40
570.77	179.96	182.33	1.32	0.83	125.92	126.84	0.73
				1.00	118.76	119.35	0.50

For non-polar or weak polar mixtures, such as the benzene–cyclohexane binary system, the isobaric heat capacities can be calculated using the Lee–Kesler mixing rules [10, 11]. Comparison between the experimental results, the calculated results and the literature data are presented in Tables 2 and 3. Figure 3 shows a direct graphical comparison.

The values measured by Sinke and Vries [1] agree with the values obtained in this work, with a deviation of 1%. However, the values calculated using the Lee–Kesler mixing rules differ from the values obtained here by more than 1%, as shown in Table 2. This may be due to errors in the calculating method, derived from a general deviation in the heat capacity, or from the mixing rules, as explained by Reid et al. [11]. Therefore, this new apparatus can yield reliable values for multicomponent vapors, as well as for single-component vapors.

As shown in Fig. 3, the plots of non-polar mixtures are nearly straight lines, whereas that of ethanol–carbon tetrachloride is slightly concave. This difference can be explained by molecular mobility.

TABLE 3

The heat capacities of benzene–carbon tetrachloride and ethanol–carbon tetrachloride vapors in J K^{-1} mol^{-1}

C_p of $xC_6H_6 + (1-x)CCl_4$ at 101.3 kPa and 383.87 K				C_p of $xC_2H_5OH + (1-x)CCl_4$ at 101.3 kPa and 437.59 K			
x	Exp.	Ref. 1	Dev. (%)	x	Exp.	Ref. 1	Dev. (%)
0.00	108.83	107.95	0.87	0.00	94.88	95.31	−0.45
0.25	105.47	104.68	0.75	0.25	93.32	92.89	0.47
0.50	100.99	100.50	0.49	0.50	91.12	90.63	0.54
0.75	97.14	96.48	0.67	0.75	89.02	88.36	0.74
1.00	93.25	92.84	0.44	1.00	87.76	87.86	−0.12

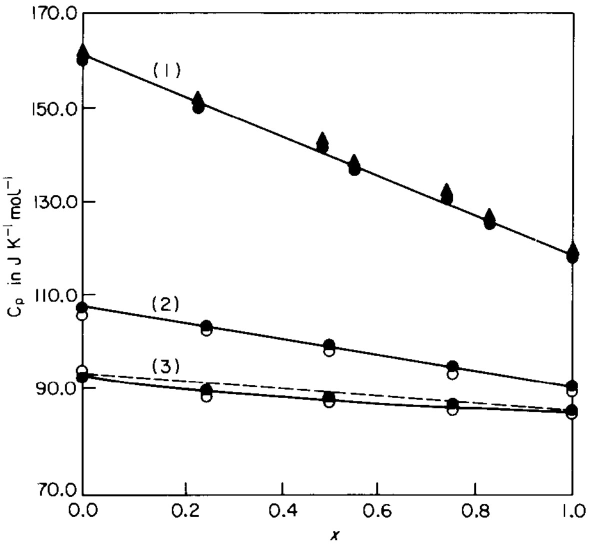

Fig. 3. The heat capacities of binary vapors at 101.3 kPa. (1) $xC_6H_6 + (1-x)c\text{-}C_6H_{12}$ at 421.30 K; (2) $xC_6H_6 + (1-x)CCl_4$ at 383.87 K; (3) $xC_2H_5OH + (1-x)CCl_4$ at 437.59 K: ▲, calculated from the Lee–Kesler mixing rules; ○, Sinke and Vries [1]; ●, this work.

Within non-polar and weakly polar molecules, such as benzene, cyclohexane, and carbon tetrachloride, the van der Waals force is the main intermolecular force. When these molecules are mixed together, the mobility of the molecules is virtually unaffected or remains consistent, because the intermolecular forces are almost unchanged by mixing. Thus, to a great extent, heat capacity of the mixtures displays linear addition. However, the ethanol molecule is highly polar, with hydrogen bonding being the predominant intermolecular force, the magnitude of which is much greater than that of the van der Waals force. Even in the vapor state, about five ethanol molecules are connected together by hydrogen bonding [12]. When such an associated vapor is mixed with non-polar vapors, the hydrogen bond is weakened and, to some extent, destroyed. In other words, the degree of association decreases, and so the molecules become more movable, which means that the vapor becomes more sensitive to heat input. Thus, the excess isobaric specific heat capacity of the mixed vapors is negative.

CONCLUSIONS

A new flow calorimeter was constructed for the determination of the isobaric specific heat capacities of multicomponent vapors. It can yield reliable values over a wide temperature range with deviations of less than 1.0% from the literature values.

The method for calculating the general departure of the heat capacity and the Lee–Kesler mixing rules can be applied for non-polar and weakly polar mixtures, with deviations of less than 1.5% of the literature values.

The excess heat capacity is nearly zero for the vapors investigated. For ethanol–carbon tetrachloride, there was a slight negative deviation which may be explained by molecular mobility.

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