

## CALORIMETER FOR DETERMINATION OF HEATS OF VAPORIZATION OF PURE SUBSTANCES

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The vaporization calorimeter for the determination of the heat of vaporization of pure substances in the temperature range of 25–100°C has been constructed. A new design of the head of calorimeter reduces substantially the needed time of experiments and the demands on their performance. The measured energy is supplied into the calorimetric vessel in the form of electric pulses of constant amplitude, which makes it possible to evaluate the energy supplied easily and accurately.

The system of control circuits is proposed in such a way that it ensures the sufficient accuracy of the measured values of heat of vaporization in whole temperature range. The values of heats of vaporization are measured with an accuracy of  $\pm 0.1\%$ .

Many methods and their modifications are known for the determination of the heats of vaporization of pure substances. Nevertheless there are only several types of calorimeters that have been developed. The reason consists in the fact that in spite of its apparent simplicity, the measurement of heat of vaporization is not easy. Testing and improving the apparatus extends considerably the development. The most often used method is the evaporation one. A typical representative of the evaporation method based on the loss in weight of the evaporating vessel is the apparatus proposed by Brown<sup>1</sup> and improved by Mathews<sup>2,3</sup>. It yields the values of heats of vaporization with an accuracy of 0.3 per cent at the normal boiling point of pure substances. The second modification of the evaporation method, the method of separate condensation proposed by Pitzer<sup>4</sup> and worked out by Waddington, Todd and Huffman<sup>5</sup> makes it possible to determine the heats of vaporization of pure substances under an arbitrary pressure and, consequently, temperature. The accuracy of the experimental data is better than 0.3 per cent. The most perfect is considered the third modification of the evaporation method, on the principle of which the apparatuses with closed system work that were worked out by Osborn, Stimson and Ginnings<sup>6,7</sup>. They were used for accurate measurements of calorimetric quantities of water in a wide temperature and pressure range. The heats of vaporization of hydrocarbons were determined at a temperature of 25°C. For the determination of heats of vaporization of small amounts of liquids under pressures, too, that are higher than the saturated vapour pressures of pure substances at the given temperature, the method of evaporation by air (or inert) flow was developed. The method proposed by Smith<sup>8,9</sup> and worked out by Hunter and Bliss<sup>10</sup> was improved by Wadsö<sup>11,12</sup>. Heats of vaporization were measured at a temperature of 25°C with an accuracy of 0.3–0.5%. Condensation methods are abandoned at present. They are characterized by the simplicity of the calorimeter design but the accuracy of the data does not correspond to the requirements of our days. This method is connected with the works of Swietoslawski and Zielenkiewicz<sup>13,14</sup> and lately Svoboda, Hynek and Pick<sup>15</sup>.

In spite of the considerable effort of many research institutes, there are very few experimental data on heats of vaporization of pure substances. The aim of this work was to design and test the vaporization calorimeter for measuring in the temperature range of 25–100°C. Its design should enable a quick carrying out of experiments without reducing the requirement of simplicity and accuracy of the data on heats of vaporization.

## EXPERIMENTAL

### Design of Calorimeter

The schematic diagram of the calorimeter is given in Fig. 1. The evaporating vessel is of cylindrical shape with a diameter of 30 mm and height of 60 mm. It is made of brass and gold plated. The inside of the evaporating vessel 11 is made of silver. Above the upper part of the vessel, the teflon head 10 with leads of manganin heating and platinum resistance thermometers for the temperature control of evaporating vessel and adiabatic jacket is fixed. The resistance thermometers and heatings are wound bifilarly. The electrical insulation of walls of the vessel and winding was made up by successive coating and polymerizing the electroinsulating varnish S 901. The evaporating vessel is attached to the cover 9 of the adiabatic jacket 2, which is an aluminium cylinder of inside diameter of 120 mm, wall thickness of 12 mm and height of 150 mm. The surface of the aluminium jacket was anodized and then coated with several layers of cured electroinsulating varnish S 901. On the outside surface of the jacket, double heating made of manganin wire and a platinum resistance thermometer are wound. The head of the calorimeter is made

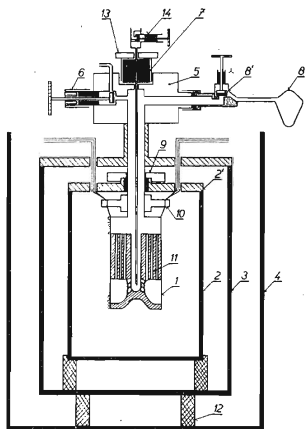


FIG. 1

Schematic Diagram of Vaporization Calorimeter

1 Evaporating vessel, 2 adiabatic jacket, 2' cover of adiabatic vessel, 3 thermostat, 4 outside jacket, 5 head of calorimeter, 6 vacuum valve, 7 stopper, 8 condensation vessel, 8' valve of condensation vessel, 9 cap nut, 10 teflon head, 11 inside of evaporating vessel, 12 teflon supports, 13 cap nut of closure, 14 filling valve.

up of brass. It is equipped with the vacuum valve 6 for the evacuation of the inside space of the evaporating vessel, with the filling hole with stopper 7 from fluorinated silicone rubber which serves for filling the evaporating vessel and with the vessel 8 for condensation of evaporated liquid. The accessories of the calorimeter are the device for heating the calorimeter head and the thermometer for measuring its temperature. The apparatus is further equipped with a thermal fuse protecting it from an excessive heating in case of the thermostats failure. All mechanical joints 12 between jackets as well as insulations, bushings of electrical leads and packings were made of teflon.

### Measuring and Control System of Calorimeter

When designing and constructing the control systems of the calorimeter, our starting point were the papers<sup>16-21</sup>. From the point of view of control engineering, it is the question of three coupled control systems: 1. temperature control of the evaporating (calorimetric) vessel, 2. temperature control of the adiabatic jacket according to the temperature of the evaporating vessel (cascade control), 3. temperature control of the outside jacket.

The structure of the control systems is apparent from the block diagram of measuring and control systems of calorimeter (Fig. 2). The temperature  $T_1$  is controlling quantity of the control system of evaporating vessel (controlled system  $S_1$ ),  $T_3$  is controlling quantity of the control system of outside jacket ( $S_3$ ). The elements  $Z_{21}$  and  $Z_{23}$  represent the action of the controller  $R_2$  on the system  $S_1$  and of the controller  $R_3$  on the system  $S_2$ , resp. For right function of the apparatus it is necessary to fulfil the inequality  $T_1 > T_2 > T_3$ . The temperature control of the

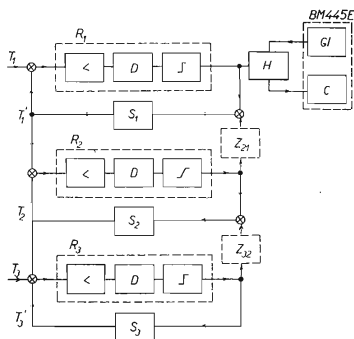


FIG. 2

### Schematic Diagram of Measuring and Control Systems of Calorimeter

Temperatures:  $T_1$  of evaporation vessel,  $T_2$  of adiabatic jacket,  $T_3$  of outside jacket (controlling quantities, controlled variables are denoted by the same symbols with primes); temperature controllers:  $R_1$  of evaporation vessel,  $R_2$  of adiabatic jacket,  $R_3$  of outside jacket; controlled systems:  $S_1$  evaporation vessel,  $S_2$  adiabatic jacket,  $S_3$  outside jacket;  $D$  synchronous detector,  $H$  gate,  $G1$  pulse generator 1 kHz,  $C$  pulse counter.

adiabatic jacket is adjusted so that the difference of temperatures of evaporating vessel and adiabatic jacket,  $T_1 - T_2$ , may be minimum but always positive. The temperature  $T_3$  is adjusted approximately  $1^\circ\text{C}$  lower than the temperature  $T_2$  or  $T_1$ , in order that the control system of adiabatic jacket may operate all the time in the proportional band. The controllers  $R_1$ ,  $R_2$ , and  $R_3$  have a similar structure; they consist of alternating current amplifier, synchronous detector and the third member of the controller is either a non-linear amplifier (relay) with the controllers  $R_1$  and  $R_3$  or linear direct current amplifier with the controller  $R_2$ .

The temperature control of evaporating vessel is the non-linear on-off control. The temperature detecting element is the platinum resistance thermometer whose resistance at  $25^\circ\text{C}$  is about  $160\ \Omega$ . The counting circuit for making up the control deviation is the Wheatstone bridge with the parasitic capacity compensation. The required temperature is adjusted by a decade resistor Metra XLL that is connected parallel to a fixed resistor of  $500\ \Omega$  in one arm of the bridge. In this arrangement an adequately fine temperature adjustment is reached.

Wheatstone bridges for measuring temperature are fed from three independent outputs of the sinusoidal voltage 375 Hz generator. The stabilization of the supply voltage of the bridges is carried out similarly to that of oscillator<sup>17</sup>. The outputs of single bridges are amplified by the alternating current amplifiers that differ as for single control channels only in the amplification factor and in the transmitted frequency band width. All amplifiers are terminated by a synchronous detector for distinguishing the sense of the bridge off-balance. The output voltages of synchronous detectors are treated in a different way according to the kind of the control of heating power.

The alternating current amplifiers of the controllers  $R_1$  and  $R_2$  are identical. Their amplification is continuously adjustable and its maximum value amounts to  $2 \cdot 10^6$ . The selectivity is determined by a tuned circuit with resulting quality factor  $Q = 10$ . The amplifier of the controller  $R_3$  is simpler, it has no tuned circuit and its maximum amplification is  $10^4$ .

The signal of the synchronous detector of the controller  $R_1$  controls by means of the Schmitt circuit the relay for switching the heating power. The measurement of electric work  $W = \sum UI \cdot \Delta t$  falls into the measurement (by means of a compensator QLK) of constant voltage and current across the manganin heating resistor (of about  $22\ \Omega$ ) and into the measurement of  $\sum \Delta t$  by an Universal Counter Tesla BM 445 E that makes it possible to distinguish the time interval of 1 ms. The temperature control of the adiabatic jacket can be considered a linear cascade control in a narrow proportional band. Two platinum resistance thermometers ( $160\ \Omega$  at  $25^\circ\text{C}$ ) are connected in the adjoining arms of the Wheatstone bridge, one for measuring the temperature of adiabatic jacket, the second for measuring the temperature of evaporating vessel. The remaining two arms are formed by manganin resistors and between them a resistor of about  $0.2\ \Omega$  is connected, bypassed with a  $250\ \Omega$  helipot for the accurate adjustment of the bridge balance. The control deviation is given by the difference in temperatures of the evaporating vessel and the adiabatic jacket. The signal of synchronous detector is power-amplified by the direct current amplifier with the power-amplifier transistor KU 601; its load is the heating resistor wound on the adiabatic jacket. The minimum proportional band of the controller (in case of the maximum amplifier gain) corresponds to about  $0.05^\circ\text{C}$ . An auxiliary heater is wound on the adiabatic jacket, too, which enables a quicker reaching of steady state on increasing temperature.

The temperature control of the outside jacket is a typical on-off control. The temperature detecting element is a platinum resistance thermometer connected in one arm of the Wheatstone bridge Metra MLL. The signal of synchronous detector controls, by means of a Schmitt circuit, a multivibrator that oscillates at a basic frequency about 3 kHz. By this alternating voltage, a thyristor KT 704 is controlled through a separating transformer. On constructing the electronic circuits especially amplifiers, the minimum interfering signal on the output of the synchronous detector was obtained by a suitable spacing of components.

When constructing the Wheatstone bridges for measuring temperature, the following principles were kept: 1. An induced interfering signal was suppressed by the bifilar winding of all bridge resistors and by the arrangement of the bridge connections to form minimum loops. 2. For suppressing the effects of temperature changes on the resistance of the bridge connections, the feeding and output nodal points of bridges were chosen with respect to a partial temperature compensation. 3. An effect of temperature changes of surroundings on all manganin resistors (including resistance boxes) was suppressed by coupling always one fixed and one variable resistor in adjacent arms to the pair placed in a common space with equalized (levelled) temperature.

### Materials Used

*Methanol* (analytical grade reagent) was boiled with the Grignard reagent and then distilled over on an 1.5 m long column packed with stainless steel saddles. The measured physical constants of methanol are: n.b.p. 64.56°C (lit. 64.51–64.65),  $d_4^{25}$  0.7866 (lit. 0.78657–0.78668),  $n_D^{25}$  1.3266. The weight per cent of H<sub>2</sub>O as determined by the Fischer method amounted to less than 0.01%. The results obtained by means of a mass spectrometer proved that the content of impurities is less than 0.01%. *Benzene* (analytical grade reagent, thiophene-free) was distilled over with metallic sodium on an 1.5 m long column packed with stainless steel saddles. The measured physical constants for benzene are: n.b.p. 80.10°C (lit. 80.07–80.106),  $d_4^{25}$  0.87368 (lit. 0.87366–0.87368),  $n_D^{25}$  1.4979 (lit. 1.4979–1.4981). The weight per cent of water as determined by the Fischer method amounted to less than 0.007%. The content of impurities determined by means of a mass spectrometer was less than 0.01%. *Cyclohexane* (chemical grade reagent) was distilled over on a forty-plate bubble-cup column. The formaldehyde test for benzene was negative. The measured physical constants of cyclohexane are: n.b.p. 80.7°C (lit. 80.75),  $d_4^{25}$  0.7739 (lit. 0.77383–0.77389),  $n_D^{25}$  1.4236 (lit. 1.42354 to 1.42358). The weight per cent of water as determined by the Fischer method amounted to less than 0.003%. The content of impurities determined by means of a mass spectrometer was less than 0.01%. The measured physical constants of pure substances were in good agreement with the literature data<sup>22</sup>. As well the results of tests for water and impurities content are satisfactory.

### Procedure

The calorimeter is heated up to a working temperature. The filling valve 14 is inserted into the calorimeter head and tightened by the cup nut of the cup 13 so that a vacuum tightness may be ensured. The calorimeter head is overheated by 1–2°C above the working temperature and the calorimeter is evacuated. The condensation vessel is closed by the vacuum valve 8' and by means of the filling valve, the measured liquid (approximate amount 5 ml) is forced into the evaporation vessel. Then the filling valve with capillary tube is pulled out of the calorimeter. Usually 1–1.5 h after filling the temperature course of calorimeter does not vary. The evaporation of the measured substance starts with opening the valve of the condensation vessel. On evaporating 1–3 ml of the measured liquid, the valve is closed. Simultaneously the time of evaporation  $\tau_0$  and, by the counter BM 445 E, the total heating period  $\tau_1$  are measured. At the same time, the heating input power (voltage and current) is measured. The amount of condensate is determined by weighing.

### Calculation of Heat of Vaporization and Estimation of Measuring Error

The heat of vaporization of a pure substance was calculated from the relation

$$\Delta H_v = (W - q_1 - q_2)/m, \quad (I)$$

TABLE I  
Heats of Vaporization of Pure Substances  
Selected measurements.

Substance	°C	$\tau_0$ , s	$\tau_1$ , s	$N \cdot 10^3$ cal s <sup>-1</sup>	$U$
Cyclohexane	80.7	1 201	528.15	1.218	5.4980
Benzene	80.1	1 500	810.23	1.505	5.7074
	25.0	780	359.59	1.568	5.7410
Methanol	64.7	1 500	720.01	1.382	5.7480
	25.0	3 002	1 964.60	0.613	3.8681
Water	100.0	1 804	1 051.62	4.273	5.8256

where  $\Delta H_v$  is heat of vaporization of pure substance in cal/g,  $m$  weight of evaporated liquid in g and  $W$  total heat amount in cal supplied into the evaporation vessel during evaporating:

$$W = 0.239 UI\tau_1, \quad (2)$$

$q_1$  is correction for the "course" of the calorimeter in cal. By the "course" of the calorimeter is meant a steady heating input power  $N$  that compensates the heat losses due to both the heat conduction by electrical leads and the transfer of heat from the evaporating vessel to the adiabatic jacket. Its value was measured always before evaporating and it was proved experimentally that even during evaporating it did not vary. It is a quantity adjustable in advance and it is given by the relation

$$q_1 = N\tau_0. \quad (3)$$

In Eq. (2)  $I$  is current in A,  $U$  voltage across the heating resistor of the evaporating vessel. The term  $q_2$  is a heat correction for an increase in vapour space of the evaporating vessel on vaporization of  $m$  grams of liquid at a temperature  $T$ :

$$q_2 = (W - q_1) h; \quad h = \frac{d_g}{d_g + d_c} = \frac{PM/zd_cRT}{(PM/zd_cRT) + 1}, \quad (4)$$

where  $d_c$ ,  $d_g$  are densities of liquid and vapour at the temperature  $T$ ,  $P$  is saturated vapour pressure of pure substance at the temperature  $T$ ,  $M$  molecular weight of the substance,  $z$  compressibility factor of the substance at the given  $T$ ,  $P$  and  $R$  is gas constant. The quantity  $h$  was calculated from the orthobaric densities<sup>22</sup> or the  $PVT$  data<sup>23</sup> of corresponding substances:

Methanol:	$h = 1.567 \cdot 10^{-3}$ (64.7°C);	$0.219 \cdot 10^{-3}$ (25°C)
Cyclohexane:	$h = 4.151 \cdot 10^{-3}$ (81.7°C);	$0.575 \cdot 10^{-3}$ (25°C)
Benzene:	$h = 3.337 \cdot 10^{-3}$ (81.1°C);	$0.461 \cdot 10^{-3}$ (25°C)
Water:	$h = 0.624 \cdot 10^{-3}$ (100°C)	

For estimating the error in measurement it is suitable to rearrange Eq. (1) to the form

$$\Delta H_v = (UI/m)(\tau_1 - \tau_2)(1 - h).$$

TABLE I  
(Continued)

<i>I</i> , A	<i>W</i> , cal	<i>q</i> <sub>1</sub> , cal	<i>q</i> <sub>2</sub> , cal	<i>m</i> , g	$\Delta H_v$ , cal g <sup>-1</sup>
0.25431	176.48	1.46	0.73	2.0418	85.36
0.26813	296.34	2.26	0.99	3.1146	94.13
0.26950	132.97	1.22	0.06	1.2731	103.44
0.26610	263.21	2.07	0.41	0.9910	263.09
0.18158	329.79	1.84	0.07	1.1738	279.33
0.27000	395.33	7.71	0.24	0.7183	539.30

TABLE II  
Comparison of Measured and Published Data on Heat of Vaporization of Pure Substances

Measurement (tempera- ture, °C)	$\Delta H_v$ , cal/g		Measurement (tempera- ture, °C)	$\Delta H_v$ , cal/g	
	this work	literature (ref.)		this work	literature (ref.)
	Cyclohexane			C <sub>6</sub> H <sub>6</sub>	
8 (80.7)	85.35 ± 0.03	85.43 (25) 85.62 (2) 85.40 (26) 84.72 (27)	4 (25) 5 (80.1)	103.48 ± 0.03 94.14 ± 0.02	103.57 (7) 103.22 (24) 94.35 (30) 94.35 (2) 94.09 (31) 94.14 (24)
	CH <sub>3</sub> OH			H <sub>2</sub> O	
6 (25)	279.35 ± 0.08	278.40 (11) 279.25 (24) 279.18 (28)	3 (100.0)	538.63 ± 0.49	539.49 (7) 539.66 (32) 539.49 (33)
15 (64.7)	263.17 ± 0.12	263.10 (24) 263.79 (29) 263.40 (2)			

Thus, the error of measurement (in per cent) is

$$\left| \frac{\delta(\Delta H_v)}{\Delta H_v} \right| \cdot 100 = \left( \left| \frac{\delta m}{m} \right| + \left| \frac{\delta U}{U} \right| + \left| \frac{\delta I}{I} \right| + \left| \frac{\delta(\tau_1 - \tau_2)}{(\tau_1 - \tau_2)} \right| + \left| \frac{\delta(1-h)}{(1-h)} \right| \right) \cdot 100.$$

According to our calculations, the value of the first term on the right-hand side of the equation is  $4 \cdot 10^{-4}$ , the sum of the second and third one is  $3 \cdot 10^{-4}$ , the fourth one  $2 \cdot 10^{-4}$  and the last

one  $5 \cdot 10^{-5}$ . The error in determination of  $\tau_1$  is 0.01% and  $\tau_2$  1%. From the given analysis of errors it follows that the heats of vaporization of pure substances were determined with an error of 0.1%. From the measured values, a standard deviation follows being on the average 0.05% (in case of less than five measurements, instead of the standard deviation just the mean deviation was calculated).

## RESULTS

The calorimeter was tested by measuring the data on the heats of vaporization of pure substances methanol, benzene, cyclohexane and water, at their normal boiling points and of two substances — methanol and benzene — at a temperature of 25°C. In Table I some typical measurements are presented for comparison. The correctness of the measured results was checked-up by changing the conditions of evaporating. It was found that the accuracy of the results does not depend on the time of evaporation as far as it is within 10–30 min, further on the choice of the heating input power within the range of 0.7–1.5 W and on the evaporation rate as far as the supplied power is sufficient for the maintenance of the temperature of evaporation vessel. There is also a certain freedom in the choice of the value of the calorimeter course. The limiting criterion is the relation between the temperature of adiabatic jacket and evaporation vessel on measuring the course of calorimeter and the average temperature of evaporation vessel during vaporization. Table II shows a good agreement of measured values of the heats of vaporization of pure substances with the data given in the literature.

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