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Microcalorimetry in a Historical Aspect, State of Art and Prospects. Part 1.

This article scrutinizes the development of calorimetry since the 17th century on. It shows how calorimetry methods changed depending on the acquisition of new knowledge about the nature of heat and thermal processes. The influence of the industrial revolution on the development of calorimetric methods is reflected. The achievements of microcalorimetry in the 20th century and at this stage are demonstrated. The main applied directions of practical use of microcalorimeters are shown. A prospect of possible promising achievements in the field of microcalorimeters and an analysis of the ways to achieve them is made.

Keywords: microcalorimetry, types of calorimeters, characteristics of calorimeters, application of calorimeters.

Introduction

A large number of processes of various nature: physical, chemical, biological, where one type of energy is converted into another, are accompanied by the absorption or release of heat. Hence, information about the quantitative assessment of thermal effects and the nature of their occurrence is essential both for scientific research and for the control of multiple technological processes. Since thermal processes are informative about many important characteristics of substances, in particular enthalpy, internal energy, entropy and other state functions, as well as about heat capacity and thermal conductivity, their study underlies such fundamental laws of nature as the law of conservation of energy and the first principle of thermodynamics.

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The power of thermal processes is most accurately determined when using calorimeters, i.e., – devices that measure thermal effects in special reaction chambers.

The term calorimetry at different stages of the development of physical science obtained different interpretations. Currently, calorimetry is a method of measuring the amount of heat, absorbed or released, which accompanies various physical and chemical processes, including those occurring in biological systems.

When it comes to a small amount of matter and minor thermal effects, research is carried out using microcalorimeters, which are characterized by speed, high accuracy and the ability to work in a wide temperature range.

Although the history of calorimetry dates back to the mid-1700s, the potential applications of microcalorimeters still remain relatively new and unexplored. Its new characteristics are still inspiring innovative possibilities.

History of Calorimetry

The 18th century witnessed the development of the first calorimeters, devices designed specifically to measure heat transfer. This period is characterized by the collaboration of several key figures whose innovations laid the foundation for understanding thermal measurements and paved the way for future advances.

The first calorimeters were simple vessels that allowed experiments with the quantitative determination of thermal changes. These initial designs, although imperfect, enabled researchers to conduct comparative studies of thermal processes in different substances.

It is Joseph Black, a Scottish chemist and physicist, who is considered to be the founder of calorimetry. By heating white magnesia (magnesium carbonate), Black discovered in 1754 that “bound air”, i.e. carbon dioxide, was released in this process, and burnt magnesia (magnesium oxide) was formed. Based on these experiments, the scientist concluded that the difference between carbonic and caustic alkalis is that the former contain carbon dioxide. Black's discovery of carbon dioxide initiated pneumatic chemistry (the chemistry of gases). Black isolated and weighed the gas released when lime or magnesia was heated. He called it “bound air” because he could dissolve it in lime water and thus restore the original carbon without loss of weight. In this way, Black showed that gas can be a component of a solid, that it is strictly material and does not contain anything mystical, as was previously believed.

In 1757, Black introduced the concept of latent heat, discovering the heat of melting and vaporization, although these works were published only in 1779. In the period from 1759 to 1763, the scientist discovered the difference between the amount of heat and its temperature, and introduced the concept of heat capacity. In 1761, Black noticed that ice absorbs heat when melting without increasing its temperature. From this he concluded that the heat particles combine with ice particles and become latent (hidden) heat and showed that different substances have different latent heat (specific heat of melting).

The beginning of the development of experimental calorimetry can be attributed to the works of French scientists Lavoisier and Laplace [1]. The world's first ice calorimeter, made in the winter of 1782 – 1783 by Antoine Lavoisier in collaboration with the mathematician Pierre

Simon de Laplace, was intended to estimate the heat associated with various chemical changes; their calculations were based on Joseph Black's previous discovery of latent heat.

Laplace, who was interested in the mechanics of the celestial spheres, was also concerned with earthly problems, such as the study of the thermal effects of reactions and the development of methods for measuring heat. Heat energy was the quantity next to impossible to measure. In Laplace's time, the study of processes that occur with the absorption or release of heat was considered a field of study in chemistry, since the greatest amount of heat was visibly and clearly released in combustion processes. At that time, it was believed that the release of heat during combustion was a consequence of the release of phlogiston, which is contained in different quantities in different materials. Obviously, the changes in mass that accompanied the combustion processes did not fit well into the phlogiston theory. For example, the increase in the mass of the combustion product of a metal compared to the pure metal could only be explained by the negative mass of phlogiston. The experiments of Laplace's contemporary, Lavoisier, showed that no change in mass occurs at all in combustion processes, i.e., matter does not appear or disappear. A reasonable question arose about the nature of heat and the possibility of its measurement.

Meanwhile, in Scotland, Joseph Black and his colleague William Irwin had already begun to measure certain types of heat, namely the amount of heat required to change the temperatures of materials that do not enter into chemical reactions. In these experiments, Black discovered an interesting and paradoxical phenomenon at that time, although the temperature did not change in the process of melting a substance, the corresponding material needed to be heated for melting. The nature of this phenomenon still had to be understood, but the experimenters decided to practically use the incomprehensible phenomenon: Black suggested that the amount of melted ice could be used as a tool for measuring heat. Antoine Lavoisier was not informed about these experiments; at that time he was interested in combustion processes, and not in physical phenomena in which the composition of substances and materials does not change. Laplace and Lavoisier met after Joseph Priestley's public demonstration of experiments with "dephlogisticated air", which Lavoisier later called oxygen. The scientists quickly installed friendly relations and began working together in Lavoisier's laboratory. When Black's work reached France in 1780, Laplace decided to use the proposed idea of measuring heat.

Laplace developed a device (Fig. 1) in which a chamber with a sample was surrounded by ice. The heat from the chamber where the reaction was taking place melted the ice, and the water flowed through a hole into a weighing glass. The second ice jacket of the device

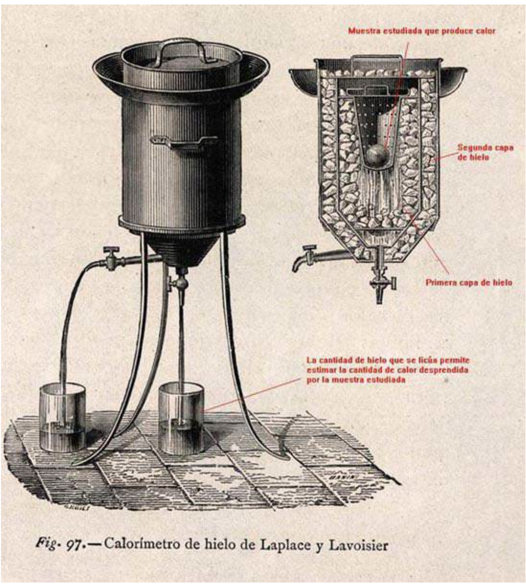

Fig. 1. Laplace and Lavoisier calorimeter

provided thermal insulation of the melting ice from external factors. With the help of this device (by weighing the water melted by the heat of the chemical process), Laplace and Lavoisier were able to estimate the heat of combustion of sugar, sulfur, and phosphorus.

Afterwards, experiments were conducted on living organisms: test animals were placed in the device for several hours and the amount of water they melted was compared with the volume of carbon dioxide released. This enabled establishing a relationship between “animal heat” and chemical processes, leading to an assumption that living processes are some special form of combustion.

The device thus developed and tested Laplace later called a “calorimeter”, apologizing to the scientific community for combining the Latin (calor – heat, Lat.) and Greek (meter – measurement, Gr.) roots. The ties between scientists were destroyed by the French Revolution [2].

It is now believed that it was A. Lavoisier who made a huge contribution to calorimetry. His systematic approach to experimentation and emphasis on measuring heat transfer laid a solid foundation for understanding the relationship between heat and chemical reactions. Lavoisier's methodology marked a shift from philosophical speculation to empirical science, which contributed to the development of this field. He conducted a large number of experiments on the calorimetry of respiration and combustion, emphasizing the correlation between heat and chemical reactions. Through his work, Lavoisier provided evidence that chemical reactions, such as combustion, are exothermic – they release heat – while others, such as the formation of a solution, can be endothermic – they absorb heat. This led to a deeper understanding of the energy involved in various reactions.

Lavoisier's systematic approach to experimentation helped formalize calorimetry as a scientific discipline. One of Lavoisier's most notable contributions was the introduction of quantitative analysis into calorimetric studies. By carefully measuring the reactants and the heat released during reactions, he demonstrated that heat was a measurable quantity, integral to understanding chemical processes. His innovative experiments centered on the concept that heat could be transferred and quantified, establishing the fundamental principles of calorimetry. These principles include:

1) the law of conservation of mass: the mass in a closed system remains constant, and this principle was adapted to the study of heat. He recognized that energy released or absorbed in reactions corresponds to changes in the state of matter, reinforcing the relationship between mass and energy;

2) heat as a form of energy. By linking heat to chemical changes, Lavoisier helped to understand heat as a physical property of matter that could be measured. Lavoisier not only contributed to the theoretical understanding of calorimetry, but his discoveries had practical implications in various scientific fields.

These principles helped develop industrial applications that required accurate thermal measurements, creating a stronger foundation for modern processes such as:

- Thermodynamics, which influenced future research into energy systems.

• Chemical engineering: Lavoisier's quantitative approach informed manufacturing methods, ensuring the efficiency of reactions important to the manufacturing and energy sectors.

• Biochemistry: Data from calorimetric studies of respiration laid the foundation for understanding metabolic processes in living organisms.

In other words, innovations during this period transformed calorimeters from simple containers into more sophisticated instruments capable of accurately measuring heat transfer. Some important features and designs of that time include:

1) Insulation techniques to minimize heat loss to the environment, thereby increasing accuracy. Double-walled structure was used to reduce heat transfer.

2) The use of water as the calorimetric medium due to its high specific heat capacity. This made water an ideal medium for measuring heat transfer. Such choice also facilitated consistent comparisons between experiments.

3) Beginning of development of measurement scales and methods for quantifying energy changes, focusing on determining the specific heat values for various substances.

The next milestone in the development of thermodynamics leads us to the concept of heat as a form of energy. In the 1790s, Sir Benjamin Thompson established that heat is a form of energy.

In 1841, the English physicist and mathematician James Prescott Joule made an accurate measurement of the mechanical equivalent of heat. Joule's work was a huge step forward in the development of thermodynamics. From a philosophical point of view, his work proved that heat is a measurable form of energy [3]. Joule's measurements showed the importance of maintaining an isolated system for experiments. All of these concepts are still used nowadays.

The study of the heat of chemical reactions begun by Lavoisier and Laplace later led to the establishment of the fundamental law of thermochemistry: the Law of Constant Heat Summation (G.I. Hess, 1840). Hess stated that the total enthalpy during the course of a chemical reaction is the same regardless of the number of intermediate states between the initial and final states. In other words, a chemical process does not depend on the path, but depends only on the initial and final states of the system at constant pressure and that the amount of heat released during the reaction can be a measure, as they said then, of chemical affinity. This law underlies the estimation of the standard enthalpy of formation using direct synthesis calorimetry, which we measure up to now.

A number of consequences follow from Hess's law, namely the first law of thermochemistry of Lavoisier – Laplace, which was discovered prior to Hess's law. It also follows from Hess's law that if, as a result of a series of successive chemical reactions, the system enters a state that completely coincides with the initial one, the sum of the energy effects of these reactions is equal to a sphere. If two chemical processes occur that lead from different initial states to the same final ones, the difference between the energy effects is equal to the energy effect of the transition from one initial state to another. On the contrary, if two chemical processes occur that lead from the same initial states to different final states, the difference between the energy effects is equal to the energy effect of the transition from one final state to the other.

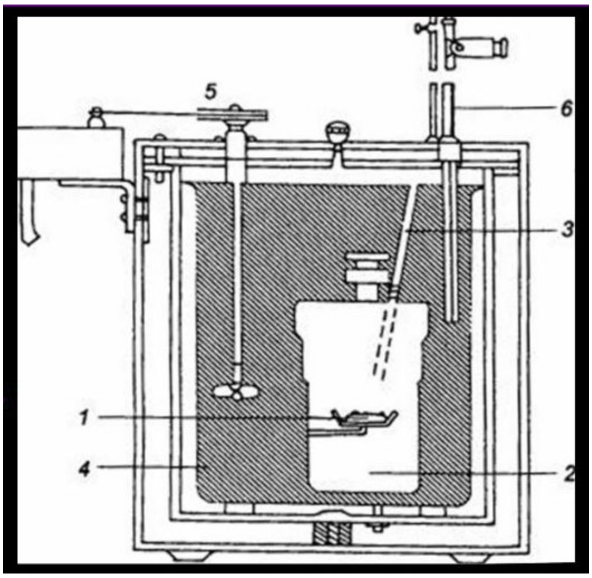

Fig. 2. Berthelot calorimeter for combustion studies:
1 – food sample; 2 – chamber;
3 – oxygen-filled igniter; 4 – water;
5 – stirrer; 6 – thermometer

The results obtained by scientists contributed to the creation of the first modern bomb calorimeter by Pierre Eugène Marcellin Berthelot in the 1870s [4]. It was a thick-walled steel vessel, lined with platinum or enamel on the inside, immersed in water, used to determine the heat of combustion of the substances under study in an oxygen atmosphere. A platinum wire heated by some electric current was inserted inside the vessel (Fig. 2). It was later realized that measurements on such a device were inaccurate due to the need to take into account several systematic measurement errors, so a new methodology was later developed using a reference substance (benzoic acid).

Although we spontaneously associate the name Berthelot with the "calorimetric bomb" for combustion studies, the history of thermochemistry says that this bomb was invented by Paul Viey, who later became a scientist at the Central Powder Laboratory [5].

The name Berthelot is also associated with the quasi-adiabatic water calorimeter (Fig. 3), which in France is called the "Berthelot calorimeter", but the English call it the "Thomson calorimeter", and Świętoslavski called it the "ordinary calorimeter". In fact, several decades before Berthelot, it was used by Favre and Silbermann, Thomson, Regnault and Hess.

The merit of Berthelot, who was an inventive experimenter, is that he used these two calorimeters effectively and managed to involve numerous colleagues and students in the invention of the instruments necessary for specific measurements.

Berthelot is therefore at the origin of numerous experimental results not only in combustion calorimetry, but also in mixing, dissolution, evaporation, and heat capacity calorimetry. The quantity and quality of these results are astonishing. The French National Standards Bureau in 1952 provided the first information on chemical thermodynamics, citing no less than 223 publications authored or co-authored by Berthelot. He is also the author of 1.200 patents.

The Berthelot calorimeter, long used in practical work on thermodynamics, often appeared as equipment from another era, with its small "calorimeter bucket" and wool felt insulation.

It must be acknowledged that the literature on calorimetry is far from using a uniform terminology, and even the concept of heat, which could be considered fundamental in calorimetry, covers very different realities from one scientist to another. However, we know that the production or absorption of thermal energy associated with the vast majority of physical, chemical, and biological transformations makes this energy measurement a nearly universal way to monitor and quantify these phenomena. This has led to more than a century of continuous improvement and modernization of calorimetry and its applications.

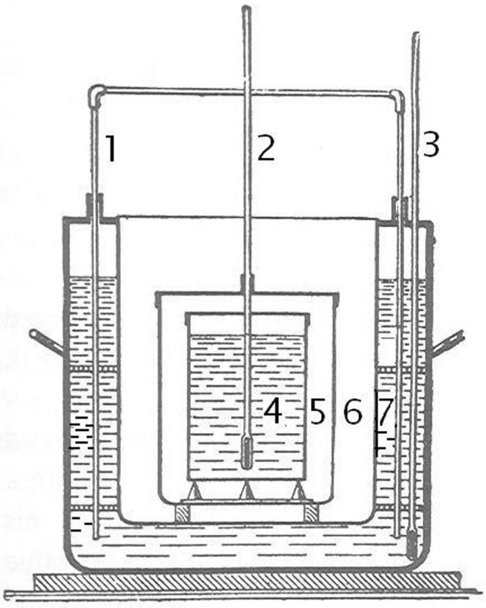

Fig. 3. Quasi-adiabatic water calorimeter. Air vanes (5 and 6) provide thermal insulation of the calorimeter bucket (4). A vertical stirrer (1) equalizes the temperature of the thermostatic housing. Thermometers (2 and 3) measure the temperatures of the calorimeter beaker and the thermostat

The 19^{th} century saw significant advances in calorimetric techniques, driven by increased scientific interest and technological innovation. As chemists and physicists delved deeper into heat measurement, several different designs and methodologies emerged, each with its own specific application. These advances not only increased the accuracy of calorimetric measurements, but also expanded the scope of heat-related experiments. As the scientific community adopted methods that improved the accuracy of measurements, the stage was set for calorimetry to become an indispensable tool for analyzing and understanding energy transformations in both chemical and physical processes.

The Industrial Revolution, having taken place in the late 18th and early 19th centuries, was a transformative era that profoundly impacted various scientific disciplines, including calorimetry and thermal measurement. As industry developed, the demand for accurate energy measurements grew exponentially, leading to significant advances in calorimetric methods and applications. The main impacts of the Industrial Revolution on calorimetry can be summarized as follows:

1) Increased energy consumption: The development of steam engines and the expansion of factories required an understanding of energy efficiency. Accurate calorimetric measurements became vital to optimizing fuel use in these new technologies, supporting an evolving industrial landscape.

2) Innovation in materials: The search for new materials, such as improved insulators and heat-resistant materials, sparked interest in calorimetry. Industry sought materials that could withstand high temperatures for use in manufacturing and engineering, leading to improved calorimetric methods for assessing thermal properties.

3) Advances in the food industry: A better understanding of caloric value and heat transfer facilitated methods for preserving food (e.g., canning and refrigeration). Calorimetry facilitated the determination of the nutrient content and energy value of foods, influencing the science of diet and public health.

4) Environmental awareness: As industrial processes evolved, awareness of energy use and waste increased. Calorimetry began to play a role in assessing the thermal efficiency of processes and their environmental impacts, contributing to sustainable development initiatives.

The evolution of calorimetry during that era was marked not only by improvements in instrumentation but also by an expanded understanding of the role of heat in chemical reactions. As the eminent chemist William Thomson, later known as Lord Kelvin, said, if you can't measure it, you can't improve it.

This principle proved to be a guiding principle as calorimetric data became an integral part of innovation and efficiency.

Notable innovations during the Industrial Revolution included:

- Improvement of the bomb calorimeter for industrial use, which allowed for precise measurements of the combustion of various fuels. This advancement helped industries carefully estimate the energy input required to compare productivity in production.
- Integration with thermodynamics: The synergy between calorimetry and thermodynamics became more clearly understood, helping industry to comprehend energy conversion. Rigorous study of heat transfer facilitated energy conservation research.
- Expanding the curriculum: The integration of calorimetry in educational programmes helped to shape a new generation of scientists with thermal analysis skills.

The Industrial Revolution thus acted as a catalyst, accelerating the development of calorimetry and thermal measurement, which has had a lasting impact on both science and society. With an emphasis on energy conservation, researchers continue to innovate in calorimetry, contributing to advances in energy efficiency and other practices across sectors.

Microcalorimetry of the 20th century and today

Microcalorimetry as a separate field began to take shape in the early 20th century. The founder of the thermochemistry of organic compounds, Wojciech Świętoslavski, developed microcalorimeters in the 1920s that operated under isothermal and adiabatic conditions. These devices allowed the measurement of very small amounts of heat, which was useful for the study of radioactive substances and organic compounds [6].

The 20th century experienced significant progress in calorimetry, driven by rapid technological innovation and an expanded understanding of thermodynamics. As scientists developed sophisticated instruments and methodologies, calorimetry became a highly precise science serving various fields, including materials science, biochemistry, and ecology, among others.

Masuo Kawakami in the period 1927–1930. measured the heat of mixing of some binary liquid alloys in the temperature range from 110 °C to 1200 °C. Using three different calorimeters, the heat of mixing was determined for different systems of binary alloys of such metals as mercury, potassium, sodium, tin, cadmium, bismuth, zinc and antimony [7].

In 1939, Kubashevsky and Walter in Germany constructed an adiabatic reaction calorimeter that operated at temperatures up to 700 °C to measure the processes of direct synthesis of intermetallic compounds. The measurement process used pressed granules of powder mixtures that were thrown into the calorimeter. It should be noted that adiabatic conditions in such an experiment were difficult to maintain [8].

The history of heat measurement, thermometry and calorimetry, starting from ancient Greek times, was described in 1943 by K. Boyer in connection with the 350th anniversary of the invention of the thermometer and the 200th anniversary of the Celsius scale [9].

The term “microcalorimetry” is also inextricably linked with the name of E. Calvet, who significantly improved the first Tyana calorimeters based on the measurement of energy flow, and developed the theory of the method. Therefore, calorimeters manufactured according to his developments are often called Calvet calorimeters in the thermochemical literature. French scientists E. Calvet and A. Prat in 1956 published a monograph in which they described in detail the basic principles of constructing microcalorimeters with thermoelectric temperature sensors, and also presented the design of calorimeters and the main results of their application for studying the thermogenesis of microorganisms, plants and other biological objects. It was shown that the characteristic difference between the thermograms of bacteria, yeasts, and fungi is that the heat production of bacteria is greater than that of fungi and yeasts, and is also non-monotonic [10].

The widespread use of the term microcalorimetry was also facilitated by the publication of a monograph in English by E. Calvet and A. Pratt under the title “Recent progress in microcalorimetry”, dedicated to the method they developed [11].

Of great importance was probably the fact that devices for measuring small amounts of energy, made on the basis of Calvet's developments and manufactured by the Setaram company (France) in various designs, are usually called microcalorimeters. Therefore, especially recently, the term “microcalorimeter” has been used for calorimetry, founded by Calvet and a number of other scientists.

A Calvet-type calorimeter can be described as an integrated heat flow microcalorimeter, in which changes in enthalpy in the sample are measured by the heat flow between the outer surface of the cell and the shell surrounding it. The most important task here is to measure the heat flow through a thermopile. Accordingly, calorimeters operating on the principle of measuring heat flow or, more precisely, heat power, are usually called heat flow calorimeters, or heat conduction calorimeters. In principle, the term “heat flow calorimeters” better conveys the essence of the method, but it is usually extended to a large number of different calorimeters of industrial manufacture, including numerous devices for differential thermal analysis.

Therefore, researchers more often use the term "heat conduction calorimeters" to emphasize that it mainly concerns precision calorimeters manufactured according to the ideas of Tian-Calvet. In cases where it is appropriate to emphasize the principle of measurements, the text sometimes uses the more general name: "heat flow calorimeters".

A conduction calorimeter was developed to track the growth of microbes. The calorimeter is a double structure that has thermopile plates as temperature sensors. Heat release during microbial growth at the required temperature can be observed as an output voltage generated at the terminals of the thermopile. Fig. 4 shows an image of a microcalorimeter with a Tian-Calvet type heat fluxmeter.

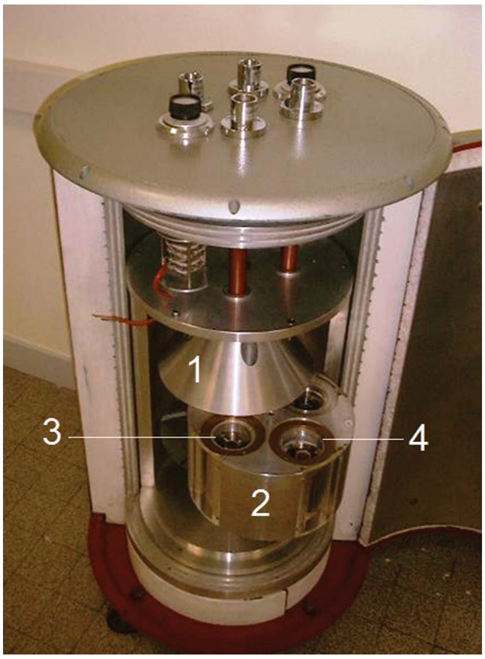

Fig. 4. Microcalorimeter with a Tian-Calvet type heat fluxmeter. 1 – cone of equal temperature distribution, 2 – central cylinder of the thermostat containing thermopiles 3 and 4 (the other two are located behind) with approximately a thousand chromel-alumel junctions each

Shortly after the publications of Calvet and Prat, a period of improvement of the Calvet microcalorimeter began. The quasi-adiabatic calorimeter is a refinement of the Calvet microcalorimeter (1955) by Kleppa. In this design, a hollow cylindrical shell with a constant temperature is enclosed in a heated furnace with a high resistance. The temperature was controlled by a commercial temperature controller. Due to the large amount of insulating material between the shell and the heating system, a constant temperature of the shell can be ensured. The actual thermal effects occur in a removable crucible inside the calorimeter unit in the central compartment of the shell. The temperature is measured by several thermocouple junctions, with one set of junctions located in the central unit and the other on the shell [12].

In 1952, Tichnor and Bever created the first calorimeter that was designed to use the technique of solution calorimetry [13]. This methodology is widely used in many countries for accurate calorimetric measurements.

In 1959, Kleppa developed a double microcalorimeter for the study of molten salt systems at 350–450 ºC [14]. For alkaline nitrate systems, the heats of liquid-liquid mixing and interaction were measured, studying the effects of ionic size, the effects in reciprocal mixtures, and short-range order. And in 1962, Kleppa built another new calorimeter at the University of Chicago, using a nickel block. Nickel is a relatively poor conductor compared to copper, silver, or aluminum, but is a better choice than nichrome or other refractory compounds. This calorimeter operated at 700–800 °C. The nickel unit option was also economical, since the silver unit, which would have been better, was prohibitively expensive, weighing 300 pounds.

Darby et al. A silver unit calorimeter was built at the Argonne National Laboratory, which gave very good results [15]. The article describes the design and principle of operation of a double Calvet-type liquid metal solution calorimeter for use up to 1173 K. The calorimeter is well suited for the study of alloys containing transition elements. A means of automatic data recording is described. The satisfactory operation of the calorimeter was demonstrated by determining the heat of dissolution of noble metals and palladium in liquid tin at 698 K. The results were in good agreement with existing data.

To the significant applications of microcalorimetry can be added the measurement of α-, β- and γ-radiation in nuclear reactors using various absorbers (lead, graphite, beryllium, etc.) placed in Tian-Calvet thermoelectric batteries. These so-called “Calvet dosimeters” were systematically introduced in the late 1960s in nuclear reactors built not only in France. The high reliability of these thermopillars has allowed them to remain in operation to this day. Only the reading and writing system, which remains external to the reactor, has been periodically changed, as electronics and then computers have progressed significantly over the years.

Swedish scientists under the guidance of Ingemar Wadsö made significant contributions to the development of isothermal microcalorimetry in the 1960s and 1970s. They developed and tested a microreaction calorimeter, designed primarily for studying biochemical reactions using small sample volumes. Electrical calibration experiments indicate achievable accuracy of 0.05 % for large amounts of heat and better than 1 % if 0.001 cal is released (fast processes). The calorimeter is useful for processes lasting at least an hour [16].

Soon after, I. Wadsö and J. Suurkuusk developed and tested an improved precision drop calorimeter for measuring the heat capacity of small samples, designed for precise work with small solid or liquid samples (≤ 1 g) and designed for a temperature range of 273 to 343 K. The accuracy of the results with samples weighing 1 g was 0.01 [17].

In the 1970s, a conductive microcalorimeter used for applied research was created in Ukraine, [18,19].

Microcalorimeters of that time significantly expanded the range available for high-quality thermochemical work with expensive or hazardous materials, with compounds that are poorly soluble or have low volatility, and with reactions involving high-molecular compounds. Other important areas of microcalorimeters included monitoring of life processes at the cellular level and processes occurring in technically important materials [29].

In 1985, Kleppa built a new calorimeter in which the thermocouple for the furnace was replaced by Pt13Rh [21]. The modern furnace uses Kanthal wire. This calorimeter can operate in the temperature range up to 1200 °C.

Swedish designers S. Thorén, J. Suurkuusk, B. Holma in 1989 reported the development of a multichannel microcalorimetric system operating in the micro-submicron range [22].

Monitoring heat flux values below 4 μW in microcalorimetry required unconventional experimental solutions to achieve high accuracy and reproducibility. With 5 mL ampoules, stable baselines were achieved in 70 min if a three-step pre-temperature procedure was used and if the gas phase above the liquid was reduced to 0.5 mL or less.

Cacciamani et al. in 1995 described several commercial and laboratory devices based on the droplet method and incorporating an isoperibolic differential detector [23]. Their device consists of two cells, one above the other, located in ceramic and metal tubes for thermal equalization. The temperature difference between the two cells (working and reference) is measured by a 20-pair thermocouple. The calorimeter is housed in a furnace with three independent controlled zones that can be heated to 1200 °C. A typical run consists of dropping a small capsule containing about 2 g of the metal mixture from a room temperature thermostat. The thermal effect is estimated by dropping several weighed samples of silver before and after the capsule is dropped. Subsequently, in a second run, the same capsule containing the reacted sample is dropped back into the calorimeter. The difference between the thermal effects obtained in the two runs gives the heat of formation of the alloy at room temperature.

Wadsö I. and Goldberg R.N. in 2001 reviewed the basic calorimetric principles used in isothermal microcalorimetry [24]. Their article discusses various chemical calibration and test reactions with emphasis on reactions suitable for ambient conditions; reactions initiated by mixing liquids (including titration microcalorimetry), dissolution of solids and sparingly soluble gases, photochemical processes and heat power signals released over a long period of time. At present, isothermal microcalorimetric measurements are mainly carried out at room temperature or slightly elevated temperatures, and a significant part of the measurements are carried out on aqueous solutions. This is due to the fact that most of the proposed calibration and test reactions are primarily intended for use under such conditions. It is obvious that there is a need for standard reactions carried out at higher temperatures on solid materials, which are required by some of the most important practical applications, as well as for reactions carried out in organic liquids, which pose special problems due to evaporation effects and possible interaction with seals, etc. It is noted that there is a serious shortage of standard materials suitable for calibration and test reactions in connection with all types of sorption measurements.

The book [25] reviews the development of highly sensitive calorimetry from a specialized method used by a few experts to a mainstream commercially available tool aimed at understanding molecular interactions and stability. As a result, the number of studies and the range of experiments to which calorimetric methods was applied have increased. Applications range from small molecule and solvent biophysics, through drug screening to whole cell analyses. The technology has evolved to include higher levels of sensitivity (and therefore lower sample size requirements) and the pursuit of high-throughput technologies.

Many scientific and industrial applications require quantum-efficient microcalorimeters with high energy resolution to measure faint X-ray sources in which few photons reach the detector. Astrophysical applications of these microcalorimeters include measurements of the composition and temperature of stellar atmospheres and diffuse interstellar plasma. Other applications include the measurement of X-ray fluorescence of industrial or scientific samples. For such studies, efforts have been made to develop microcalorimeters with an energy resolution of a few eV, since many sources (such as celestial plasma) contain combinations of elements that produce emission lines that are only a few eV apart. A model of the microcalorimeter is presented in [26], which extends the previous theory of microcalorimeters to include additional current-dependent effects. Predictions regarding the effects of various forms of noise are evaluated.

In the field of pharmaceuticals, especially solid-phase pharmaceuticals, microcalorimeters have proven to be an invaluable tool for determining the stability, compatibility, and amorphousness of drug substances [27].

Jung et al. in Korea in 2003 developed a Kleppa-type microcalorimeter to measure the heat change in a reaction tube at $T > 1300$ K. To verify the operation of the new calorimeter, the standard enthalpies of formation for NiSi and Ni_3Al were measured by direct synthesis in the calorimeter at $T = 1323$ K. The results obtained confirmed the performance and stability of such a calorimeter [28].

In [29], a method for measuring the complex impedance of calorimeters with a transition edge sensor is described. Using this method, the impedance of a calorimeter with a superconducting Mo/Au transition edge sensor was measured. The impedance data fit well into the presented linear calorimeter model. Unprecedentedly accurate measurements of the heat capacity and resistance gradients with respect to temperature and calorimeter current throughout the phase transition were obtained. The measurements investigate the internal state of the superconductor during the phase transition and are useful for characterizing the calorimeter.

The book [30] combines the past, present, and future outlook for the use of calorimeters. It explores the history, foundations, methodologies, and applications of biocalorimetry. It covers the use of calorimetry for the study of cell membranes, nucleic acids, and proteins.

In [31], technical details of chip calorimeters are discussed, including information on calibration and correction, as well as recommendations for proper sample preparation for analysis. Examples of individual applications of fast scanning chip calorimeters are given. In particular, for polymers, examples of analysis of crystallization kinetics, crystal nucleation, crystal reorganization, and melting are given. In addition, the relationship between relaxation of polymer glasses and nucleation of homogeneous crystals is highlighted. Using biological and pharmaceutical molecules as an example, it is shown that rapid heating can overcome the degradation of temperature-sensitive substances to study their behavior during melting. The analysis of the degradation of macromolecules at the earliest stages, even if this does not lead to mass loss in thermogravimetric measurements, is described, as well as the use of chip calorimeters to assess the kinetics of evaporation of liquids with low volatility, etc.

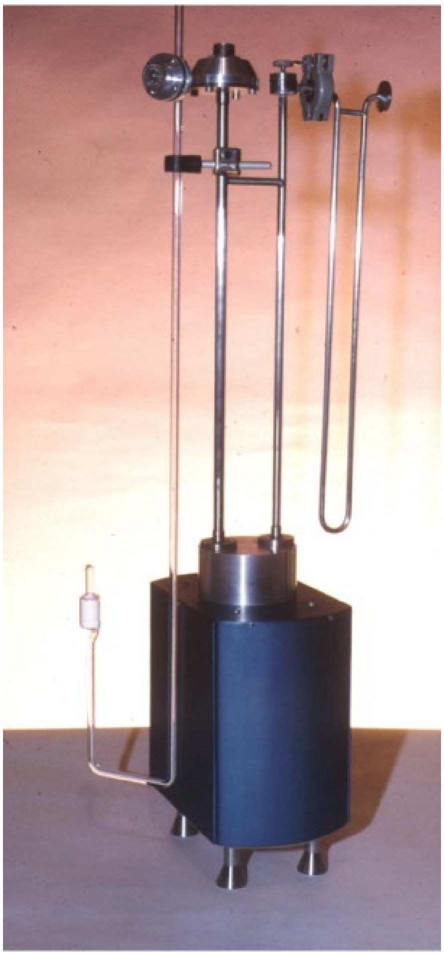

Fig. 5. Gas adsorption microcalorimeter operating at 77 and 87 K outside its cryostat

In Marseille, at the MADIREL Institute, a large fleet of microcalorimeters is in operation, including the only two microcalorimeters in the world capable of conducting isothermal gas adsorption measurements at 77 or 87 K (Fig. 5) [32, 33]. It contains two thermopiles of a thousand thermocouples each, filled with helium. The sample canister (in the figure next to the microcalorimeter) is inserted into one of the two thermopiles through the lower opening.

Alternatively to routine thermal process evaluations, there are also very precise measurements of combustion energy, carried out by only a few university laboratories in the world, aimed at determining the binding energies in new molecules, especially when they undergo several conformations. To achieve high-order precision (since the energy difference between two conformations is small compared to the combustion energies), these laboratories use the so-called “rotating bomb”. This allows any solid combustion residues that might have settled on the wall to be dissolved in order to obtain a well-defined final state, which is necessary for an accurate thermodynamic calculation. The relative error can then be reduced to a few tens of parts per thousand, making this method one of the most outstanding in experimental thermodynamics.

A vivid illustration of the modernity of calorimetry is the measurement of cosmic ray energy (in particular, Higgs bosons) using the ATLAS detector, 46 meters long, 25 meters in diameter, and weighing 7.000 tons, installed in 2004 at CERN in Geneva at a depth of 100 meters underground. The dimensions of the ATLAS detector calorimeter are: 8 meters in diameter and 12 meters along the beam axis (Fig. 6). The first measurements using this detector were carried out in 2007. In 2012, the ATLAS experiment was conducted at CERN, the European Organization for Nuclear Research, to search for superheavy elementary particles. The detector (Fig. 7) includes two calorimeters designed to measure a wide spectrum of particle energies that arise when protons collide in the center of the detector which is the inner electromagnetic calorimeter and external hadron calorimeter [34].

The electromagnetic calorimeter absorbs the energy of charged particles and photons and determines its quantity with high accuracy. The absorber materials are lead and stainless steel, and the sensitive substance is liquid argon. To prevent argon evaporation, the calorimeter is placed in a cryostat. The energy of the particles that have passed through the electromagnetic calorimeter is absorbed by a hadron calorimeter, which is less accurate. The energy absorber is steel. Due to the large size of the device, cost-effective materials were chosen for the manufacture of the calorimeter.

Fig. 6. CERN ATLAS detector calorimeter under construction

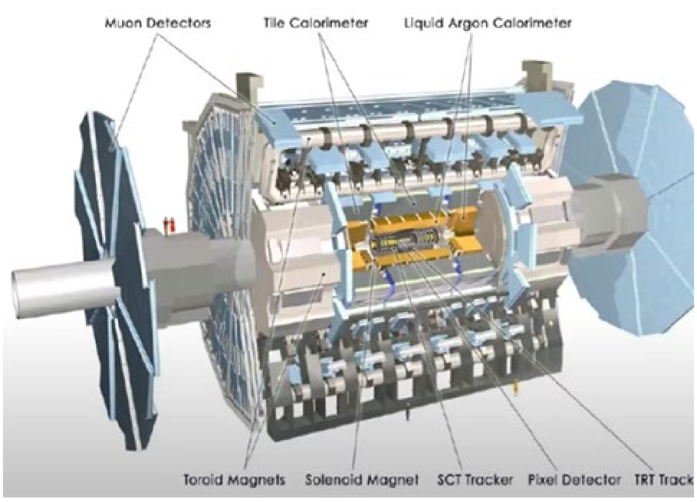

Fig. 7. Overall diagram of the ATLAS detector

Regarding the classification of calorimeters

The term “calorimeter”, introduced by Laplace, can hardly be considered very successful. First, it (like the name of calorimeters after their inventors) does not give an idea of the method of measurements and therefore does not allow including these devices in the framework of any classification. Secondly, the allocation of these devices into a separate group, based on the amount of energy measured, can lead to misunderstandings. Even before the advent of calorimeters, many thermochemists set themselves the task of measuring small amounts of energy. Their ideas were implemented in a number of calorimeters of various types (adiabatic, isothermal, differential, etc.).

Many of these devices are described in the monograph of V. Svientoslavsky. However, calorimeters built according to Calvet's ideas are not described at all. Therefore, it is most appropriate to single out the calorimeters created by Calvet et al., which are described in the book [10], to base them on the measurement method characteristic of this group, and to call them heat-conducting or conductive microcalorimeters. The term “microcalorimeter” is inextricably linked with the name of Calvet, who significantly improved the first Tian calorimeters based on the measurement of energy flow, and developed the theory of the method. These calorimeters are often called “Calvet” calorimeters in the thermochemical literature. The fact that devices for measuring small amounts of energy, manufactured on the basis of Calvet's developments and manufactured by the Setaram company (France) in various designs, are usually called microcalorimeters, probably played a great role. Therefore, the term "microcalorimeter" is used for calorimeters founded by Calvet and a number of other scientists. Calvet calorimeters differ from the above-mentioned variable-temperature calorimeters with an isothermal or adiabatic shell, primarily in that the main part of the energy released in the reaction chamber is not spent in them on increasing the temperature of the calorimeter system, but is removed from the reaction zone through a system of thermopillars. Therefore, calorimeters operating on the principle of measuring heat flow or, more precisely, heat power are usually called heat flow calorimeters or heat conduction calorimeters. The first term is adopted, for example, in the book by G. Höhne and W. Hemminger, the second revised edition of which was published in 2003 [35].

The term "heat conduction calorimeters" is used in the book by E. Calvet and A. Prat [10]. In principle, the term "heat flow calorimeters" better conveys the essence of the method, but it is usually extended to a large number of various industrially manufactured calorimeters, including numerous devices for differential thermal analysis (DTA). Therefore, many researchers often use the term "heat conduction calorimeters" to emphasize that it mainly concerns precision calorimeters manufactured according to the ideas of Tian-Calvet. In cases where it is appropriate to emphasize the principle of measurements, the more general name is also used: "heat flow calorimeters". The main advantages of the heat conduction calorimeter are as follows:

1. It allows only very small temperature changes (but the effect of temperature changes on the kinetics of chemical reactions and the development of the living organisms under study is very large).
2. The device can be used according to the zero method with strict compensation of heat release by the Peltier effect. In this case, it will be almost isothermal.
3. It is very convenient to use and allows for quick and continuous recording of the heat released in the calorimeter.
4. The sensitivity of the device is very high (it allows measuring thermal power at the level of the order of 0.1–0.5 μW), and the reliability is such that it can be used with confidence for measurements of practically unlimited duration (a month or more).

What are the main types of calorimeters and their applications? For a simple and general classification of the approximately one hundred calorimeters invented during the last two centuries [36], two broad categories are distinguished, which in turn are divided into active and passive [37].

In adiabatic calorimeters, an attempt is made to eliminate the heat exchange between the sample and the thermostat surrounding it. Passive adiabatic calorimeters use only thermal insulation for this purpose, which is never perfect, and can be called "quasi-adiabatic". Their archetype is the Berthelot calorimeter. These calorimeters are used mainly when the thermal effect is noticeable and, above all, short-term (to limit the necessary corrections due to imperfect adiabatism): combustion calorimetry (main industrial application), dissolution, and mixing. To overcome their imperfections, the temperatures of the sample and the standard placed in the same thermostat are constantly compared and any difference is immediately compensated for by means of a compensating power generated by the Joule or Peltier effect: this is the principle of differential scanning calorimetry (DSC) with power compensation where, in addition, the standard is subject to temperature changes. In active adiabatic calorimeters, it is the temperature of the thermostat that is adjusted according to the temperature of the sample to compensate for the heat exchange. They are particularly appreciated for studies of materials at low and very low temperatures (from 4 to 250 K), where heat exchange by radiation is minimal and where adiabatism is therefore excellent, and also for studies of safety (self-heating) from room temperature.

In diathermic (heat conduction) calorimeters, on the contrary, heat exchange between the sample and the thermostat is favoured. In passive diathermic calorimeters, this is achieved by good thermal conductivity, either to a material where the two phases in equilibrium (water and ice for the Lavoisier-Laplace (and later Bunsen) calorimeter) change proportion depending on the thermal energy exchanged (a principle that has now been practically abandoned), or by means of a heat fluxmeter, according to the principle of the Tian-Calvet microcalorimeter with thermopiles (Fig. 4). Thanks to its “differential” design, which uses two thermopiles connected in opposition (one containing the sample, the other the standard), this last type of calorimeter is today the most common in both fundamental and applied research. This is due to its sensitivity, long-term stability (several months if necessary), temperature range (from 77 to 1500 K) and adaptation to open systems thanks to the differential knot that enables, without disturbing the measurement, easy introduction of a gaseous, liquid or solid reagent or removal of a reaction product. In miniature form, DSC devices with heat flow utilize the same principle. In active diathermal calorimeters, which are not that common, the result of good heat exchange with the thermostat is simulated by a compensation power at the sample level (which is the measured quantity), i.e. the temperature of the sample is controlled by the temperature of the thermostat. Some newer calorimeters, which we will call hybrids, can operate either as diathermal or as adiabatic, but not simultaneously. These are known as reaction calorimeters (Fig. 8) and are used for the controlled conduct of chemical reactions.

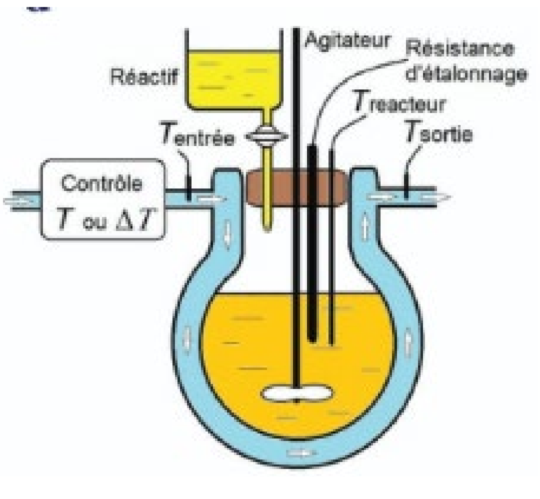

Fig. 8. Reaction calorimeter

Reaction calorimetry allows the study of chemical reactions or physical processes and provides important information on process safety, scalability and criticality. Factors of interest include reaction kinetics (rate constants, activation energies, heat/mass transfer) as well as thermodynamic aspects (enthalpies of reaction and adiabatic temperature rise) [38].

For example, a microstructured flow reactor and a flow reaction calorimeter were used to study the continuous synthesis of diazoacetonitrile, collecting heat and reaction rate data [39], which is important because diazo compounds are of interest due to their potential for more environmentally friendly synthesis routes.

Continuous flow microcalorimetry as a tool for studying catalytic hydrogenations has been applied to CO_2 methanation [40].

A review of current methods and procedures for high-temperature calorimetry is provided in [41].

Characteristics and parameters of microcalorimeters

It should be noted that due to the variety of calorimetry, a single approach to describing the properties of microcalorimeters has not yet been established. In the literature, there are different, often contradictory views on their main parameters and characteristics, which most often determine only individual properties of the devices and do not allow comparing microcalorimeters by their maximum possible values. There are large discrepancies not only in the definition of parameters and characteristics, but even in the terminology used.

In brochures and catalogues of companies that produce microcalorimeter equipment, to characterize these devices, a parameter called sensitivity is most often indicated. However, this term in different sources denotes different physical characteristics of the microcalorimeter. Three parameters are most often used: volt-watt sensitivity, i.e., the ratio of the EMF of the microcalorimeter sensor to the thermal power released in the reaction chamber, V/W; current sensitivity, namely, the ratio of the current in the sensor circuit to the thermal power released in the reaction chamber, A/W; current sensitivity in the Peltier effect compensation mode which means the ratio of the Peltier current in the compensation circuit to the thermal power released in the reaction chamber, A/W. In determining the current sensitivity, it is assumed that the sensor and the recorder input are resistance-coupled.

These three parameters are essentially the ratio of the sensor output signal (EMF or current) to the measured value (thermal power) and do not characterize the accuracy of measurements in themselves. The threshold sensitivity parameter of a microcalorimeter, measured in watts or joules, is also widely used; most often it is defined as the minimum thermal power (for calorimeter integrators as the amount of heat) that creates a signal at the recorder input equivalent to a relative measurement error of 100 %.

The refusal to use the adjective “threshold” leads to terminological confusion: the concepts of minimum detectable power and noise-equivalent power, which are sometimes close in meaning, are sometimes equated with threshold sensitivity. The quantity inverse to threshold sensitivity is called detection (sometimes resolution) power.

The speed of microcalorimeters is determined by a time constant, which characterizes the inertia of the microcalorimeter as a dynamic system. In some sources, the time constant is called the time of the transition process, that is, the time for the transition characteristic of the microcalorimeter to reach the set value with a given accuracy. The time constant, of course, depends on the measurement conditions and has different values for an unloaded reaction chamber, for a chamber loaded with the measurement object and in the Peltier effect compensation mode. In multiple sources, the conditions under which the inertia of the microcalorimeter is determined are not specified, so information about the speed becomes ambiguous. When characterizing microcalorimeters, the operating temperature range (especially for scanning microcalorimeter devices), the volume of the reaction chambers, the electrical resistance of the sensor, and the minimum temperature difference registered by the sensor are also given. In addition to the main parameters considered, sometimes the reproducibility of measurements, stability (zero drift) at a given temperature, Peltier constant (W/A), relative and absolute measurement errors, etc. are indicated.

Table 1 presents some commercially available calorimeters and their technical characteristics at the end of the 20th century [42]:

Table 1

Type	**Device**	**Manufacturer**	**Available temperature range (°C)**	**Scanning speed ($K·min^{-1}$)**	**Resolution**
PC DSCe	Pyris	Perkin Elmer	– 170 to + 725	500	0.2 μW
CHF DSCf	DSC 12E	Mettler	– 40 to 400	20	10 μW
	DSC 821	Mettler	– 150 to 700	100	0.7 μW
	DSC 200	Netzsch	– 170 to 530	40	4 μW
	DSC 6	Perkin Elmer	– 120 to 450	50	
	Exstar 6000	Seiko	– 150 to 1500	100	0.2 μW
	DSC 141	Setaram	– 150 to 600	100	10 μW
	DSC 50	Shimadzu	20 to 725	100	10 μW
	DSC 2920	TA Instr	– 180 to 725	200	0.2 μW
	DSC 2010	TA Instr	– 180 to 725	200	1 μW
FFHF DSCg	DSC 404	Netzsch	– 120 to 1500	50	8 μW
FFHC DSC + TG	STA 409	Netzsch	– 160 to 2000	100	8 μW
	Labsys	Setaram	20 to 1600	100	10 μW
C DSCh	DSC VII	Setaram	– 45 to 120	1.2	1 μW
	DSC 111	Setaram	– 120 to 830	30	5 μW
Bomb	1425	Parr	Ambient mode	–	4 J
	1271	Parr	Ambient mode	–	2 J
	C 5000	IKA	Ambient mode	–	6 J
	C 7000	IKA	Ambient mode	–	0.5 J
Solution	1455	Parr	0 to 70	–	0.4 J
Calvet	MS 80D	Setaram	20 to 200	–	0.1 μW
	HT 1000	Setaram	20 to 1000	1	10 μW
Process	RC1	Mettler	– 50 to 300	30	
	BFK	Berghof	20 to 60	–	40 μW
Micro	LCM-2526	Xensor	Ambient mode	–	0.1 μW

The resolution of the calorimeter is estimated here as the vendor specification or twice the rms noise value for the most accurate system.

Major advances in calorimetry in the 20th century and up to now

1. Differential scanning calorimetry (DSC): This revolutionary technique enabled accurate measurements of the heat flows associated with phase transitions in materials. DSC has allowed researchers to monitor thermal events in real time, providing important data on such characteristics as melting points, glass transition temperatures, and crystallization rates, providing a dynamic view of the behavior of a material under different temperature conditions. DSC allows the quantification of specific heat capacities and enthalpy changes during phase transitions, which is important for determining thermodynamic parameters critical in various chemical processes.
2. For example, the important achievement of DSC in achieving a balance between process safety and chemical yield in optimizing the ruthenium-catalyzed coupling reaction of catechol with a terminal alkyne to form the key benzodioxolane intermediate to lotigliprone using a thermally hazardous reagent is reported in [43].
3. Isothermal titration calorimetry: By measuring the heat change in a sample during the addition of reagents, isothermal calorimetry has become invaluable for studying binding interactions in biochemical systems. This method plays a crucial role in drug development, allowing scientists to investigate the energetics of molecular interactions, which is a primary factor in understanding enzyme kinetics and receptor-ligand binding [44, 45, 46, 47].
4. *X*-ray microcalorimetry is the use of non-dispersive spectrometers that measure the heat generated by the thermalization of a single photon in an absorber with a low heat capacity [48].
5. Nanocalorimetry encouraged scientists to study thermal properties in the nanoscale, including thin films. Microchip-based nanocalorimeters were developed for small-scale and high-speed thermal measurements. Nanocalorimeters allow us to see how thermal properties scale with size, provide direct measurements of high-speed and multi-step reactions in complex media, and surface effects, even on samples below a monolayer [49, 50].
6. Improved sensitivity and automation: The emergence of electronic data acquisition and automated calorimeters gave a chance to increase the sensitivity of measurements, reducing human error and obtaining accurate calorimetric data. Automation of these processes meant that samples can be measured continuously and under different conditions, thus facilitating large-scale studies.

Authors’ information

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References

1. Lavoisier A.L., & De Laplace P.S. (1780). Memoire sur le chaleur. *Memoires de l'Académie des Sciences*, 355–408. https://catalog.library.vanderbilt.edu/discovery/fulldisplay/alma991015206499703276/01VAN_INST:vanui
2. Quoi de neuf depuis la calorimétrie de Lavoisier et de Berthelot? (2019). *L'ACTUALITÉ CHIMIQUE,* 441, Juin. https://new.societechimiquedefrance.fr/numero/quoi-de-neuf-depuis-la-calorimetrie-de-lavoisier-et-de-berthelot-p15-n441/
3. Joule J.P. (1843). On the calorific effects of magnetic electricity and on the mechanical value of heat. *Philosophical Magazine,* 23, 263–276, 347–355, 435–443. https://www.abebooks.fr/calorific-effects-magneto-electricity-mechanical-value-heat/31374983144/bd
4. Berthelot M. (1879). *Essai de mécanique chimique fondée sur la Thermochimie, I. Calorimetrie.* Dunod. https://gallica.bnf.fr/ark:/12148/bpt6k903010.texteImage
5. Médard L., & Tachoire H. (1994). *Histoire de la Thermochimie.* Publications de l'Université de Provence, pp. 209–211. https://doi.org/10.1006/jcht.1995.0110
6. Świętosławski W. (1946). *Microcalorimetry.* Reinhold Publishing Corporation, p. 199. https://www.google.com.ua/books/edition/Microcalorimetry/r8ggAAAAMAAJ?hl=uk&gbpv=0&bsq=inauthor:%22Wojciech%20%C5%9Awi%C4%99tos%C5%82awski%22
7. Kawakami M. (1927). Die Mischungswärme von Metallen. *Zeitschrift für anorganische Chemie,* 167(1), 345–363. https://doi.org/10.1002/ZAAC.19271670128
8. Kubaschewski O., & Walter A. (1939). Ein Adiabatisches Hochtemperaturcalorimeter zur Bestimmung der bei der Legierungsbildung auftretenden Wärmetönungen. *Zeitschrift für Elektrochemie,* 45(8), 630–636. https://www.periodicos.capes.gov.br/index.php/acervo/buscador.html?task=detalhes&id=W1957172836
9. Boyer C.B. (1943). History of the measurement of heat I. Thermometry and calorimetry. *The Scientific Monthly,* 57(5), 442–452. http://www.jstor.org/stable/18161
10. Calvet E., & Prat H. (1956). *Microcalorimétrie; applications physico-chimiques et biologiques.* Masson & Cie. https://odebuplus.univ-poitiers.fr/discovery/fulldisplay?docid=alma991000749359706171&context=L&vid=33UDP_INST:33UDP&lang=fr&search_scope=MyInst_and_CI&adaptor=Local%20Search%20Engine&tab=Everything&query=sub,exact,%20Calorimetry%20,AND&mode=advanced&offset=0
11. Calvet E., & Prat H. (1963). *Recent progress in microcalorimetry* (H.A. Skinner, Ed.). The MacMillan Co. https://shop.elsevier.com/books/recent-progress-in-microcalorimetry/calvet/978-0-08-010032-6
12. Kleppa O.J. (1955). A thermodynamic study of liquid metallic solutions. VI. Calorimetric investigations of the systems Bismuth-Lead, Cadmium-Lead, Cadmium-Tin, and Tin-Zinc. *Journal of Physical Chemistry,* 59, 175–181. https://pubs.acs.org/doi/10.1021/j150524a020

13. Ticknor L.B., & Bever M.B. (1952). Heats of solution of group IB metals in liquid tin. *JOM,* 4(9), 941–945. https://doi.org/10.1007/bf03397751
14. Kleppa O.J. (1955). A thermodynamic study of liquid metallic solutions. VI. Calorimetric investigations of the systems Bismuth-Lead, Cadmium-Lead, Cadmium-Tin, and Tin-Zinc. *Journal of Physical Chemistry,* 59, 175–181. https://pubs.acs.org/doi/10.1021/j150526a018#citeThis
15. Darby J.B., Jr., Kleb R., & Kleppa O.J. (1966). Twin liquid metal solution calorimeter. *Review of Scientific Instruments,* 37(2), 164–167. https://doi.org/10.1063/1.1720119
16. Wadsö L. (1968). Design and testing of a microreaction calorimeter. *Acta Chemica Scandinavica,* 22, 927–937. https://doi.org/10.3891/acta.chem.scand.22-0927
17. Suurkuusk J., & Wadsö L. (1974). Design and testing of an improved precise drop calorimeter for the measurement of heat capacity of small samples. *Journal of Chemical Thermodynamics,* 6(7), 667–679. https://doi.org/10.1016/0021-9614(74)90117-7
18. Anatychuk L.I., & Luste O.Y. (1978). Limiting potentialities of microcalorimeters. *Journal of Engineering Physics,* 35, 1178–1186. https://doi.org/10.1007/BF00860381
19. Anatychuk L.I., Demchuk B.M., & Luste O.J. (2003). Particularly sensitive thermoelectric microcalorimeters with eddy thermoelements. *Proceedings of the 22nd International Conference on Thermoelectrics (ICT'03)*, IEEE, 652–654. https://doi.org/10.1109/ICT.2003.1287436
20. Wadsö I. (1984). Microcalorimetry. In Ribeiro da Silva, M. A. V. (Ed.), *Thermochemistry and Its Applications to Chemical and Biochemical Systems*
21. Kleppa O.J. (2001). Evolution and application of high-temperature reaction calorimetry at the University of Chicago from 1952 to 2000. *Journal of Alloys and Compounds,* 321, 153–163. https://doi.org/10.1016/S0925-8388(01)00964-1
22. Thorén S.A., Suurkuusk J., & Holma B. (1989). Operation of a multichannel microcalorimetry system in the micro-submicrowatt region: Some methodological aspects. *Journal of Biochemical and Biophysical Methods,* 18(2), 149–156. https://doi.org/10.1016/0165-022X(89)90076-6
23. Cacciamani G., Borzone G., & Ferro, R. (1995). On a simple, high-temperature direct reaction calorimeter. *Journal of Alloys and Compounds,* 220, 106–110. https://doi.org/10.1016/0925-8388(94)06024-X
24. Wadsö I., & Goldberg R.N. (2001). Standards in isothermal microcalorimetry. *Pure and Applied Chemistry,* 73(10), 1625–1639. https://doi.org/10.1351/pac200173101625
25. Ladbury J., & Doyle M. (Eds.). (2004). *Biocalorimetry II: Applications of calorimetry in the study of biological systems.* John Wiley & Sons. https://doi.org/10.1002/0470011122
26. Lindeman M. (2000). *Microcalorimetry and the transition-edge sensor.* University of California, Davis. https://books.google.com.ua/books/about/Microcalorimetry_and_the_Transition_edge.html?id=Tv1jbqar4oQC&redir_esc=y

27. Phipps M., & Mackin L. (2000). Application of isothermal microcalorimetry in solid-state drug development. *Pharmaceutical Science & Technology Today,* 3(1), 9–17. https://doi.org/10.1016/S1461-5347(99)00227-8
28. Woo-Gwang Jung, & Mira Yoo. (2003). Kleppa type calorimeter for the study of high-temperature processes. *Journal of Chemical Thermodynamics,* 35(12), 2011–2020. https://doi.org/10.1016/j.jct.2003.08.001
29. Lindeman M., Bandler S., Brekosky R., Chervenak J., Figueroa-Feliciano E., Finkbeiner F., Li M., & Kilbourne C. (2004). Impedance measurements and modeling of a transition-edge-sensor calorimeter. *Review of Scientific Instruments,* 75, 1283–1289. https://doi.org/10.1063/1.1711144
30. Bastos M. (Ed.). (2016). *Biocalorimetry: Foundations and contemporary approaches.* Taylor & Francis Group, LLC.
31. Schick C., & Androsch R. (2018). Chapter 2 - Fast scanning chip calorimetry. In *Handbook of Thermal Analysis and Calorimetry, Volume 6* (pp. 47–102). https://doi.org/10.1016/B978-0-444-64062-8.00018-8
32. Llewellyn P., Grillet Y., & Rouquerol J. (1994). Effect of T(III) zoning in MFI-type zeolites on the adsorption isotherm and differential enthalpies of adsorption at 77 K. *Langmuir,* 10. https://doi.org/10.1021/la00014a038
33. Giordano F., Denoyel R., & Rouquerol J. (1993). Influence of porosity on the adsorption of a non-ionic surfactant on silica. *Colloids and Surfaces A: Physicochemical and Engineering Aspects,* 71, 293–298. https://doi.org/10.1016/0927-7757(93)80044-F
34. The ATLAS Detector. https://atlas.cern/Discover/Detector
35. Höhne G.W.H., Hemminger W.F., & Flammersheim H.-J. (2003). *Differential scanning calorimetry.* Springer. https://link.springer.com/book/10.1007/978-3-662-06710-9
36. Médard L., & Tachoire H. (1994). *Histoire de la Thermochimie.* Publications de l'Université de Provence. https://doi.org/10.4000/books.pup.1747
37. Rouquerol J., Rouquerol F., Llewellyn P., & Denoyel R. (2015). *Calorimétrie: Principes, appareils et utilisation.* Techniques d'analyse. https://doi.org/10.51257/a-v1-p1202
38. Soritz S., Sommitsch A., Irndorfer S., Brouczek D., Schwentenwein M., Priestley I.J.G., Iosub A.V., Krieger J.P., & Gruber-Woelfler H. (2024). Thermokinetic analyses of metal-sensitive reactions in a ceramic flow calorimeter. *Reaction Chemistry & Engineering,* 9(7), 1805–1815. https://doi.org/10.1039/D4RE00014E
39. Baldan M., Blauth S., Bošković D., Leithäuser C., Mendl A., Radulescu L., Schwarzer M., Wegner H., & Bortz M. (2024). Continuous synthesis of diazo acetonitrile: From experiments to physical and grey-box modeling. *Chemie Ingenieur Technik,* 96(5), 658–670. https://doi.org/10.1002/cite.202300191
40. Mateo Rosado Y., Ledoux A., Balland L., & Polaert I. (2024). Continuous flow microcalorimetry as a tool for studying catalytic hydrogenations: Application to CO_2 methanation. *Journal of Thermal Analysis and Calorimetry,* 149(6), 2631–2642. https://doi.org/10.1007/s10973-023-12849-z

41. Scharrer M., Bonatti L., Geraci T., Ushakov S.V., Majzlan J., Bustamante M., Kojitani H., Guo X., Xu H., Zhang L., Lilova K., Hayun S., Subramani T., & Navrotsky A. (2025). The joys and jitters of high-temperature calorimetry. *Journal of the American Ceramic Society, 108*(6). https://doi.org/10.1111/jace.20381
42. van Herwaarden S. (1999). *Calorimetry measurement.* CRC Press LLC. https://dsp-book.narod.ru/MISH/CH36.PDF
43. Clarke J., Farr D., Wang J., Ingram H., Chapman C., Field H., Breen C.P., Gulotty E.M., Mason S., Russell G., Williams O., Kumta S., Britto J., & Ping L.-J. (2025). Thermally hazardous 1,3-dioxolane coupling reaction required for a pharmaceutical candidate starting material, made safer by employing process safety data as key design of experiments output variables. *Organic Process Research & Development, 29*(3), 836–845. https://doi.org/10.1021/acs.oprd.4c00519
44. Claveria-Gimeno R., Vega S., Abian O., & Velazquez-Campoy A. (2019). Tinkering with binding polynomials in isothermal titration calorimetry. *Methods in Molecular Biology, 1964*, 185–213. https://doi.org/10.1007/978-1-4939-9179-2_14
45. Mosebi S. (2022). Calorimetry to quantify protein-ligand binding. *Applications of Calorimetry, IntechOpen.* http://dx.doi.org/10.5772/intechopen.102959
46. Migliore R., Zavalishin M.N., Gamov G.A., et al. (2022). Isothermal titration calorimetry investigation of the interactions between vitamin B6-derived hydrazones and bovine and human serum albumin. *Journal of Thermal Analysis and Calorimetry, 147*, 5483–5490. https://doi.org/10.1007/s10973-022-11200-2
47. Migliore R., Biver T., Barone G., & Sgarlata C. (2022). Quantitative analysis of the interactions of metal complexes and amphiphilic systems: Calorimetric, spectroscopic, and theoretical aspects. *Biomolecules, 12*, 408. https://doi.org/10.3390/biom12030408
48. Quilty C.D., West P.J., Li W., Dunkin M.R., Wheeler G.P., Ehrlich S., Ma L., Jaye C., Fischer D.A., Takeuchi E.S., Takeuchi K.J., Bock D.C., & Marschilok A.C. (2022). Multimodal electrochemistry coupled microcalorimetric and X-ray probing of the capacity fade mechanisms of nickel-rich NMC – progress and outlook. *Physical Chemistry Chemical Physics.* https://doi.org/10.1039/D1CP05254C
49. Yi F., & LaVan D.A. (2019). Nanocalorimetry: Exploring materials faster and smaller. *Applied Physics Reviews, 6*(3), 031302. https://doi.org/10.1063/1.5098297
50. Diulus J.T., Corbella C., & Yi F. (2025). Nanocalorimetry for plasma metrology relevant to semiconductor fabrication. *Journal of Vacuum Science and Technology B: Nanotechnology and Microelectronics, 43*(2). https://doi.org/10.1116/6.0004294

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Мікрокалориметрія в історичному аспекті, стан та перспективи. Частина 1.

У цій статті розглянуто розвиток калориметрії починаючи з XVIII століття. Показано, як змінювалися методики калориметрії у залежності від отримання нових знань про природу тепла і теплових процесів. Відображено вплив промислової революції на розвиток калориметричних методів. Продемонстровані досягнення мікрокалориметрії у XX столітті та на даному етапі. Показані основні прикладні напрямки практичного використання мікрокалориметрів. Зроблено прогноз можливих перспективних здобутків в області мікрокалориметрії і аналіз шляхів їх досягнення.

Ключові слова: мікрокалориметрія, типи калориметрів, характеристики калориметрів, застосування калориметрії.

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