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A new flow calorimeter for the determination of the isobaric heat capacity of vapors

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Abstract

A new flow calorimeter has been constructed to determine the isobaric heat capacity of vapors, especially multicomponent vapors. The calorimeter is capable of operation up to 673 K and 20 MPa. A novel design encloses the innermost part of the calorimeter within a double set of thick-wall, aluminum shields, replacing the traditional constant temperature bath, to minimize heat loss and precisely control the calorimeter temperature. An upper copper block within the outer shield is used to preheat the fluid while a lower copper block within the inner shield further heats the fluid to the operating temperature. Such a structure and temperature-controlling arrangement allow easy component replacement and operation. The apparatus was tested by determining the heat capacity of benzene and the benzene–carbon tetrachloride binary system at atmospheric pressure with an experimental error of less than 0.7%. Results for the two binary systems benzene–chloroform and benzene–acetone at 101.3 kPa and about 515.0 K are also given.

Keywords: Binary system; Calorimeter; Flow calorimeter; Heat capacity; Instrument; Isobaric heat capacity; Novel

1. Introduction

Accurate knowledge of the heat capacity of organic vapors, C_p, is an important part of the thermodynamic description of real gases, and necessary for the calcula-

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tion of thermodynamic processes. Therefore, the direct measurement of the heat capacity is of technical interest.

Flow calorimetry is the most direct and widely used method. By the early 1960s, several kinds of glass flow calorimeter, reviewed by McCullough and Waddington [1], had been set up, mainly to measure the heat capacity of pure organic vapors at low pressures and temperatures. Over the last two decades, although many calorimeters capable of operation up to high temperatures and pressures have been constructed, only a few of them can be directly used to measure the heat capacity of vapors. Moreover, most of these calorimeters, such as those constructed by Ernst and co-workers [2–4] and Miyazaki et al. [5], have to make use of an external air bath, application of which to operations at high temperatures is hard because of the poor heat conductivity of air. As a result, Sandarusi and Yasavage [6] used a unique concentric coil design with passive metal radiation shields, both to control the calorimeter temperature and to heat the fluid instead of an external air bath. However, their calorimeter has a complicated structure and its construction is difficult.

The differential flow calorimeters of White et al. [7] and Rogers et al. [8] are of particular note. They replaced the external air bath with two thick-wall metal shields to maintain the calorimeter temperature and two blocks to heat the fluid. This new idea enables easy design, construction and operation of the apparatus. We incorporate this in the design of our calorimeter.

In the present paper, a description of the new calorimeter is given. The apparatus is tested by determining the heat capacity of benzene and the benzene–carbon tetrachloride system at 101.3 kPa. The following paper will present the results for the benzene–acetone and benzene–chloroform systems with respect to compositions at about 515.0 K and 101.3 kPa.

2. Experimental

2.1. Materials

The analytical reagents, benzene, carbon tetrachloride, acetone and chloroform, were all purified by fractional distillation using a 1.5 m long column packed with glass rings. Their densities and refractive indices agree well with those reported in the literature [10]. Binary systems were prepared by weighing and mixing their respective components. The uncertainty of the measured composition is estimated to be less than 0.02%.

2.2. Calorimeter design

A cross-section of the present calorimeter is schematically shown in Fig. 1. The basic design of the calorimeter involves six parts: an innermost section, two blocks (upper D and lower E), two shields (inner C and outer B), and a stainless steel vacuum jacket with a lid.

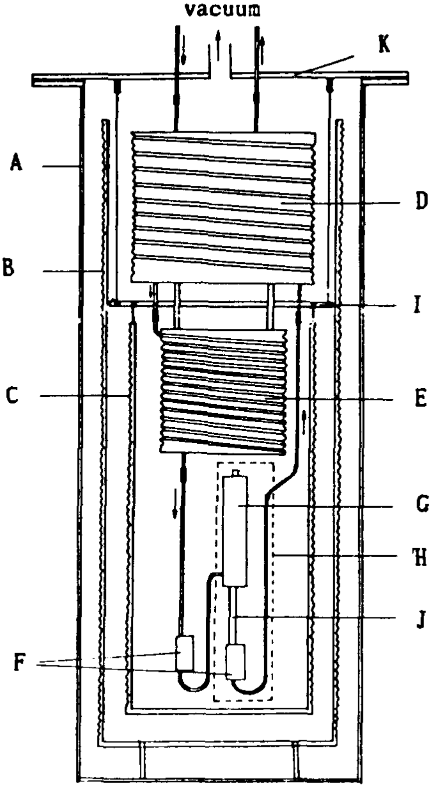

Fig. 1. Schematic diagram of the calorimeter. The parts are labeled as follows: A, vaccum jacket; B, C, outer and inner shields; D, E, upper and lower blocks; F, inlet and outlet thermometer bars; G, heater sub-section; H, radiation shield; I, round plate; J, tubulence promoter; K, calorimeter lid.

The innermost section consists of two copper bars, a heater sub-section, a radiation shield, a turbulence promoter and about 1.8 m length stainless steel thin-wall tubing ($\varnothing$ 3 × 2.4 mm). The tubing is cut into two parts which are installed before and after the heater sub-section respectively, and further bent to give two "U" type figures. The copper bars, as shown in Fig. 2, are mounted tightly on a branch of each "U" figure and placed, nearly at the same height, right below the heater sub-section to avoid direct radiation from the heater. Two miniature, secondary standard, platinum resistance thermometers are inserted into copper bars to indirectly detect the inlet and outlet temperatures of the fluid. Rough evaluation shows that the indirect measurement of temperatures results in an error of less than 0.001%, so the measured temperatures need no calibration.

The heater sub-section is of most significance, containing three stainless steel tubes and a capsule type heater as shown in Fig. 3. Two bottoms of the outer tube are soldered with silver on to the outer surface of the inner tube and middle tube respectively. The lower bottom of the inner tube is also sealed by silver welding. A

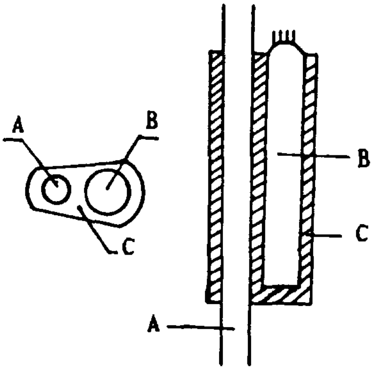

Fig. 2. The thermometer bar: A, tubing; B, Pt resistance thermometer; C, copper bar.

folded path is formed to let the fluid flow in two opposite directions, in order to increase the flow length and to heat the fluid more efficiently.

The turbulence promoter is mainly used to smooth the fluid temperature. The radiation shield surrounds the heated part, including the heater sub-section and the outlet thermometer bar, to reduce radiative heat loss. The heat radiated from the shield to the colder surroundings does not represent any heat loss. In addition, both

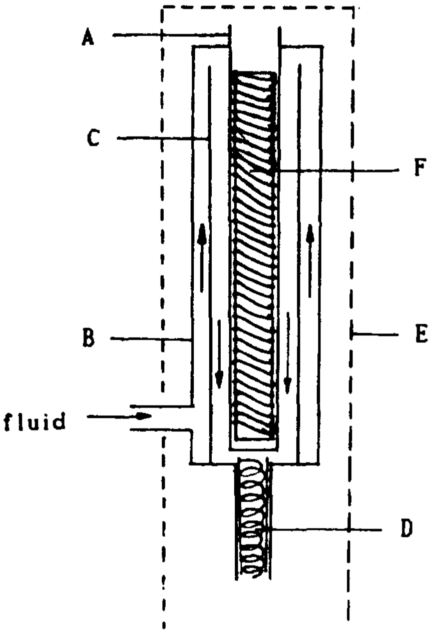

Fig. 3. Schematic diagram of the heater sub-section: A, inner tube; B, outer tube; C, middle tube; D, tubulence promoter; E, radiation shield; F, heater.

the heater and the thermometer wires lead out of the calorimeter through wrapping on the tube in order to reduce conductive heat loss.

The accuracy of the heat capacity measurements depends on the fine control of the fluid temperature and the temperature stability of the calorimeter. This is achieved by using two copper blocks and two aluminum shields with guard heaters. The lower block, used for final temperature control of the fluid, is a cylinder (65 mm diameter and 78 mm length) controlled, to within ±0.005 K in one determination (30 min) and ±0.02 K over 2 h in another, with a central catridge heater (75 W) and precision thermopile. To obtain good temperature equilibration between the fluid and the block, a 1.5 m length of the flow tubing is swaged tightly into grooves cut on the surface of the block. The upper block (80 mm diameter and 90 mm length), of similar design as the lower block, is used to preheat the fluid using a heater (100 W) and a series-connected, differential thermopile. The temperature is relatively well controlled at 1 K below that of the lower block. Two grooves paralleling each other are cut into the surface of the block to swage two flow tubings; one is used to carry the colder entering fluid while another is linked with the tubing coming from the outlet thermometer bar, and carries the heated fluid out of the calorimeter. Such an arrangement provides fine control of the temperature.

Between the two blocks is a round plate which is used to fix the blocks and the inner shield. The plate itself is hung from three rings soldered onto the inner surface of the calorimeter lid by stainless steel wires, and further stabilized by having a diameter equal to the inner diameter of the outer shield. Such structural design provides relative stability, and components can be easily replaced by pulling the plate out. The two shields are of similar design and function. They are hollow, thick-wall (12 mm), aluminum cylinders with bottom plates. Insulated heating wires are inserted into grooves cut into their exterior surfaces which are further banded with multilayer insulation. The outer shield provides most of the power required to operate the calorimeter at high temperature. In addition, the temperature of the inner shield is relatively well controlled at ±0.02 K and 0.5 K below that of the lower block in the outer shield case, and ±0.2 K and 4 K below.

All functional parts are installed in the vacuum jacket. The jacket is kept under vacuum (<0.1 Pa) to reduce convective heat loss, and all lead wires exit the calorimeter through the lid.

2.3. *Flow system*

In the present investigation to determine C_p under atmospheric pressure, the flow system is simple. It consists of a sample tank, a flash boiler [9], a water condenser, a WGP-6 type high pressure metering pump (Zhejiang Scientific Instrument Corp.), and the calorimeter.

The liquid sample in the tank is pumped into the flash boiler. Since constancy of the flow is critical to our design, pump calibrations are conducted and show that the volumetric flow rate is stable to within 0.05%. In addition, the sample tank is thermostated to ±0.01 K by a water bath, and the pump is enclosed in an air bath controlled to within ±0.1 K and at the same temperature as the tank. This is necessary for calculation of the liquid density which allows the volumetric flow rates to be converted into the required mass flows.

In the chamber of the flash boiler, the liquid is completely and rapidly vaporized into a steady stream of vapor. After exiting the calorimeter, the heated vapor is cooled to a liquid by a water condenser and re-collected in the sample tank to form a flow circuit.

2.4. *Experimental method and evaluation*

In a flow calorimeter, for the determination of C_p, a constant mass flow F of gas is heated by an electric power Q resulting in a temperature rise ΔT at pressure p. Because heat loss is unavoidable at high temperatures, we actually measured the apparent heat capacity, $C_{p(\mathrm{app})}$. An integral mean value of the real heat capacity, C_p, may be obtained by extrapolating $C_{p(\mathrm{app})}$ to $1/m \to 0$, as shown in the equation

$$C_{p(\mathrm{app})} = \frac{Q}{F\,\Delta T} = \frac{Q_1 + Q_2}{F\,\Delta T} = C_p + \frac{Q_2}{F\,\Delta T} \qquad (1)$$

where Q_2 is the power loss and $Q_1 = Q - Q_2$. Q may be obtained by measuring the drops in voltage of the heater and a 1 Ω standard resistor using a digital multimeter; the uncertainty in the measured Q is estimated to be less than 0.05%. In this investigation, C_p is assigned to the pressure $p = 101.3$ kPa and to the average temperature:

$$\langle T \rangle = T_1 + \frac{1}{2n} \sum_{i=1}^{n} (\Delta T)_i \qquad (2)$$

where n represents the number of the $C_{p(\mathrm{app})}$ determination, T_1 is the inlet temperature, and $(\Delta T)_i$ is the temperature rise for the ith flow rate.

The temperature rise is about 4 K. There is also a temperature difference of several mK between the two thermometers of the calorimeter when the heater is switched off ($Q = 0$). This small temperature difference is due to the change in the potential energy of the fluid, to the Joule–Thompson effect according to the small pressure drop, and perhaps to the small errors of the two thermometers. To eliminate all these influences, a heater-on experiment with a temperature rise of ΔT_{h} and a heater-off experiment with a temperature rise of ΔT_{b}, but with all other conditions unchanged, are carried out. The relationship $\Delta T = \Delta T_{\mathrm{h}} - \Delta T_{\mathrm{b}}$ can then be used.

3. Results and discussion

In the design of the calorimeter, the quantitative influence of the heat loss on the experimental results for $C_{p(\mathrm{app})}$ must be checked. Table 1 is a typical example of the determination of $C_{p(\mathrm{app})}$ for benzene at 101.3 kPa and 471.6 K. The results show that $C_{p(\mathrm{app})}$ varies linearly with $1/F$, leading to the conclusion that heat loss at a

Table 1
The apparent heat capacities of benzene at 101.3 kPa and 471.6 K

$1/F$ in s mol^{-1}	Q in W	ΔT in K	$C_{p(\mathrm{app})}$ in J mol^{-1} K^{-1}	$C'_{p(\mathrm{app})}$ [a] in J mol^{-1} K^{-1}	$C_{p(\mathrm{app})} - C'_{p(\mathrm{app})}$ in J mol^{-1} K^{-1}
3751	0.17002	4.206	144.35	144.31	0.04
2142	0.27376	4.195	139.78	139.80	−0.20
1623	0.35735	4.192	138.35	138.40	−0.05
1276	0.44402	4.112	137.78	137.35	0.43
811.7	0.68353	4.088	135.72	135.94	−0.22
$C_p = 133.47$					

[a] Correlated heat capacity according to Eq. (1).

Table 2
The heat capacities of benzene at 101.3 kPa and different temperatures

$\langle T \rangle$ in K	$C_{p(\mathrm{obs})}$ in J mol^{-1} K^{-1}	$100(C_{p(\mathrm{lit})} - C_{p(\mathrm{obs})})/C_{p(\mathrm{obs})}$		
		Ref. [11]	Ref. [12]	Ref. [13]
413.8	118.54	−0.13	0.09	−0.40
432.6	122.65	−0.24	−0.08	0.33
455.8	129.81	−0.46	−0.25	−0.66
471.6	133.47	−0.29	−0.05	−0.42
493.5	138.54		0.04	−0.30
522.0	144.42		0.31	−0.10
565.3	153.68		−0.43	

[a] Interpolation value from the literature.

Table 3
The heat capacities of the $(1-x)C_6H_6-xCCl_4$ system at 101.3 kPa and 373.2 K in J mol^{-1} K^{-1}

X	$C_{p(\mathrm{obs})}$	$C_{p(\mathrm{lit})}$ [14]	Dev. in %
0.0000	107.65	107.05	0.28
0.1972	105.14	105.38	0.23
0.4060	101.63	102.18	0.44
0.5791	99.08	99.30	0.22
0.7982	96.12	95.68	−0.46
1.000	93.30	92.84	−0.50

given temperature is constant, and that C_p may be obtained by linear extrapolation of $C_{p(\mathrm{app})}$ to $1/F \rightarrow 0$.

As a test of the apparatus, the real heat capacities of benzene and the benzene–carbon tetrachloride binary system, with respect to composition, are determined at different temperatures. The results are summarized in Tables 2 and 3. It is found

Table 4
The heat capacities of the $(1-x)C_6H_6$-$xCHCl_3$ and $(1-x)C_6H_6$-xC_3H_6O systems at 101.3 kPa and 515.0 K in J mol^{-1} K^{-1}

$(1-x)C_6H_6$-$xCHCl_3$				$(1-x)C_6H_6$-xC_3H_6O			
x	$C_{p(\mathrm{obs})}$	$C_{p(\mathrm{cal})}$	Dev. in %	x	$C_{p(\mathrm{obs})}$	$C_{p(\mathrm{cal})}$	Dev in %
0.0	143.26			0.0	143.26		
0.1998	130.58	128.08	−1.15	0.1026	140.46	137.19	−2.3
0.3467	122.34	120.88	−1.20	0.2046	137.15	134.10	−2.2
0.5116	112.09	111.00	−0.97	0.2801	134.51	131.80	−2.0
0.6495	104.06	103.09	−0.92	0.3530	132.47	129.54	−2.2
0.8005	92.76	92.49	−0.29	0.4955	127.90	124.72	−2.2
1.0	81.21			0.6435	122.76	120.62	−1.7
				0.8028	117.03	116.23	−0.7
				1.0	110.54		

that the observed values are in good agreement with the interpolation values from the literature, with a deviation of less than 0.7% and typically below 0.5%. Therefore, the apparatus can be used to measure the heat capacity of pure substances and mixtures. In addition, although the test is conducted under atmospheric pressure, a measurement accuracy of less than 1.0% may be expected when the apparatus is operated at high pressures.

Error analysis shows that the uncertainties of parameters such as Q, F, and ΔT add up to about 0.25%. Other errors also arise from the extrapolation in obtaining the real heat capacity. Therefore, more careful consideration on how to make the apparatus adiabatic is needed to further enhance the measurement accuracy.

The heat capacities of the two binary systems benzene–chloroform and benzene–acetone with respect to composition at 515.0 K and 101.3 kPa are measured. The observed values and the calculated values from the Lee–Kesler method [15,16] are shown in Table 4. An almost linear relationship between the heat capacities and the compositions in these two systems is found. This indicates that the excess heat capacity of the two systems is a weak function of the composition. Besides, the comparison shows that all the calculated values are smaller than the observed values, with maximum derivations of 1.2% and 2.3% respectively. This may be ascribed to the inaccuracy of the Lee–Kesler method in calculating the heat capacity of polar substances.

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