**G. J. Kabo, A. V. Blokhin,
A. G. Kabo**

INVESTIGATION OF THERMODYNAMIC PROPERTIES OF ORGANIC SUBSTANCES

The main problem of chemistry is to determine how deeply the matter can be transformed. Such ability is characterized by the limiting (equilibrium) degree of conversion under given conditions and the time it takes to get the necessary yield [1]. The quantitative characteristics of the reactivity of substances can be obtained unambiguously if the parameters of the potential energy surface $G(r_i)$ for the given set of molecules (particles) are known. The surface geometry depends on the properties of the interacting particles, external conditions, presence of solvent, catalysts etc. The minima on the surface correspond to the stable states (molecules). The concentration of the reagents can be determined from the ratio of the minima:

$$\Delta_r G^o = -RT \ln K_r,$$

where $\Delta_r G^o = G^o_{(A)} \quad G^o_{(B)}$ is the standard Gibbs energy change in the chemical transformation; $K_r = a_A/a_B$ is the equilibrium constant, which defines the equilibrium ratio of the reagents (a_A, a_B are the activities or fugacities of the components A and B in the equilibrium mixture $A \leftrightarrow B$). The maxima on the reacting paths define the time the transformation takes. One of the main and very difficult problems of physical chemistry is the determination of the overall surface geometry. The minima are found from thermodynamic experiments: measurement of enthalpies of combustion, or other devaluation reactions, and calculation of enthalpies of formation and reactions; measurement of heat capacity from (5 to 700) K, enthalpies of phase transitions, saturated vapor pressures followed by the calculation of the entropy $S^o(T)$ and the Gibbs energy $\Delta G^o = H^o - T\Delta S^o$. These values are of great importance for theory, technology, and engineering.

For example, in USA it is recognized as necessary to perform thermodynamic analysis for all important processes and reactions related with the human activity on the Earth. These data are necessary to make sure of that the activity is put into practice at the conditions providing maximal thermodynamic efficiency [2].

Investigation of thermodynamic properties of substances is extremely time-consuming and expensive. The comprehensive thermodynamic studies have been carried out only for one thousand compounds among about 10 million of the synthesized ones. So, first, the comprehensive thermodynamic investigations for the series of key compounds are one of the main tasks of chemical thermodynam-

ics. They allow us to find out the correlations between structure and properties of molecules and to develop the methods for the serial calculations of thermodynamic properties. Second, thermodynamic properties of substances are basic characteristics, which depend on their structure and energy levels. This circumstance is used sometimes to get the information on the molecular structure. Third, substantiation of the most thermodynamically reasonable conditions is especially important for industrial chemistry, because millions tons of chemicals are processed at many chemical plants. Knowledge of optimal conditions leads to the least expenses and ecological danger of chemical plants.

The investigations in these three directions are carried out at the Laboratory of Thermodynamics of Organic Compounds (LTOC) of the Institute for Physical Chemical Problems of Belarusian State University. The subjects to study are chosen in agreement with either theoretical aims, or the needs of technology.

EXPERIMENTAL INVESTIGATION OF THERMODYNAMIC PROPERTIES OF SUBSTANCES

The substances were additionally purified by fractional distillation and sublimation under ambient and reduced pressure, fractional crystallization, and preparative chromatography with the PAKhV-08 chromatograph.

The purity of the samples was controlled chromatographically with the TSVET-800 chromatograph equipped with a flame-ionization detector and a katharometer.

Heat capacity in the range (5 to 320) K and enthalpies of phase transitions in the condensed state are measured with an automated adiabatic calorimeter TAU-1 made by VNIIFTRI (Moscow, Russia) [3–5]. It was modified at the Laboratory using modern measuring instruments and computers. The scheme of the calorimeter and the measuring cell are given in Fig. 1. The calorimeter was equipped with the nitrogen and helium immersion thermostats. The ordinary for adiabatic calorimetry intermittent heat input was used. The temperature of the adiabatic shield was kept close to that of the calorimeter. The calorimeter containers had small volume (1 to 2) cm^3. That is why the Fe-Rh resistance thermometers TSZhRN-3 ($R_0 = 45.32$ and $R_0 = 101.83$ Ω) were placed into copper tubes located on the inner surface of the adiabatic shield. The thermometers were produced and calibrated by VNIIFTRI. The temperature difference between the calorimeter and the adiabatic shield was determined with the four-junction differential thermocouple (Cu + 0.1 % Fe) / Chromel. The computer-controlled potentiometric scheme was used for measurement of the input power and the information processing. The calorimeter was verified in the C_S measurements with benzoic acid of K-1 grade (99.995 mol % purity). It was shown that the uncertainty of the measurements was < 2.0 % at (5 to 10) K, (1.0 to 1.5) % from (10 to 20) K, (0.6 to 0.5) % from (20 to 40) K and 0,4 % above 40 K. With this calorimeter the heat capacities have been measured for more than 100 substances [6–10]. For some substances the results agree well with those obtained in the leading foreign laboratories of Japan and USA [11, 12].
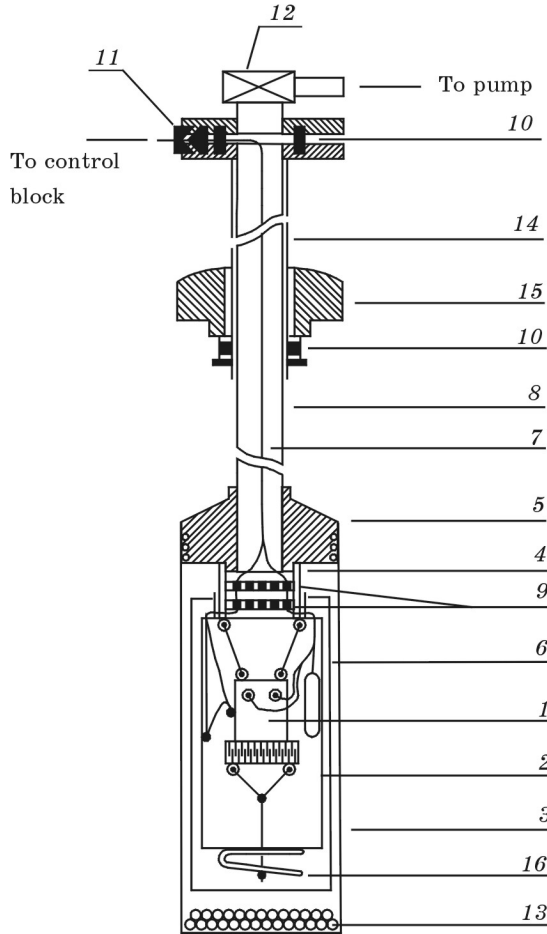
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Fig. 1. Adiabatic calorimeter TAU.
1, calorimeter; *2*, adiabatic screen; *3*, vacuum cup;
4, textolite tube; *5*, copper flange; *6*, radiation
screen; *7*, wires; *8*, stainless steel tube;
9, contact collar; *10*, resign compaction;
11, hermetic socket; *12*, vacuum gate;
13, coal adsorber; *14*, stainless steel tube;
15, screw-nut; *16*, spring

The scanning calorimeter of the heat bridge type was used at the Laboratory for the measurements of heat capacities and enthalpies of phase transitions in the temperature range (250 to 650) K. The method is based on the condition of correspondence of heat flows to the cells with the tested sample and the reference substance [13]. It was noted [14] that it was reasonable to use the configuration of the calorimeter with only two cells (Fig. 2). The calorimeter cells ($V \sim 1$ cm^3) were made of copper and were placed on the constantan rods of 3 mm diameter and 15 mm height. The rods were stayed on a heater block of high mass. The copper cells, the rods and the copper heater block formed two differential thermocouples, electro-
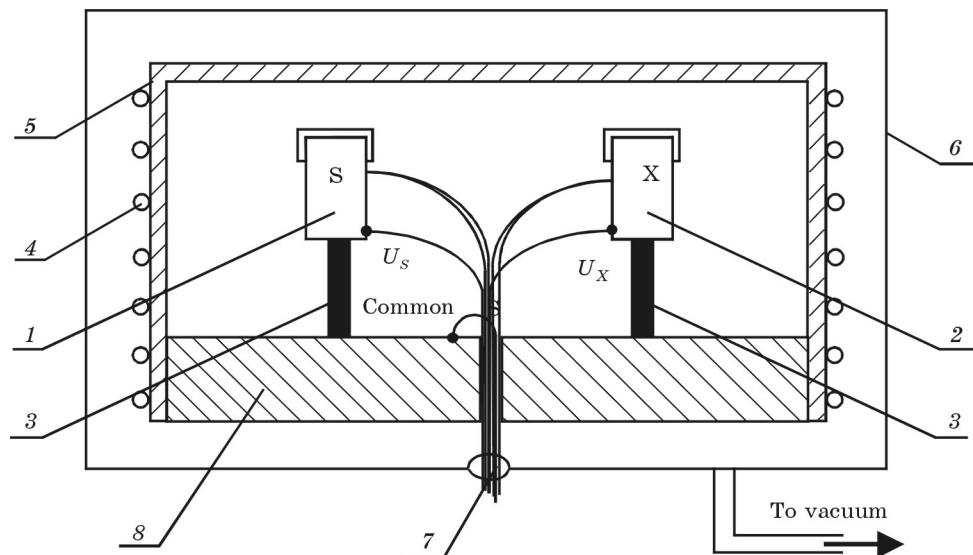
Fig. 2. Differential scanning calorimeter of triple heat bridge type.
1 is reference cell; 2 is sample cell; 3 are Constantan rods; 4 is heater; 5 is cover;
6 stainless steel shield; 7 are thermocouples; 8 is copper heater block

motive forces (e.m.f.) of which were proportional to the heat flows and, therefore, the heat capacities of the substances loaded into the cells. The described cell was covered with a steel dome. The dome was filled with argon. Its pressure was kept about 2 kPa in the experiment. The heat capacity of the tested sample C_X was calculated from the equation

$$C_X \quad A(T)\frac{U_X}{U_S} \quad B(T),$$

where U_X and U_S are e.m.f. of the differential thermocouples with sample cell and reference cell, respectively; $A(T)$ and $B(T)$ are the factors determined by the calibration against the reference substances. The temperatures of the cells were measured with the copper-constantan thermocouples calibrated against the platinum resistance thermometer.

The U_X and U_S values were measured with a digital nanovoltmeter. The heating rate was (0.8 to 0.9) K min^{-1} and reproducibly depended on temperature. The heat capacity measurements for copper (99.995 mas %), aluminium, benzoic acid (K-1 grade) showed that the error of C_S measurements was within (1 to 2) %. The error depends significantly on the purity of the external surface of the cells and the emitting parts of the calorimeter, because the heat exchange due to radiation became dominant at $T > 450$ К. That is why before every series of measurements the surfaces were preliminary reduced with hydrogen at 700 K and then evacuated. The reliability of the measurements was also supported by the agreement of C_s values with those obtained with the adiabatic calorimeter [15, 16]. The good agreement of the values of enthalpies of phase transitions from DSC and adiabatic calorimetery should also be noted [17].
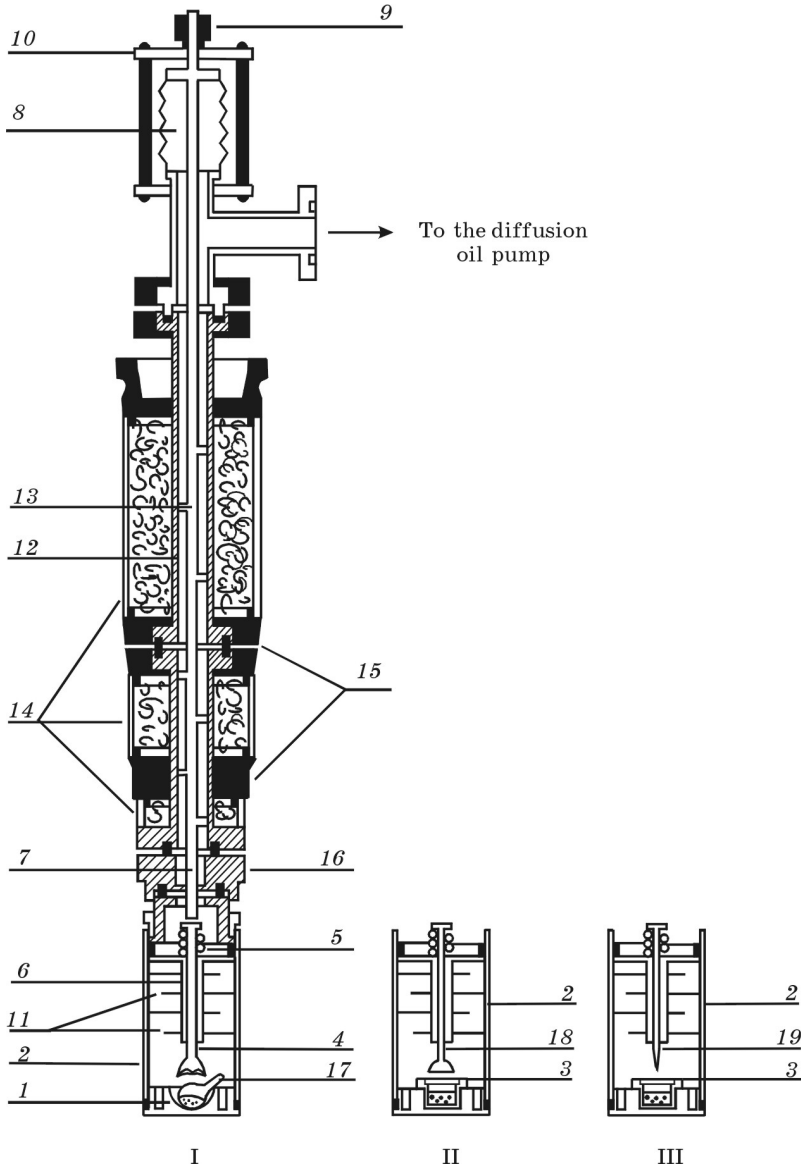
Fig. 3. The scheme of the calorimetric cell
for the differential microcalorimeter.

1, the lower lid; *2*, evaporation chamber; *3*, effusion cell with a sample;
4, metal rod; *5*, spring; *6*, directing channel; *7*, subsidiary rod; *8*, bellows;
9, fixing screw; *10*, limiting strap; *11*, metal shields; *12*, Teflon tube;
13, segmental shields; *14*, thermoisolating coats; *15*, *16*, metal contacts
for thermostating, *17*, glass cell; *18*, metal rod with a seal band;
19, metal rod with a spire; I, evaporation chamber with crushed ampoule;
II, evaporation chamber with effusion cell closed by metal rod; III, evaporation
chamber with effusion cell obtained by piercing the membrane.

The heat flow differential microcalorimeter of the Calvet type for determination of enthalpies of evaporation was designed at LTOC based on the commercial MID-200 calorimeter («Etalon» plant, Alma-Ata, Kazakhstan). We designed the special calorimetric cell [18] (Fig. 3), according to the following requirements: a) maximal thermal contact in the measuring zone; b) prevention of heat loss from the measuring zone; c) keeping of thermophysical properties of the MID-200 thermostating shields. The evaporation occured either from the broken glass ampoules, or from the special metal ampoules through the orifice in the thin nickel membrane. The glassy ampoule was crashed with a metal rod. The latter was fixed on a spring, which was moved with an auxiliary Teflon rod. After the ampoule being broken the main and the auxiliary rods did not contact directly to prevent heat loss related with heat-conductivity of the rod. Earlier, if the metal ampoules were used, the orifice was made before the experiment start and was covered with a silicon cap placed on the butt-end of the metal rod. The hole was opened when the measurements had started. Now the membrane is pierced with a needle placed on the rod during the experiment.

Four segmental metal shields were established into the evaporating chamber (fig. 3). It was done to prevent the carryover of the condensed substance and to increase the path of the vapor in the evaporating chamber. The latter excludes the carryover of the supercooled gas from the chamber. The power of the heat flow W is evaluated from the relation

$$W = \frac{\Delta E}{K},$$

where ΔE (mV) is the e.m.f., which corresponds to the temperature difference between the core of the calorimeter and the evaporating camera; K (mV $\cdot$ W^{-1}) is the thermal constant of the cell.

The constants for two cells K_A and K_B were determined from the results of measurements of enthalpies of vaporization for the reference substances (bidistilled water, decane, naphthalene, and benzoic acid):

$$K = \frac{1}{\Delta_{vap(sub)}H} \int_0^{\tau_{fin}} \Delta E \, d\tau,$$

where $\Delta_{vap(sub)}H$ is the enthalpy of vaporization (sublimation) for the reference substances:

$\Delta_{vap}H$ (H$_2$O, 298.15 К) = (44.016 ± 0.042) kJ mol^{-1},
$\Delta_{vap}H$ (C$_{10}$H$_{22}$, 298.15 К) = (51.33 ± 0.13) kJ mol^{-1},
$\Delta_{sub}H$ (C$_{10}$H$_8$, 298.15 К) = (72.6 ± 0.3) kJ mol^{-1},
$\Delta_{sub}H$ (C$_7$H$_6$O$_2$, 298.15 К) = (90,4 ± 0.5) kJ mol^{-1};

τ is the time of the experiment (of thermal equilibration).

The time for complete evaporation of the samples of the reference substances differed significantly. In spite of that the thermal constants of the cells $K_A = (185.6 ± 0.4)$ and $K_B = (200.0 ± 0.6)$ remain about unchanged and agreed with

the results of calibration with electric current [18]. The signal ΔE was registered with the V2-38 nanovoltmeter with the uncertainty of $\pm$ $(10^{-3}$ to $10^{-4})$ mV depending on the value of the signal. The intervals between the readings was $(0,7$ to $1.5)$ s. The large drift in the K_A and K_B values occurred if the device was not used for long periods. That is why the calibration procedure was repeated before every series of experiments. The error of the enthalpies of evaporation was better than $\pm$ 0.5 % .

The calorimeters for combustion of organic substances (Figs. 4, 5) were designed based on the commercial V-08-MA calorimeters («Etalon» plant, Alma-
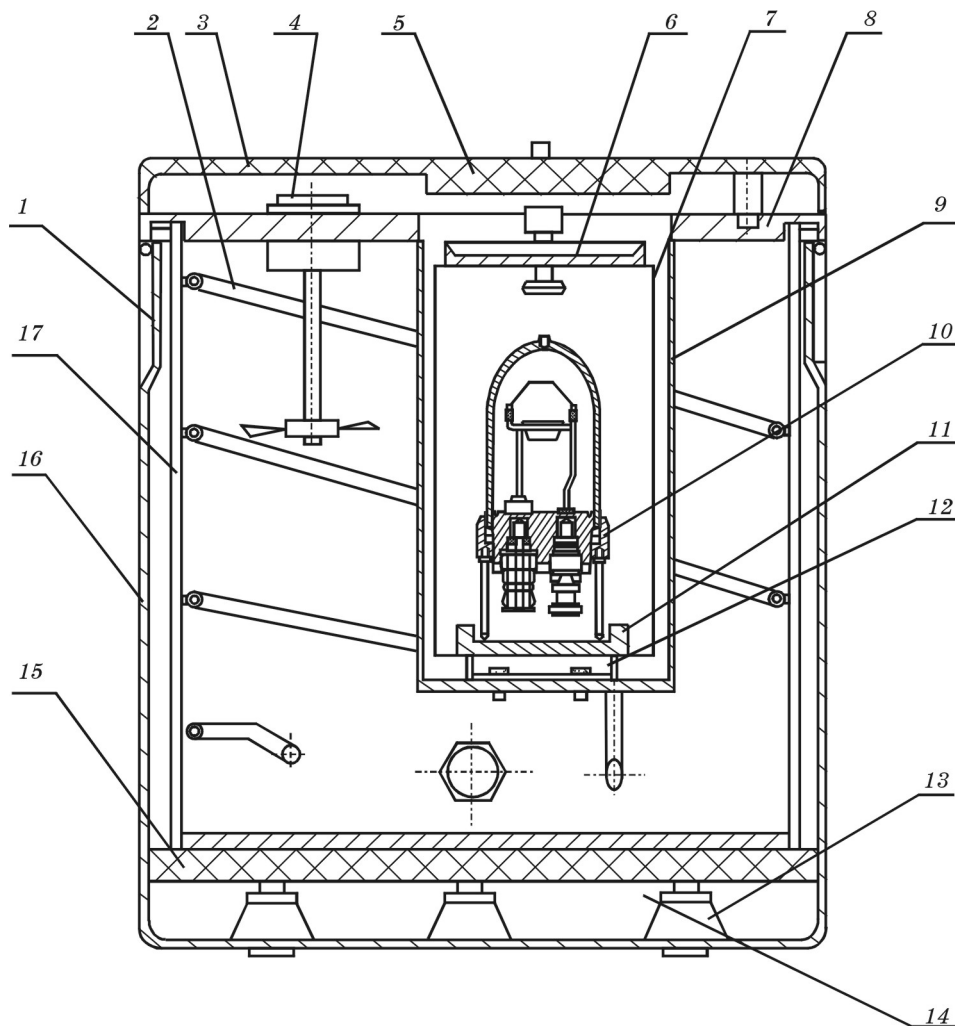

Fig. 4. Calorimeter V-08-M.
1, folding handle; *2*, pipe; *3*, cover of calorimeter; *4*, shell mixer; *5*, cover;
6, cover of the calorimetric vessel; *7*, calorimetric vessel; *8*, higher textolite plate;
9, socket of calorimetric vessel; *10*, calorimetric bomb; *11*, metal support;
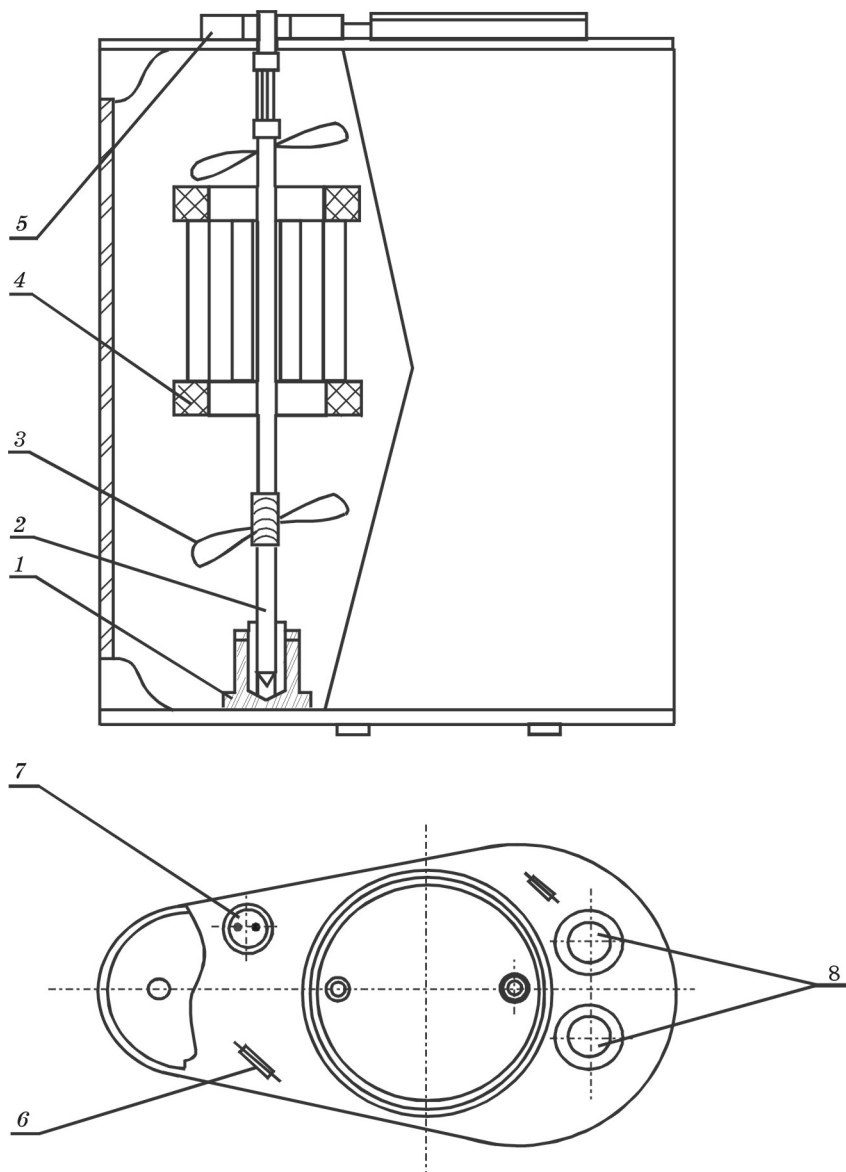*12*, pedestal; *13*, legs; *14*, pallet; *15*, textolite plate; *16*, coat; *17*, shell

Fig. 5. Calorimetric vessel.
1, bearing; *2*, axis of the mixer; *3*, impeller; *4*, heater; *5*, bush; *6*, lug;
7, bayonet clamp; *8*, sockets for the platinum resistant thermometers

Ata). The thermostating bath, the ignition scheme were improved. The calorimetric vessel and the device for the gas rinsing of the bomb for the analysis of the gaseous combustion products were sealed [19]. The steel crucible was changed to the platinum one.

The temperature in the calorimetric shield was kept constant to within ± 0.01 K. The electric energy spent to ignite the substance is measured by the discharge of the 9.0 mF capacitor bank. The platinum wire of 0.05 mm is used for the ignition. The temperature of the calorimetric vessel is measured with the 100 W platinum resistance thermometer using the bridge scheme. The unbalance is registered with the digital Sch-1516 voltmeter with uncertainty of ± 0.0002 V.

The original electronic device for the automation of the measuring process was designed. The primary information is sent to the computer, and all the necessary calculations are made: corrections for heat exchange, Washburn corrections, energy of combustion of the substance. The oxygen used to fill the bomb is purified in the apparatus with heated CuO, a pipe cooler and tubes with ascarite. The samples of the substances in the form of pellets or polyethylene ampoules were weighed with accuracy of $\pm\ 2 \cdot 10^{-5}$ g. Then the mass was reduced to vacuum. The content of the dissolved nitrogen oxides in the bidistilled water ($1\ cm^3$) put in the bomb was determined by titration.

The gaseous products of the calorimetric experiment were analyzed gravimetrically. The system of the absorbing traps filled with activated MnO_2 and ascarite. The thermal value of the calorimeters (Table 1) was determined in the experiments with benzoic acid (K-1 grade). Its heat of combustion is

$$\Delta_C U^o\ (298.15\ K) = (26460.6 \pm 4.6)\ J \cdot g^{-1}$$

for weighing in air.

The absence of systematic errors and the reliability of the calorimeter were verified in experiments on combustion of crystalline carbamide (Table 2).

The combustion energies for hundreds of C, H, O, N-containing substances and materials have been determined in the described calorimeters.

Table 1

Technical characteristics of the combustion calorimeters

Calorimeter	Mass of the calorimetric vessel with the bomb, kg	Volume of the bomb, dm^3	Temperature of the shield, K	Voltmeter readings at 298.15 K, V	Heat value, $J \cdot V^{-1}$
1	7.9837	0.3205	300.65	0.7940	14889.9 ± 6.4
2	8.0000	0.3210	300.41	0.7518	14936 ± 4.6

Table 2

Standard enthalpy of combustion for carbamide (CH_4ON_2)

Authors (year)	Purity, mas %	$-\Delta_C U^o$ (298.15 K), kJ $\cdot$ mol^{-1}
Huffman [20] (1940)	–	638.99 ± 0.18
Mannson, Sunner [21] (1963)	–	632.57 ± 0.10
Jonson [22] (1975)	99.70	633.02 ± 0.17
Aleksandrov, et al [23] (1979)	99.83	632.82 ± 0.54
Minas de Piedade, et al [24] (1992)	99.90	632.57 ± 0.48
Our data [25] (1990)	99.92	633.30 ± 0.65

The effusion Knudsen method for determination of vapor pressure of organic substances. Vapor pressure P_{sat} is one of the most important physical chemical properties of the substance. It is the key value in the calculation of the ideal-gas entropy. The P_{sat} values are necessary for many kinds of technical calculations. The method of vapor pressure measurements is chosen based on its value, thermal stability of the substance, how accurate should the data be and some other factors.

The vapor pressure of most of the substances we have studied is below 200 Pa in the range where they are thermally stable (200 to 450 K). The Knudsen method fits for measurements in this range. It is based on the measurements of the effusion rate from the cell filled with saturated vapor through the orifice of known diameter. Knudsen analyzed the effusion process under such conditions and received the following equation

$$P_{sat} = \frac{m}{K\,S\,\tau}\sqrt{\frac{2\,RT}{M}},$$

where m is the mass loss in the experiment; S is the orifice square; τ is the exposition time; K is the Clausing coefficient; T is the temperature; M is the molar mass of the substance. This relation holds if the mean free path of the molecules of the gas is larger than the size of the effusion cell. The Clausing coefficient considers the non-zero thickness of the orifice. In many cases it can be evaluated from the equation

$$K = \frac{1}{1+\dfrac{l}{2r}},$$

where r is the radius of the orifice; l is the membrane thickness.

The integral version of the Knudsen method is used in LTOC. The experiments take more time, provides better thermostatting of the sample than in the differential method, where the cell is suspended in vacuum.

A scheme of the apparatus for P_{sat} measurements by the integral effusion Knudsen method is shown in Fig. 6 [26, 27]. The cylindrical effusion cell of 1 cm diameter and 1 cm height was made of stainless steel 1Kh18N9T. The thicknes of the walls is 1 mm. The membrane is made of 0.05 mm nickel foil and is fixed with a gasket. The cell was sealed with a Teflon ring, as a washer. The copper washer was put on the membrane to lower the temperature gradients. The effusion orifices were made by drilling of the foil fixed between two steel plates. Then the orifice was additionally treated with a steel needle and Capron thread. The orifice diameter was determined with the modified horizontal compare circuit by rotation of the membrane with step of 15°. The magnification was 3000^{x}. The average diameters were (0.2483 ± 0.0006); (0.8254 ± 0.0004) mm etc.

The studied substance of (0.3 to 0.5) g mass was charged into the cell with a steel punch. The system (Fig. 6) was evacuated, filled with helium to 101 kPa pressure, and thermostated within ± 0.01 K for 30 minutes. The temperature of the thermostat was measured with the platimun resistance thermometer using the opposition method.
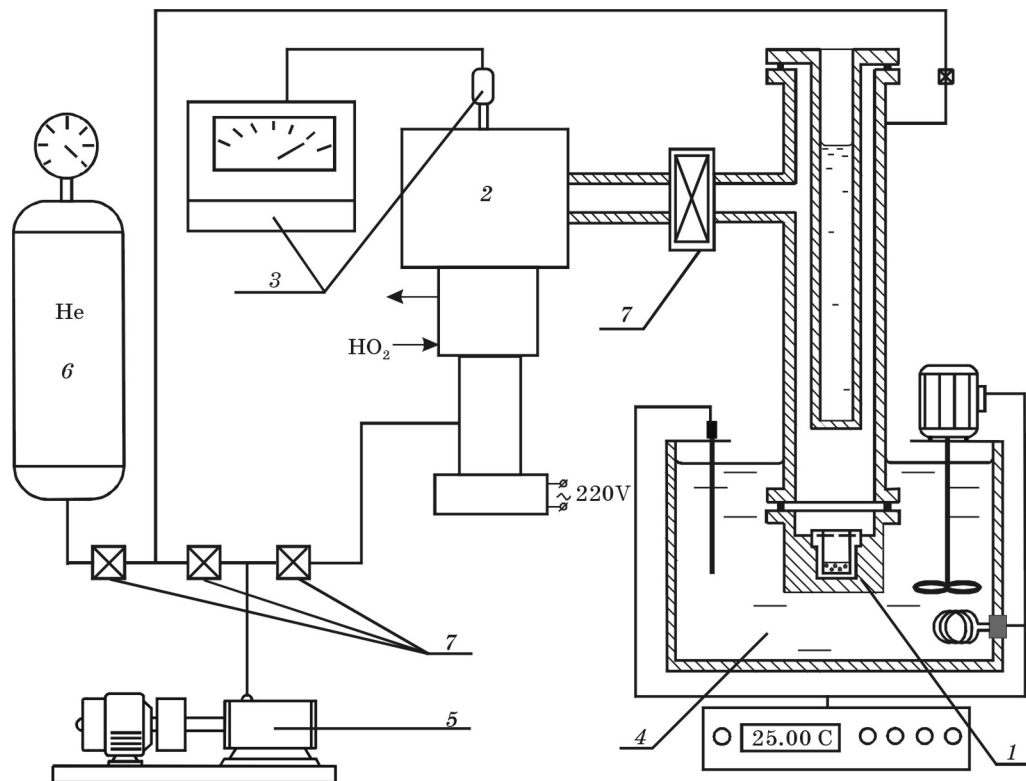
Fig. 6. The scheme of the apparatus for vapor pressure measurement by Knudsen method:
1, measuring block (effusion cell with a sample, vacuum connection, cold finger);
2, diffusion oil pump; *3*, vacuum measuring gauge; *4*, liquid thermostat;
5, roughing-down pump; *6*, helium cylinder; *7*, bellows gates

In the special experiments it was demonstrated that the temperature difference between the sample and the thermostat was about 0.03 К. It will not introduce the error in the P_{sat} values larger than 0.5 %. The system was evacuated with an oil diffusion pump and a roughing-down pump. The residual pressure was less than 10^{-3} Pa.

After the exposition the system was filled with helium to 101 кPa, thermostat was removed, and the cell was cooled down under helium pressure. After keeping in air to constant mass the cell was weighed with uncertainty $\pm 2 \cdot 10^{-5}$ g.

The mass loss during the thermostatting procedure was determined in the special experiments. This correction depended on the nature of the substance, thermostatting time, and P_{sat} values.

The exposition time depended on the evacuating mode. When turning the oil diffusion pump after the roughing-down pump had worked for 10 s the uncertainty in the mass loss due to the non-stationary conditions was compared with the uncertainty of weighing.

To determine how the results depend on the orifice square and to extrapolate them to the «zero» orifice the special experiments were carried out. It was found

that the relation $P_{sat} = k(d) \cdot P_{ef}$, where P_{ef} is the effective vapor pressure for the membrane of $d = 0.258$ or 0.832 mm diameter, can be used for evaluation of P_{sat}. For the membranes $k(d) = 1.01$ and 1.10 respectively. It did not depend on the P_{ef} values and the nature of the substance.

The apparatus was verified with the K-1 grade benzoic acid. The probable error in P_{sat} was estimated to be $\pm 5,0$ %. However, the values of enthalpies of vaporization (sublimation) calculated from the $P_{sat} = f(T)$ dependence were systematically (3 to 5) kJ·mol^{-1} higher than those obtained from calorimetric measurements. We found out that the calorimetric $\Delta_{vap(sub)}H$ values did not depend on the way the evaporation was initiated, from the broken ampoule, or through the pierced orifice in the membrane. The described contradictions were resolved using the Wahlbeck theory [28] for taking into account the anisotropy failure in the vicinity of the effusion orifice.

The orifice transmission probability $K_W = f(l, d, \lambda)$ is a function of the orifice dimensions (length l and diameter d) and the mean free path of molecules λ. At the Knudsen numbers Kn $= (\lambda / d) > 10$ the K_W values are close to those calculated according to Clausing. However, at high temperatures $\lambda(P, T)$ decreases, and Kn < 10. As a result, the K_W values can differ significantly from the Clausing coefficient. The P_{sat} values are (20 to 30) % underestimated. We demonstrated that the calculation of $\Delta_{vap(sub)}H$ from the P_{sat} values evaluated with respect to the anisotropy failure in the Knudsen cell removed the contradiction with the results of the calorimetric measurements [29].

Thus, all the experimental apparatuses of LTOC allow us to measure thermodynamic properties of substances and calculate the values of $C_P(T)$, $\Delta_f H$, $S°(T)$ for crystals, glasses, liquids, and gases.

RESULTS OF INVESTIGATION OF THERMODYNAMIC PROPERTIES OF SUBSTANCES AT LTOC

Below the main results in the thermodynamics of organic substances obtained at LTOC are reviewed shortly.

Equilibria of reactions. The chemical equilibria and thermodynamic properties for some classes of organic substances were studied. They are haloalkanes [30-32], alkenes [33], alkyl and phenyl carbamides [35], nitrogen containing hetrocycles, substituted cycloalkanes [8, 10, 35] etc. Many qualitative rules for the organic reactions, for example, Zaitsev, Markovnikov, Flavitsky rules were explained and quantitatively described based on the thermodynamic calculations for the corresponding conversions.

Additivity of thermodynamic properties. The methods for calculation of thermodynamic properties were created. The physical chemical properties is considered as a sum of the increments of properties of effective atoms, bonds, or interactions in molecules:

$$P \qquad \sum_i n_i P_i,$$

where P_i is the part of the property (increment) for i effective atoms, i bonds, or i groups, and n_i is their number in the molecule.

From the experimental data the values of increments were found. The increments allowed for calculation of the thermodynamic properties of the substances, the number of which is thousands times more than the number of the substances studied in experiments. The computational techniques based on the substitutive procedure were proposed. «Cyclicity» is proved to be an important feature for classification by effective atoms. It characterizes the size of cycles and the type of contacts between them [36, 37]. This characteristic is very important as it can be applied to describe chain and cyclic compounds in the unified manner.

It was first proved that the additive methods based on the classical theory of molecular structure can be used for prediction of the thermodynamic properties for both gases and crystals [34]. The numerical values of the increments for crystalline alkanes, alkenes, ketones, alcohols, alkyl carbamides were found. The limitations for such calculations were also determined.

Thermodynamics of isomerization. One of the most important phenomena in chemistry, isomerism, was thermodynamically described on the basis of the experimental investigations performed [38]. Different types of isomeric transformations were systematically analyzed [39–41], and some thermodynamic parameters of the isomerization reactions were generalized. The new understanding of the term «pure substance» developing the van-der-Waals idea was given.

Plastic crystals. The thermodynamic properties of plastic crystals were investigated. In these compounds the restricted overall rotation of molecules in the lattice sites occurs. The transition to this state is characterized by spontaneous change in physical properties of the substance: density, dielectric permittivity, optical properties etc. So, this phenomenon can be applied in engineering. We proved that the ability to form plastic crystals cannot be predicted from simple analogies in the molecular structures [42, 43]. It was found that the transition «plastic crystal → rigid crystal» is accompanied by the spontaneous simplification of the confomational composition of the substance. It was shown that the sum of entropies of solid-to-solid transitions and fusion in the series of such compounds is approximately constant. This rule can be used for prediction of thermal behavior of crystalline substances, which are not examined completely.

Thermodynamic properties of ionic liquids. The investigation of thermodynamic properties of the room-temperature ionic liquid (IL) $[C_4mim][PF_6]$ (1-butyl-3-methylimidazolium hexafluorophosphate) is inspired by the possible use of ILs as ecologically friendly reagents, reaction media, catalysts [44]. We validated the technique for the additional purification of the $[C_4mim]PF_6$ sample manufactured by Covalent Associates, Inc. The C_s and $\Delta_{trs}H$ values in the temperature range (5 to 550) K, density in the range (298 to 353) K were measured. The thermodynamic properties for the separate ions and the ionic pair in the ideal gas state were calculated by the statistical thermodynamic method. The vapor pressure was estimated

It is demonstrated that:

1. The fractional melting technique in an adiabatic calorimeter is the efficient way to determine the purity of ILs.

2. The ratio $T_g/T_{fus} = 0.67$, $\Delta_{fus}S^o = 69.13$ and $S^o(gl, T \to 0 \text{ K}) = 14.6 \text{ J} \cdot \text{K}^{-1} \text{ mol}^{-1}$ are usual for the low-molecular organic substances.

3. Below 40 К the crystalline and glassy [C_4mim]PF_6 have anomalously high specific heat capacity compared with C_s for molecular and some inorganic ionic crystals. This phenomenon can be caused by the mechanical properties of the crystalline and glassy [C_4mim]PF_6 and hence, low values of $\Theta_D = 62.7$ K and 49.5 K is due to the low packing density of the ions of different size in the lattice. It is also possible that below 40 K the electron contribution to C_s of [C_4mim]PF_6 is comparatively large. This contribution is changed with temperature more slowly than the vibrational contribution.

From the statistical calculations and calorimetric measurements $\Delta_{vap}S^o(298.15 \text{ K}) = = 175.3 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$ was evaluated. $\Delta_{vap}H^o(298.15 \text{ K}) = 161 \text{ kJ} \cdot \text{mol}^{-1}$ was found from the molecular dynamics simulation. According to these data, the vapor pressure for [C_4mim]PF_6 was estimated to be $P_{sat}(298.15 \text{ K}) \approx 10^{-14}$ Pa.

Statistical thermodynamics. It is extremely fruitful to use the statistical thermodynamics for calculation of thermodynamic properties of substances in the ideal-gas state. Such calculations require some molecular data: structural parameters, frequencies of normal modes, potential barriers to internal rotation and molecular inversion etc. From these data one can get the values of thermodynamic properties for organic substances under conditions not available for experimental measurements. Some computational procedures were improved: the limits for applicability of the classical approximation in calculation of contribution of molecular inversion and internal rotation were substantiated [45], the approach to calculate thermodynamic properties for the mixtures of tautomers was proposed [46]. These computational methods were used for the detailed investigation of conformational and equilibrium changes of substances, which can exist in the form of mixtures of many compounds with different molecular structure: barbituric, parabanic, cyanuric acids, biurete, tetrazole, semicarbazide etc. Using the molecular and spectral data the statistical calculations of thermodynamic properties were carried out for tens substances.

The fundamental monograph [47] was published together with Prof. G.N. Roganov, and the TRC officers K. Marsh, M.L. Frenkel, and R. Wilhoit. It reviews the results of calculations of thermodynamic properties of substances by the statistical thermodynamic method for the last 30 years, and includes the data for 1168 compounds. The book was highly estimated by the known specialists in chemical thermodynamics: E. Westrum [48], E. Domalsky [49], A. Greenberg [50] etc. They noted its value for solution of fundamental problems in physical chemistry and chemical technology.

LTOC ACTIVITY FOR THE TECHNOLOGY OF ORGANIC SYNTHESIS OF THE REPUBLIC OF BELARUS

At LTOC the comprehensive thermodynamic investigations were carried out and the results of the measurements were analyzed for the reagents, main products, and some by-products of production of caprolactam (Grodno), carbamide (Grodno), dimethyl terephthalate (Mogilev), nitryl acrylic acid (Novopolotsk). The database on chemical exergies for the substances of organic synthesis in the Repulic of Belarus was created. In the database the values of chemical exergy

$E = H - T_0 S$, (T_0 is the temperature of environment) are considered as the objective measure of thermodynamic value of the substance with respect to the environment [51]. The results obtained allowed us to substantiate the reasonable schemes of power consumption in the caprolactam and carbamide production, conditions for separate saponification of esters and hydrolysis of dianones in the caprolactam production, dessication of cyclohexanone oxime, countercurrent scheme of the heat exchanger for the reactor of cyclohexanone dehydration [52, 53] etc. Some of these recommendations were realized at the Grodno «Azot» plant.

At LTOC the technical regulation for production of the XT polymer from the wastes of cyclohexane oxidation during the caprolactam production was worked out. These resources at the Grodno «Azot» plant make it possible to produce up to 5 thousand tons of the XT polymer per year. The compoundings using the polymer were proposed. The pilot batches of lacquers, enamels, wood-protectors etc.

At LTOC the dataware for the thermodynamic substantiantion of energy and resourse saving technologies of organic synthesis in the Republic of Belarus is being developed. Technical and economical substantiation was made and the laboratory regulation for production of Diesel biofuel from rapeseed oil. This technology is going to be applied for production of biofuel at the modular plant with output of 2000 tons per year.

The main principles of thermodynamic analysis of multicomponent and multiphase systems have been developed to improve the efficiency of the plants for purification of industrial gases, design of the controlled gas media and the gas generators [54].

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