THE USE OF MIXING CALORIMETER FOR MEASURING HEAT CAPACITIES OF LIQUIDS*

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Dedicated to Professor E. Hála on the occasion of his 60th birthday.

Molar heat capacities of benzene, cyclohexane, tetrachloromethane and ethanol at temperatures 25, 35 and 45°C and of 1-propanol at a temperature of 25°C were measured in a mixing calorimeter described previously. The results are in good agreement with the best literature values. The error of measurements did not exceed 0·3%.

In keeping with the contemporary trend to measure more different quantities in one apparatus an attempt has been made to employ the previously constructed mixing calorimeter[1] for measuring heat capacities as well of pure components or mixtures. Since the control systems of the calorimeter described[1] allow not only to determine directly the endothermic heat of mixing at a constant temperature but also to increase in a programmed way the temperature of calorimetric mixing vessel, it should be in principle possible to calculate heat capacity of the vessel content from the amount of energy needed to increase its temperature. This work should verify the above-mentioned possibilities.

EXPERIMENTAL

Calorimeter. All the measurements have been carried out in the mixing calorimeter of our own design which had been discussed[1] previously in detail. It consists of a mixing vessel, an adiabatic jacket and an external thermostat. The brass calorimeter vessel of cylindrical shape has volume of 45 cm^3 and has been used without separating membrane necessary for mixing. The adiabatic jacket and external thermostat are formed by concentric aluminium cylinders on which platinum resistance thermometers and manganine heaters are wound. The measuring and control system of the calorimeter is formed by three coupled circuits: *1*) The control of adjusted temperature of the adiabatic jacket, *2*) the vessel temperature control by the adiabatic jacket temperature, *3*) the temperature control of the external thermostat by the adiabatic jacket temperature. Particulars of the function of the circuits are given in the work[1].

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The principle of measuring heat capacities is as follows: The temperature of adiabatic wall is increased proportionally by a value of ΔT. With respect to the controlling conditions the vessel temperature is increased automatically by the same difference. The amount of heat is measured required to reach again a steady state, *i.e.* the temperature equilibrium between the vessel and the adiabatic wall. The procedure is analogous to the classical adiabatic calorimetry with the distinction that the controlling quantity is here the adiabatic jacket temperature and not the vessel temperature.

Measuring procedure. The filling of the calorimeter vessel and the determination of amount of liquid was the same as in mixing experiments. For all measurements the vapour space has been minimum (approximately 1—2% total volume). The vessel content was stirred up during measurements by swinging the whole calorimeter.

After attaining the steady state (which takes 30—60 minutes according to the temperature of measurement) the temperature of adiabatic wall has been increased by 2—3°C (for higher values of ΔT, the condition of proportionality ceases to hold and systematic deviations have been found between the temperature changes of vessel and adiabatic wall). The heating rate of vessel has been $\approx 0{\cdot}01 \text{ K s}^{-1}$. Similarly to mixing, the electrical energy has been supplied in the form of pulses of constant amplitude. The total heating time has been measured by a counter Tesla PCO 04·2/5. The constant voltage across the heating resistor of the vessel and across a standard 1 Ω resistor connected in series has been checked several times during measurement by a digital voltmeter Tesla MT 100.

The evaluation of the supplied heat amount Q (with respect to the heat losses into environment) has been carried out by an analogous manner as in mixing experiments[1]. The measured heat capacities have been related to the temperature $T = T_1 + \Delta T/2$, where T_1 is the initial vessel temperature and ΔT the respective increase in temperature. The values of ΔT for single T_1 have been predetermined by means of a digital quartz thermometer HP 2801A with an accuracy of 0·001 K.

Substances used have been purified by the methods described previously[1-3], where the comparisons of some measured physical constants with the literature data were also given.

RESULTS AND DISCUSSION

The evaluation of molar heat capacities from the performed measurements requires to use a reference substance of known heat capacity. As a standard, n-heptane has been chosen for its easy purification, chemical stability and published accurate values of heat capacities in a wide temperature range[4].

The molar heat capacities c_p of substances studied have been calculated from the relation

$$c_p = \left(\frac{Q - Q_r}{\Delta T} + c_{pr}\frac{m_r}{M_r}\right)\frac{M}{m}\,, \tag{1}$$

where Q is the heat supplied to increase the temperature in the vessel by ΔT, m is the mass of substance measured and M its molecular mass. The subscript r in Eq. (*1*) denotes the corresponding values for the standard (n-heptane).

In all the measurements, the ratio of heat capacities of empty vessel and liquid has been approximately 3 : 2.

With respect to low values of ΔT, the correction for the change of c_p with temperature has been negligible[4]. For the same reason neither the heat capacity of the vapour phase nor the change in its quantity during measurements have been considered. In this way obtained heat capacities are strictly speaking the values measured along the saturation curve (c_σ) and it has been necessary to convert them to the values at constant pressure (c_p). For the given substances and temperatures, however, this

TABLE I

Molar Heat Capacities

Temperature °C	Number of measurements	Molar heat capacity J K^{-1} mol^{-1}	
		this work	literature data
		Ethanol	
25	8	112·30 ± 0·11	112·34[6]; 112·19[7]; 111·91[8]; 112·53[9]
35	7	116·16 ± 0·11	116·26[7]; 116·15[8]; 116·53[9]
45	9	120·60 ± 0·13	120·71[7]; 120·29[10]; 120·81[8]
		n-Propanol	
25	9	143·77 ± 0·19	143·87[6]; 143·8[11]
		Tetrachloromethane	
25	7	131·40 ± 0·15	131·36[6]; 131·49[7], 131·0[12]
35	8	132·05 ± 0·14	131·95[7]; 132·63[12]
45	10	132·78 ± 0·16	132·76[7]; 133·89[12]
		Benzene	
25	10	135·90 ± 0·20	135·76[6]; 136·1[13]; 136·06[14]
35	8	138·00 ± 0·19	138·01[7]; 137·6[15]; 138·32[14]; 138·01[16]
45	6	140·90 ± 0·23	140·42[7]; 140·5[14]; 140·69[16]
		Cyclohexane	
25	7	156·12 ± 0·10	156·07[6]; 156·14[8]; 155·5[15]
35	8	160·04 ± 0·18	159·97[8]; 158·7[15]
45	5	163·98 ± 0·16	163·87[8]

correction[5] has amounted to about 0·01% and therefore the molar heat capacities in Eq. (*1*) are denoted directly as c_p.

The results of measuring the molar heat capacities of ethanol, tetrachloromethane, benzene and cyclohexane at 25, 35, and 45°C and of 1-propanol at 25°C are summarized in Table I where they are compared with selected literature values.

The accuracy of the measured c_p values cannot be better than the accuracy of heat capacity of n-heptane and therefore the average absolute deviations in Table I provide rather the information about the reproducibility of measurement. The comparison with the best chosen literature values which can be considered reliable, proves the probable error of measurement lower than 0·3%.

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