

Calorimetry today

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Abstract - This lecture is one of the "Swietosławski lectures", taking place in the year of the twentieth anniversary of death of this famous scientist who was named "the father of thermochemistry in IUPAC (ref. 1). The aim of the lecture is to point out the progress which took place recently in the development of calorimetric methods.

Let the following classification of calorimetric systems be the basis of our talk (ref. 2). Let us call the calorimeters with mass exchange-open systems, and the calorimetric systems in which mass exchange does not occur - closed systems. Let us also distinguish adiabatic and non-adiabatic systems. Adiabatic are those systems, in which during the measurement heat exchange between the calorimetric vessel and shield does not occur; in nonadiabatic systems it does. Let us assume, that the heat process taking place in a calorimeter can be realized in isothermal or nonisothermal conditions. As a particular case for the course of the heat process in nonisothermal conditions, we distinguish further the case of the linear (in time) temperature rise - the temperature scanning. Thus, for open and closed calorimetric systems the following groups of calorimeters can be distinguished: adiabatic isothermal, adiabatic nonisothermal, scanning adiabatic; nonadiabatic isothermal, nonadiabatic nonisothermal and scanning nonadiabatic.

The first adiabatic nonisothermal calorimeter was constructed in 1905, that is 83 years ago. During this period adiabatic calorimetry has been applied widely.

In the present time the adiabatic thermophysical calorimetry is of great importance and is being strongly developed, enriching our knowledge by giving thousands of accurate c_p data. Low temperature thermophysical adiabatic calorimetry is widely used in the estimation of thermophysical properties of substances by analyzing the morphology of heat-capacity curves and the major contribution to them such as lattice vibration, magnetic and electronic state contribution, as well as the first and second order transition, order-disorder transitions and so on. Thermophysical adiabatic calorimetry at a temperature not far from the ambient temperature is used to obtain c_p curves of organic compounds, liquids crystals, whilst high temperature thermophysical adiabatic calorimetry is applied to study metals, ceramic materials, etc.

Adiabatic calorimetry is now not so often used to investigate thermochemical properties but it is especially important when we have to deal with processes, in which a small amount of heat is generated in long periods of time.

One of the most important features in modern calorimetry is the development of a new generation of fully automatic and computerized calorimetric systems which involve automatic digital experimental logging and automatic analogue or digital control systems. This is also true for the adiabatic calorimetry (ref. 3).

For thermophysical adiabatic calorimetry the problem of today is also to minimize the sample size. An effort in this direction has been made. Thanks to it, precise measurements of samples of one or several grams, can be now carried out in adiabatic calorimeters (ref. 3). But in cases of substances hard to synthesize or purify, or radioactive and chemically dangerous materials, this is still too much. In a paper, published in 1984 in the Research Report of Chemical Thermodynamics Laboratory Osaka University it was stated that the measurement of heat capacity of a 300 mg sample was possible. Further progress in this field is expected.

The main domain of Differential Scanning Calorimetry (DSC) applications is the determination of the temperature dependence of the heat capacity in the conditions when small samples of a substance can be used. Typical DSC heat capacity measurement has an accuracy of about 1-2 per cent, that is several times lower than in adiabatic calorimetry. Much worse conditions of reaching temperature equilibrium and reproducibility problems can be noticed. On the other hand - rapidity of measurement and accessibility for users - are without doubt the priorities

of this technique. It can be underlined, that DSC is a measurement technique, where manufactured devices are used.

DSC has a great importance, among other things, in investigations of macromolecules. DSC has proved to be a fundamental technique for studying temperature - induced conformational transitions in molecular biological systems (ref. 4). The simplest temperature induced process for bio-macromolecules is the transition between two thermodynamically stable states - the native and denatured ones. The determination of enthalpy changes of this process becomes the primary aim in DSC biocalorimetry.

In several macromolecules a more complicated process takes place, and temperature-induced transformation proceeds through a number of intermediate macroscopic states. The complex nature of a process can be perceived by the appearance of additional extremes and bends on the melting curve. Ten years ago, Freire and Biltonen proposed an original method of DSC curves deconvolution. This work is the first of several papers (ref. 5) in which the deconvolution method has been described. There are many applications of this procedure.

The first adiabatic-isothermal calorimeter was described 205 years ago, by Lavoisier and Laplace, in the famous work entitled "Mémoire sur la chaleur". At present, automatic electronic devices have created a great number of possibilities of the realization of isothermal conditions of measurements in isothermal-adiabatic as well as in isothermal-nonadiabatic calorimeters. Three ways of realization of the compensation method by means of respective electronic systems can be distinguished: a) via the application of impulse compensation; b) by proportional compensation; c) by proportional - integrating compensation. At the present moment, very interesting developments take place in this group of devices. Several open calorimetric systems which can be used at elevated pressure and temperature have been constructed (refs 6-9). These calorimetric systems are used, e.g. in the determination of the heat of mixing over the whole concentration range at pressures up to 60 MPa.

Elevated pressure and isothermal conditions were applied by J.C. Petit and L.Ter Minassian (ref. 10) in the measurement of thermal expansivity and isothermal compressibility. A few years ago Randzio (ref. 11) proposed a new method of this kind of measurements and described a new type of calorimeter, i.e. the scanning pressure calorimeter. It was shown that this kind of calorimetric system can also be useful in studying the phase transitions. The inertia of the pressure wave in the sample is without doubt lower than in the process of receiving the uniform temperature in the sample. It can be noticed, additionally, that there are several papers in which organic liquids were studied at high pressures (ref. 12).

In the nonisothermal-nonadiabatic calorimeters the generated heat effect is partly accumulated in the calorimetric vessel and partly transferred to the isothermal shield. In this group of calorimeters, we have, of course, calorimeters with mass exchange as well as closed calorimetric systems. In the first group - flow calorimeters - such as the Picker heat capacity flow calorimeter (ref. 13), labyrinth flow calorimeter elaborated by Swietosławski and Zielenkiewicz (ref. 14), LKB and SETARAM flow systems can be mentioned, as well as a large number of home-made calorimeters for the determination of the heat of reaction, heat of mixing, heat of dilution, etc. In this group of open nonisothermal nonadiabatic systems flow as well as stop-flow calorimeters for measuring rates of chemical reactions should be mentioned. R.E. Johnson and R.L. Biltonen demonstrated (ref. 15) that a flow calorimeter can be used in an accurate determination of the reaction rate for reactions whose half-times exceed only a few seconds. Roughton, Berger and Balko (ref. 16) introduced a stop-flow calorimeter to kinetic parameters measurements. These devices enable us to measure the reaction rates of the half-time lasting only milliseconds. This requires temperature sensors and measuring systems which are very precise and have small inertia. It was demonstrated, that there are thermistors and thermocouples for measuring millisecond temperature changes (refs 17, 18). However, the application of conventional sensors (thermocouples, thermistors) to the study of fast processes is limited. Most often, pyroelectric and piezoelectric detectors are used now (refs 18, 19). Similarly, a short pulse of laser beam absorbed by non-transparent sample is used to induce a short time heat effect. Laser light incident on the sample causes several phenomena, among other the appearance of a direct and indirect acoustic wave. This phenomenon called the photoacoustic effect FA was discovered more than one hundred years ago by Graham Bell - but its application appeared only a few years ago. The assumption about the proportionality between the FA signal amplitude and the magnitude of the heat effect became the basis of pulse photoacoustic calorimetry (ref. 21).

The laser technique also leads to another type of devices referred in the literature as thermal lens calorimetry devices (ref. 22).

The photoacoustic calorimeter is a nonisothermal-nonadiabatic, closed calorimeter, in which the conditions of the course of heat effects are near to adiabatic. This kind of conditions occurs in a great number of nonisothermal-nonadiabatic calorimeters. They are often called the "isoperibol" calorimeters. There is a great number of such calorimeters, used for an accurate determination of various heat effects such as heat of combustion, heat of solution, etc.

In the nonisothermal-nonadiabatic calorimeters we can of course intensify the heat exchange between the calorimetric vessel and the isothermal shield. In this way we minimize the inertia of the calorimetric system. This takes place in conduction or heat-flux calorimeters. These calorimeters are used not only for the total heat effect but also for thermokinetic determinations via measuring the time changes of heat power of a given process. These determinations are of particular interest in many fields of science—physical chemistry, biology, biochemistry, medical science, material science. The determination of this function is used to examine the metabolism of various living systems, such as the growth of bacteria and plants or for studies of thermal changes in human blood. For the determinations of thermokinetics, a great number of calorimeters constructed in many scientific laboratories and also manufactured by many companies have been used. Nevertheless, a certain problem remains. The intensive heat exchange causes conditions in which it is difficult (or even impossible) to obtain a uniform temperature distribution in the calorimetric vessel. This situation stimulated the development of various analogue and numerical methods of determinations of thermokinetics (ref. 23). The basis in the determination of thermokinetics can be the multi-body method, based on the system of heat balance equations. Until the moment when the multi-body method was worked out, the "black-box" notion was widely used, that is a mathematical model based on the assumption that a calorimetric system can be treated as an object described by a linear N-order differential equation.

It should be stressed that the development of methods of the determination of thermokinetics created the situation in which we can reproduce the thermokinetics so as if the main time constant of the device was 300 times smaller.

The reconstruction of thermokinetics is an example of applications of calorimetric models (refs 24, 25) to practical problems in calorimetry. Lately, the theory of calorimetry has been widely developed. The subject of theoretical analysis was, among other things, optimization of the device construction, analysis of disturbances connected with the measuring procedure, and providing the dependences between the various mutual localizations of heat sources and temperatures sensors.

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