LOW-TEMPERATURE CALORIMETRY:
A PARTICULAR BRANCH OF THERMAL ANALYSIS

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ABSTRACT

The history and fundamental principles of low-temperature calorimetry are outlined. The particular aspects and basic difficulties of calorimetric measurements in the temperature range $4 \ K < T < 120 \ K$ are pointed out and compared with other calorimetric techniques (DTA, DSC). Recent experimental progress and modern trends in cryogenic calorimetry are tersely reviewed: emphasis is given to the development of simple, easy-to-handle, highly flexible calorimeters and less attention has been paid to discussions of highly sophisticated arrangements dedicated to singular experiments. The future aspects and possibilities of extending the range of routine thermochemical measurements by a further decade of temperature, namely 10–100 K, are critically considered.

For the first time a new type of continuously working, non-adiabatic, differential calorimeter designed for measuring small samples, typically 10–50 mg, is described, the DISC (differential, isoperibol, scanning calorimeter).

PREFACE

The oral presentation of this invited honorary lecture contained an expression of great pleasure and gratitude to GEFTA (Deutsche Gesellschaft für Thermoanalyse) and to Dr. Emmerich from NETSCH Co., Selb, for their presentation of the NETSCH–GEFTA award, followed by an acknowledgement of the kindness of ICTAs Scientific and Organizing Committee. Thanks were also given to many colleagues and collaborators for their enthusiastic help and valuable discussions in the recent years and finally to the author's family for their understanding, prudence, generosity and renunciation during the scientific work.

INTRODUCTION

Thermal analyses encompass an extremely wide spectrum of activities and a large variety of available experimental methods. This can easily be seen

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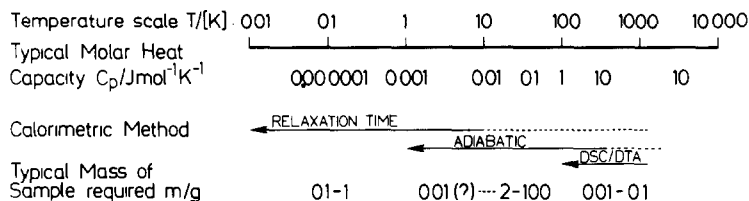Thermal Analysis Highlights, 8th ICTA, Bratislava, Czechoslovakia.

Temperature scale T/[K] 001   01   1   10   100   1000   10000

Typical Molar Heat
Capacity Cp/Jmol⁻¹K⁻¹   000 0001 0001   001 01 1   10   10

Calorimetric Method   RELAXATION TIME
                                          ADIABATIC
                                                  DSC/DTA

Typical Mass of
Sample required m/g   01-1   001(?)---2-100   001-01

Fig. 1. Logarithmic temperature scale on which are shown: typical values of molar heat capacity of solids, predominantly applied calorimetric methods, and the corresponding masses of samples required.

from the different contributions presented at this conference [1]. The specific heat is the most prominent value among the various physical and chemical parameters which can be deduced from a thermoanalytical experiment. The heat capacity c_p is the key thermal property which enables us to determine the overall energetic state of solids and liquids, to calculate directly the basic thermodynamic functions, and to characterize phase transitions and reaction kinetics. It is clear that the extreme regions of temperature — the cryogenic region below 120 K and the very high temperature range above 1500 K — are more difficult to achieve than the room temperature region and its vicinity. Nevertheless, it is astonishing (and it is not justified by any reason) that an overwhelming number of investigations in such a very old and traditional branch of science still remains restricted predominantly to one decade of temperature, namely the range from 120 to ca. 1500 K. This situation is schematically presented in Fig. 1.

A logarithmic representation of the temperature scale is shown in Fig. 1 and represents the aspect of unbounded temperature on the high temperature side and the unattainability of the absolute zero-point (NERNST theorem). From this schematic it is immediately evident why low-temperature calorimetry (LTC) is such a fascinating field of research: low-temperature calorimetry extends over several decades of temperature and every single decade contains an equivalent number of interesting and new phenomena. Thus calorimetric measurements between 0.1 and 1 K are as exciting as investigations between 100 and 1000 K. There is no physical reason to limit research to a specific decade on the temperature scale. In consequence the question arises: why does today's thermoanalysis use the capabilities offered by cryogenic calorimetrists so scarcely? A cursory glance over the present situation of calorimetry will answer this question.

In the temperature range above 120 K thermal analysis has seen a rapid development in instrumentation and automatization in the last 10–20 years. Today, this range is well equipped with commercially available instruments, and it is standard practice to achieve an accuracy of 2% or better for c_p measurements [2–4]. Calorimetric experiments below 120 K have been neglected somewhat and such measurements are still a domain of a few

cryogenic laboratories that have to use individually designed, specialized equipment and mostly depend on their own ingenuity and more or less sophisticated manufacturing, measuring, and data processing procedures. The necessary know-how for construction of simple but reliable, easy to handle calorimeters has not yet been transferred from cryogenic physicists to the range that is of practical interest (4–120 K) for thermoanalysis. This development is directly connected with the numerous and complex difficulties to be overcome in performing calorimetry between 4 and 120 K. These problems will be discussed in Section 2. It is a challenge and a duty to every low-temperature physicist to offer his knowledge and experience to other branches of science in the form of less sophisticated instrumentation. In a first step this simplification may only be achieved by reducing precision, say 1% instead of 0.1%.

There is a world-wide need for thermal data below 120 K which requires enhancement of research in the 10–100 K region, but there is less necessity for measurements at very low temperatures, i.e. below 1 K. For most materials the 10–100 K temperature range penetrates sufficiently low to include ordering phenomena and to allow precise integration of thermodynamic functions such as entropy S^0, enthalpy H^0, and Gibbs free energy G^0. The preeminent necessity of low-temperature heat capacity must first of all take into account the entropy contributions (below 120 K) which are of prominent importance because in S^0 the c_p values are divided by T; a second consideration for precise high-temperature studies is the factor TS^0 in the Gibbs energy expression $G^0 = H^0 - TS^0$.

Before outlining the principle of cryogenic calorimeters and recent progress, the following clarifying remark must be made: there is nothing extraordinary about measuring heat capacities near 4.2 K or resolving temperatures of 10^{-5} K near 4.2 K.

(i) LTC from 1 to 4 K. In the range of liquid helium, LTC is a rather simple technique, which is commonly used in many low-temperature laboratories. There is an immense amount of literature which describes such instruments; see for example references given in ref. 5. Most of these calorimeters, however, have been constructed for a dedicated purpose, such as c_p measurements on metals, superconductors or thin films, and therefore only allow restricted application in a limited temperature range for research on solids or liquids.

(ii) Quite the contrary can be said about the sub-1 K range. The determination of c_p below 1 K requires very special knowledge, very experienced scientists, expensive and high-quality equipment, and ingeniously designed cryogenic and electronic components. In consequence, c_p measurements below 1 K will remain in the exceptional domain of a few very specialized low-temperature laboratories in the future. It may be interesting to mention that c_p data as low as 20 mK and c_p values on liquid and solid helium isotopes below 1 mK have been measured.

(iii) Intermediate range from 1 to 120 K. This area, covering nearly two orders of magnitude (see Fig. 1), separates the low-temperature physicists from the other scientists working in thermal analysis. It is exactly this temperature range which offers most of the calorimetric problems. It is no wonder, therefore, that the total number of successfully operating calorimeters in this temperature range is rather limited, although it is of tremendous importance for thermoanalysis today.

Early in the '70s we became aware of this situation. We recognized the fundamental importance of $c_p(T)$ data below 100 K because of the many contacts between physicists, chemists and biologists in a large solid-state research institute and because of collaboration with employees of industrial firms. Therefore, it was our intention for many years to facilitate low-temperature calorimetry, to work out simple measuring procedures, to set up automated, computer-controlled experiments, and to design highly flexible, easy-to-handle, highly reproducible sample holder/calorimeter assemblies [5,6]. LTC should use established routine techniques that could be managed by technicians. Rapid investigation of any type of liquid or solid sample, either in crystalline or powdered form, insulators or metals, air-sensitive or volatile specimens must be possible. Such a calorimeric technique had to be offered for use to chemistry, biology, medicine and other technical branches, e.g., the earth sciences.

This paper deals with the temperature range below that covered by commercial DTA (differential thermal analysis) and DSC (differential scanning calorimetry) instruments down to liquid helium temperatures (4 K). It is my intention to (i) point out the particular aspects and basic experimental problems in the 4–120 K range, (ii) awaken interest in cryogenic calorimetry, (iii) convince the community of thermoanalysts that cryogenic measurements are necessary and (iv) make some optimistic prognoses that future thermoanalysts can hope to gather thermal results—at least c_p measurements—in a further decade of temperatures (mainly the range 10–120 K) more easily.

The paper is organized as follows. After an outline of the most frequently used LTC methods (adiabatic and non-adiabatic calorimetry) some historical remarks are given and recent trends in LTC are considered. In Section 2, the physical parameters and information which could be gained from calorimetric experiments are summarized and demonstrated by some of our recent results. In Section 3 the essential obstacles which yet hinder a general use of LTC are elucidated, and it is shown how to overcome these difficulties. In Section 4 a brief description of our calorimetric installation and recent progress is given. The last Section (5) presents the essential principles of a new type of non-adiabatic scanning calorimeter which was developed recently.

For rather obvious reasons the presentation favors the work of the author's research group. It should be emphasized that this report is focused

exclusively on the development of simple multi-purpose calorimeters which show many industrial and commercial features. This inherent subjectivity, however, neglects many of the exciting, sophisticated, and very successful constructions of calorimeters which today enable us to determine heat capacities from 50 Å thick aluminum films weighing only a few micrograms [7] (corresponding to energies of 10^{-12} J K^{-1}!), to investigate time-dependent heat capacities on the millisecond scale [8], or to operate under high pressures in excess of 20 kbar [9].

1. HISTORICAL METHODS AND RECENT TRENDS

1.1. Historical

Historically, modern thermal analysis, i.e. quantitative measurements, has begun with the experiments of J. Black [10] in 1760, J.C. Wilke [11] in 1781, and the more advanced ice calorimeter of Laplace as described by Lavoisier in 1780 [12] (portrayed in refs. 2 and 11). In the 19th century calorimetric methods were intensively developed by the rapid progress in thermodynamics, connected with J. Crawford, J.P. Joule, C. Meyer, H. Helmholtz a.o., as described in detail in Refs. 11 and 13.

1.2. Adiabatic calorimetry

The birthdate of low-temperature calorimetry (LTC) can be assigned as 1909. The paper by A. Eucken [14] gives the first description of an adiabatic
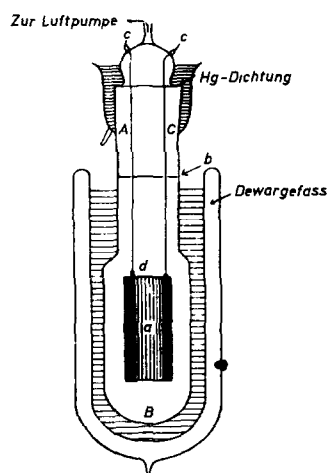

Fig. 2. Low-temperature calorimeter as proposed by W. Nernst and described by A. Eucken [14]; taken from ref. 14.
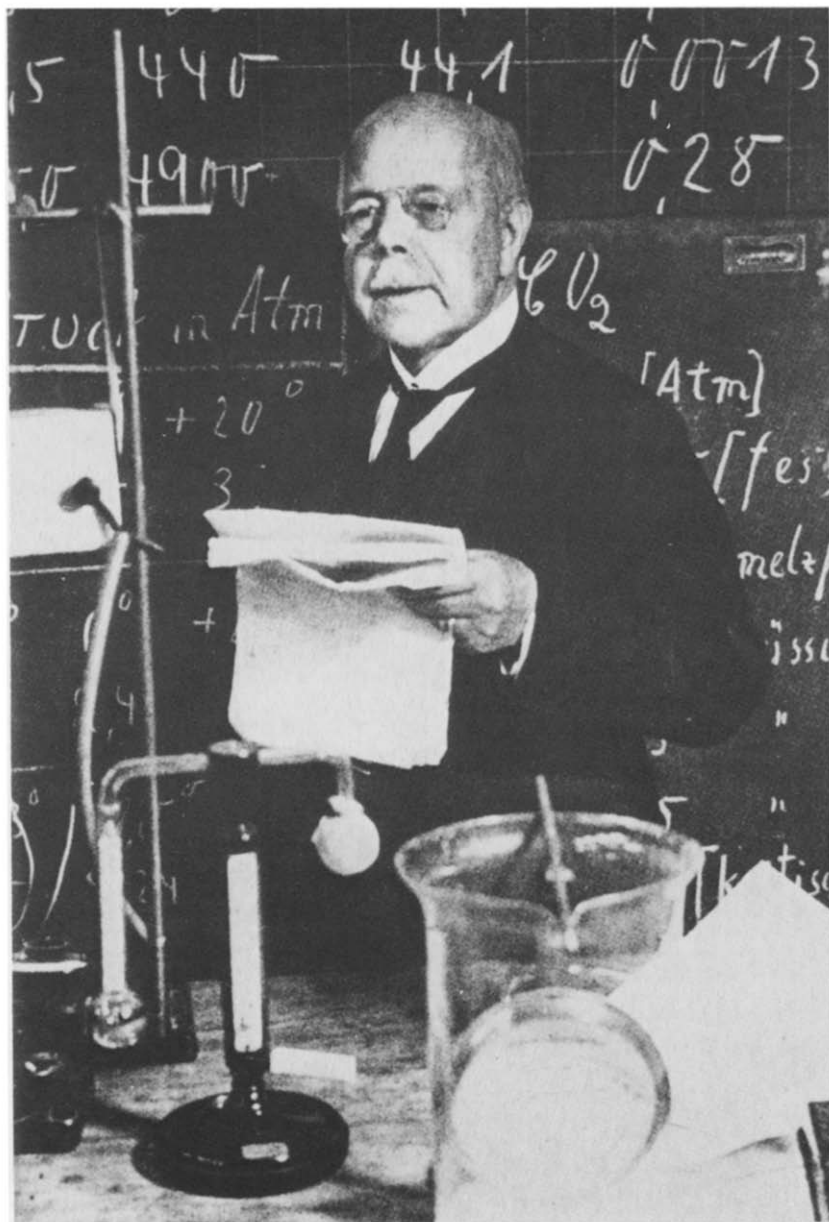
Fig. 3. Walther Nernst giving a lecture in 1922.

calorimeter as proposed by W. Nernst (this calorimeter is shown in Fig. 2); therefore, W. Nernst (Fig. 3) is the father of LTC and even today his adiabatic step-heating method is still the most precise type of calorimetric experiment for collecting heat capacity data. Most of the LT calorimeters used in the past are of this type (see refs. 5 and 15). Nernst's "pulse heating"
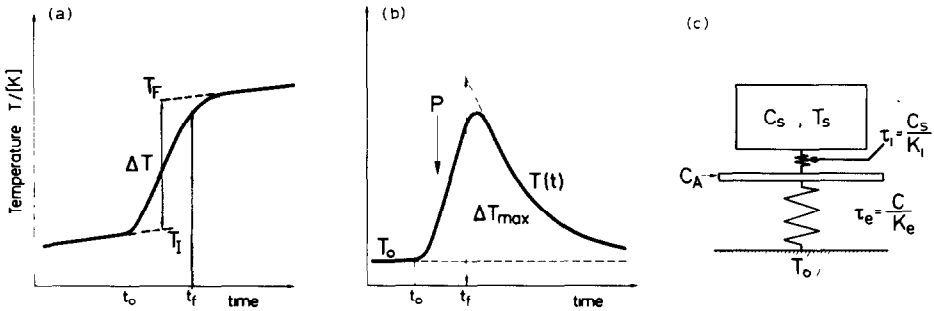
Fig. 4. Calorimetric methods and principles. (a) Nernst's (step heating) method: T_1 = initial temperature, T_F = final temperature of heating, t_0, t_f = start and end of heating period. (b) Relaxation time method: T_0 temperature of the bath, P = heating power during time from t_0 to t_f. (c) Schematic arrangement for both methods, shown in (a) and (b): C_s, T_s, heat capacity and temperature of sample; C_A, heat capacity of sample holder; T_0, temperature of bath/surrounding; τ_i, τ_e, corresponding internal and external thermal relaxation times, adiabatic calorimetry: $\tau_i \ll \tau_e$, $\tau_e = \infty$ (a), non-adiabatic calorimetry: $\tau_i \ll \tau_e$, $0 < \tau_e < \infty$ (b).

method is a direct transposition of the definition of the specific heat $c_p(T) = \lim(\Delta T \rightarrow 0)\,[Q/\Delta T]$ into a measurement; the energy Q apported to the sample/sample holder (including heater and thermometer) assembly and the temperature increment ΔT are determined as accurately as possible. The sample and its holder are thermally insulated from the surrounding (adiabatic conditions). The principle of the adiabatic measuring technique is schematized in Fig. 4a [5]. The thermal equilibrium or steady-state temperatures are determined before and after electrical heat input Q by extrapolation to the initial and final temperatures T_i and T_f, respectively, from which the temperature step $\Delta T = T_f - T_i$ is calculated. A small drift rate is allowed to occur: "quasi-adiabatic" or "slightly" isoperibol measurement. The adiabatic conditions are ensured by placing one or two thermal shields around the sample (see Fig. 13), which work either under adiabatic conditions ($T_{sample} = T_{shield}$) or under isothermal conditions ($T_{sample} \gtrless T_{shield} =$ constant). Adiabatic shield regulation is performed in the case of large sample masses ($m \geqslant 10$ g) and temperatures above 20 K, whereas isothermal conditions are preferred for experiments with small samples ($m \leqslant 1$ g) at lower temperatures ($T < 50$ K [5]). Numerous such calorimeters have been described in the literature; for further details we refer the reader to the reviews given in refs. 5, 15 and 16. Adiabatic calorimetry has progressed to a "high-precision" method in the 50s and 60s of this century; a precision of 0.1% or even better was achieved due to the construction of thermal shields which follow the sample temperature very closely, the development of extremely sensitive electronics, the application of custom-designed thermometer circuits [15,17], and the assurance of ultimate precision of mass, time, resistance, and potential calibrations.

However, calorimetry based on Nernst's method has remained a very tedious and time-consuming procedure; it is typically a thermal "equilibrium method". A run from 1.5 to 300 K may need nearly one week of measuring time. In addition, to achieve an accuracy of 0.1% rather large samples (10–100 g) are required. Both long measuring times and a large sample mass are in contrast to the intrinsic characteristics of usual DTA or DSC experiments: 1 day measurement, 10-mg samples.

1.3. Non-adiabatic calorimetry

Useful innovations and a solution to the aforementioned disadvantages have been offered in the '70s by (i) the application of the relaxation time method [18] and the a.c. (alternative current) method * [20], (ii) the introduction of computers [6], and (iii) the introduction of commercial DSC/DTA instruments.

In essence, the relaxation time method is an isoperibol-operated calorimeter, intermediate between isothermal and adiabatic principles. Originally, this technique was pioneered by Giaugue [19] and since 1972 has been widely used to determine c_p values of ~ 1-g samples below 1 K. Hence this method appears appropriate for evaluating extremely small heat capacities. The principle of this "heat-leak" method is depicted in Fig. 4b and c. A permanent thermal leak (heat conductivity K_c) between sample/sample holder (heat capacity C) and the bath T_0 is utilized. Starting from a constant temperature the sample assembly is heated by an electrical power P during a certain time $\Delta t = t_f - t_0$. If the power is cut off, an exponential decay of temperature $T(t) = T_0 + \Delta T \exp(-t/\tau_e)$ occurs with a time constant $\tau_e = C/k_c$. The time constant τ_e ranges from seconds to minutes. It must be insured that the internal thermal equilibrium time between the sample, thermometer, and heater, τ_i, is much smaller than τ_e:

$$\tau_i \ll \tau_e$$

By permanent heating a steady-state value for ΔT is reached from which the thermal conductance of the thermal link can be determined experimentally:

$$k_c = P/\Delta T$$

To shed more light on the problem of measuring small heat capacities (small sample masses), the temperature regulation of the surrounding cryogenic bath or thermal shield has to be discussed in more detail, since it represents the most important cause of heat interaction with the sample. Definitely, the suppression of the thermal link (Fig. 4b) and the measurement of large samples increases τ_e considerably, because k_e is defined by the

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* This method, introduced by Sullivan and Seidel, does not appear to be generally applicable to every type of sample and requires special conditions; therefore, it is not considered here. For details see ref. 5 and references therein.

characteristic features of the calorimeter (electrical connections to the sample) and, in consequence, adiabatic conditions are approached. Then, the relaxation time τ_e is several minutes or hours. On the other hand, when diminishing the sample masses to the 0.1 g scale, the necessary electrical heater and thermometer connections represent a limiting minimum thermal link k_e which does not allow τ_e to be kept on the minutes scale (see Section 3). As a consequence, one is obliged to accept isoperibol conditions. The desideratum to measure 1-g or 0.1-g samples implies, of course, a deviation from adiabatic conditions and therefore also from adiabatic shield control. The appropriate way to determine small heat capacities is the use of isothermal shields in connection with the isoperibol methods. Experiments have shown that the sample temperature reacts very sensitively to temperature variations of the environment. Under certain conditions calorimetry with 0.1-g samples near 80–100 K is equivalent to the measurements of 10–50-g samples below 1 K, although with the difference that at low temperatures heat conductance is the dominant type of heat transfer, whereas at high temperatures the radiational heat provides the major part of the heat transfer. Automatic, electronic, isothermal, or adiabatic shield control is now routine practice at most installations.

1.4. Automated experiments

The second important innovation in the '70s was the introduction of microcomputers [2]. Their application and use has become the rule rather than the exception. Microcomputers, as everywhere in science, play an increasing role in setting up automatic LTC; more or less automatic process control and on-line data analysis is now a routine practice [6]. In this way the time of attendance of the experimenter is shortened considerably and the precision of data is increased. In spite of our good experience with automatic LTC [5], a look at the highly developed calorimeters of the precomputer days elicits the following remarks:

(i)   The automatic "press the button" experiment always provides you with data (printed and computed results, thermodynamic functions, etc.)! The difficulty consists of interpreting the results correctly. In every instance calorimetry is based on thermal interactions, heat transfer, and heat equilibria. In consequence elaborate testing of the installation, visual (recorder) control of heating curves, observation of relaxation time-to-temperature dependence, and critical data treatment are mandatory. The critical assessment of the uncertainties must be done rigorously!

(ii)   Verification by means of standards is strongly recommended.

(iii)   In many cases a smaller degree of automatization, a semi-automatic or semi-manual operation seem to be preferable.

(iv)   The best modern electronics does not yet permit us to achieve the

TABLE 1

Comparison of advantages and disadvantages of the DSC and ADC methods

Characteristic features of:	DSC	ADC
Precision (%)	(1)–3	0.1–1.5
Stability of Calibration	Reasonable	Good to excellent
Resolution for phase transition	Very good	Reasonable
Measuring time	Hours	Days
Sample mass	1-50 mg	50 mg
Handling	Easy	Not easy
Automatization	Good	Good
Flexibility	Dependent on problem	
Systematic Errors by	Condensation of ice/exchange gas influence/dependence on heating rate	Bad thermal conductivity of sample/uncontrolled thermal radiation

accuracies currently performed with the precomputer time potentiometers. In summary, I urge that greater caution be used, particularly if dealing with automated calorimeters.

Finally, the development of several commercial calorimeters working at temperatures above 120 K has stimulated research and technology in the '70s. These instruments offer reliability, speed, and convenient operation. Table 1 gives a comparison of advantages and disadvantages of both methods, as discussed in ref. 22. Nowadays, widespread use of differential scanning calorimeters in the hands of one who has never practiced equilibrium or non-equilibrium (relaxation-time) calorimetry (see also ref. 4) can produce data in error by a factor of two; there is a still larger risk using such instruments in connection with computers. There is a strong tendency to offer the reader beautiful computer graphics but badly defined, uninterpreted data. It is worth noting that calorimetry more than other instrumentation needs permanent and consequent calibration and repetition of the measurements.

In conclusion the actual state-of-the-art of calorimetric experiments is very different in the various temperature regions with respect to methods, sample masses, and accuracy. This situation was schematically indicated in

Fig. 1. The limited space precludes us to mention many other innovations concerning thermometry, measurement of samples of low thermal diffusivity, etc.; the reader is again referred to refs. 4 and 5.

Last but not least, this first section may cause the impression that the author favors isoperibol, low-precision, and differential calorimetry. In contrast, it is a deplorable development that fewer and fewer laboratories have the means to carry out "absolute calorimetric" measurements. It is recalled that only absolute calorimeters (and in a certain instance this means adiabatically operated calorimeters) furnish the basically calibrated data for the operation of "non-equilibrium" calorimeters as DSC/DTA instruments.

2. PROSPECTS AND DIFFICULTIES

2.1. Application of low-temperature calorimetry

The specific heat reflects the distribution of the energy levels of a physical system. It is a measure of the total energy content. The overall features of the energetic contributions are given as well as a general knowledge of the different types of contributing excitations, e.g. phonons, spins, and lattice phase transitions. Heat capacity experiments do not, in general, elucidate the detailed energetic structure of a special physical system as do, for example, spectroscopic experiments. The strong connection between energy and specific heat (via the density of states and the partition function) is, at the same time, the weakness and strength of c_p measurements. Nevertheless, specific heat measurements are a powerful tool in physics and chemistry, biology, and medicine. They encompass a large variety of physical and chemico-physical properties as classified in the following:

Thermodynamic studies. In order to define the basic thermodynamic functions by simple integration of $c_p(T)$ as a function of temperature and to derive the standard values of enthalpy, entropy, and Gibbs free energy at 293.15 K.

Vibronic properties. The Debye temperature as well as the low-frequency structure of the phonon density of states can be deduced.

Electronic properties. The density of states of the electrons at the Fermi level is determined.

Magnetic behavior. Displayed by low-temperature c_p contributions of spin waves (magnons), spin interaction (spin glasses), etc.

Phase transitions enclose a broad spectrum of effects occurring whenever the thermal energy kT drops below the characteristic ordering energy E_{ord} of the physical system, $E_{ord} \geqslant kT$. The behavior of c_p gives information on the transitional energy (ΔH_t, enthalpy; ΔS_t, entropy) and, frequently, on the order of transition for: (1) electronic (e.g. superconductivity), magnetic, lattice structural (crystallographic) transitions, or melting; (2) Schottky

anomalies (two-level system), order–disorder phenomena, Verwey-, Jahn Teller effect, rotational transitions in molecular crystals.

Finally the subject includes the non-cooperative phenomena, such as: contributions from point defects, dislocations, and lattice disorder, Einstein terms, surface modes, etc.

This impressive wealth of low-temperature "specific heat effects" proves again the vital interest in performing LTC. It is worthwhile to mention that all these contributions can also be found in biological and medical samples. However, the above enumeration still leaves many phenomena unmentioned. Relatively few studies have been made on mixed phases, mechanically stressed or deformed metals and alloys, the glassy state of matter, the special properties of ionic conductors, plastic to plastic-crystalline transitions, charge-transfer phenomena, organo-metallic complexes, the change of c_p by interaction with laser light, and c_p of liquid and liquid mixtures. The effects of the purity of a material and numerous exotic behaviors are rarely explored.

A rather selective illustration of the aforementioned effects has been published in the book of Gopal [21] and in ref. 5. The following few more or less exotic examples have been chosen from recent work in our laboratory. The guideline was to select results which stimulate the reader's interest for LTC, demonstrate the necessity and prospective capabilities of LTC, and suggest that reliable information can also be collected with small samples.

A good example of how to clarify thermophysical properties is the element phosphorus. It is one of the last elements in the periodic system of elements, the specific heat of which has not yet been elucidated. Phosphorus exists in different structural modifications as black-P, red (Hittorf)-P, amorphous-P and white-P_4. It has been a matter of controversy which of the four crystallographic forms is chemically the most stable, especially whether black or red phosphorus is the modification with the lowest Gibbs free energy. This question has been decided by measuring the specific heat of each modification [22] and by calculating from it the thermochemical standard values at room temperature by integration: black phosphorus is the most stable structure. The experimental results are plotted in Fig. 5 and will be published elsewhere in more detail. There is obviously no difference in the heat capacities of the three phosphorus samples (except P_4) at temperature above 90 K. The differences in enthalpy, entropy, and Gibbs free energy are definitely produced at low temperatures. This is a nice example, which convincingly demonstrates the imminent importance of gathering data below 100 K.

In Fig. 6 the heat capacity of the superconductor Nb_3Sn is displayed. This measurement has been undertaken in order to know precisely the critical temperature T_c of transition into the superconducting state. The temperature T_c depends critically on the purity and the crystal preparation conditions of the sample. Therefore, this measurement enables us to evaluate the quality
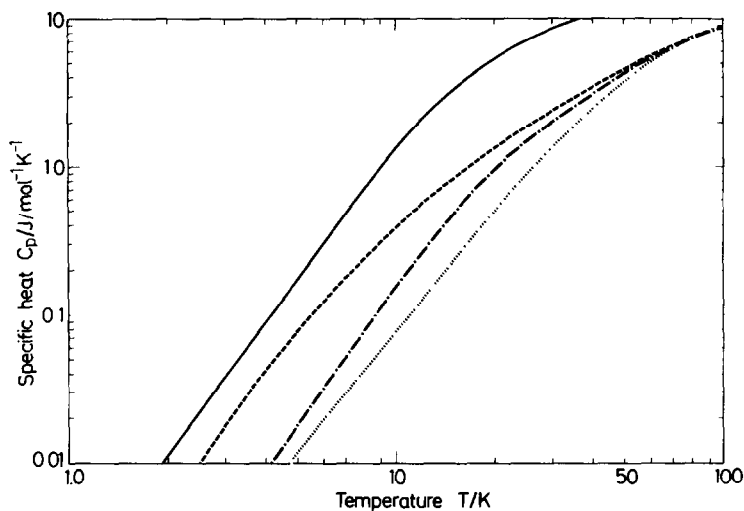
Fig. 5. Specific heat of the different modifications of phosphorus [22]: (————) white (P_4), (- - - - -) amorphous, (— · —) red (Hitdorf), (· · · · · ·) black.

of the sample by looking at the position of T_c and by calculating the transition entropy. In addition this experiment demonstrates the ultimate capability of our calorimetric installation (see Section 4). The scattering of the individual measuring points is rather high but the investigated sample [23] had a mass of only 8 mg!
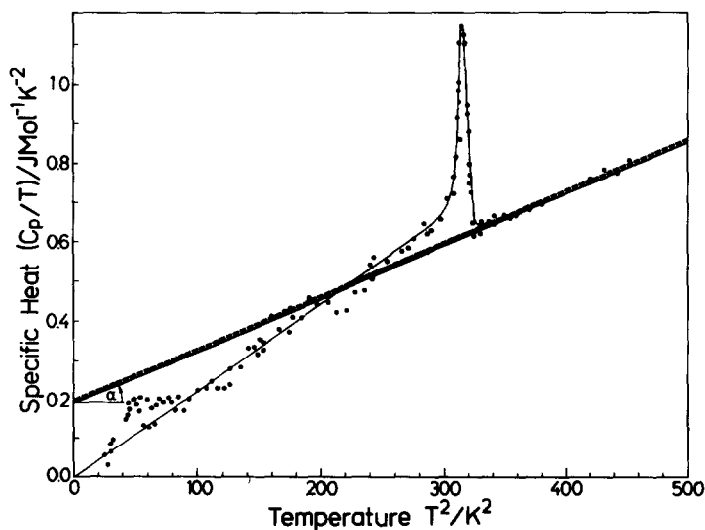

Fig. 6. Specific heat of Nb_3Sn: the superconducting transition temperature and the heat capacity were determined using a sample of only 8 mg [23].
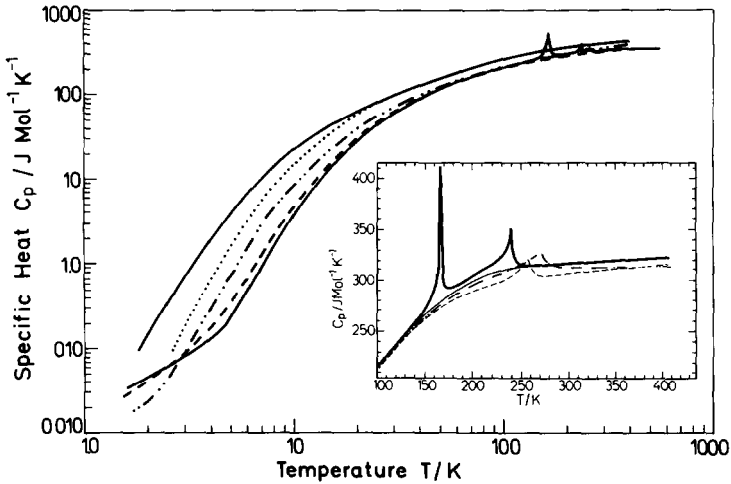
Fig. 7. Specific heat of several argyrodites [24]: (———) Cu_6PS_5Cl (lower curve), (- - - -) Cu_6PS_5Br, (— ·· —) Cu_6PS_5J, (······) Ag_7PS_6, (———) Ag_6PS_5Cl (upper curve). The inset shows crystallographic phase transitions in Cu_6PS_5(HAL) [HAL = Cl, Br, J].

The c_p data measured on different "argyrodites" (ME_6PS_5HAL and ME_7PS_6; ME = Cu, Ag; HAL = Cl, Br, I) aided significantly in the optimization of the conditions for the growth of large crystals of these interesting, partially ionic-conducting materials by chemical vapor transport [24]. The results are represented in Fig. 7. A simple measurement of $c_p(T)$ from 4 to 300 K is usually not very exciting for a physicist. These compounds, however, are a good example that nicely demonstrates how measuring an
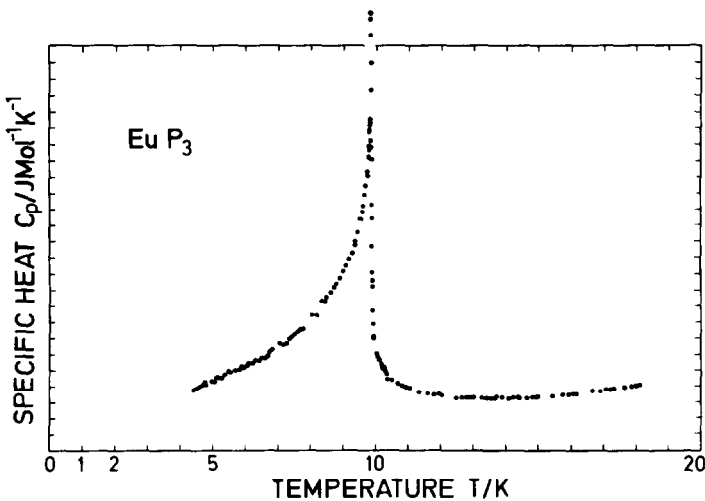
Fig. 8. Antiferromagnetic phase transition in EuP_3 [25].

expectedly smooth c_p curve as a function of temperature may cause surprises. Heretofore unknown phase transitions of the ME_6PS_5HAL compounds were revealed as shown in the insert of Fig. 7 [24]. Furthermore in Cu_6PS_5Cl the strong deviation of $c_p(T)$ from Debye's T^3 law below 5 K indicates the quantum-tunneling of Cu ions from one free lattice site to the next, a phenomenon which at high temperatures is called ionic conduction.

Specific heat studies on semimetallic $EuAs_3$, β-EuP_3, and their mixed crystals have significantly contributed to elucidating the magnetic behavior of these materials by determining the transition enthalpies and entropies. Knowledge of the spin-wave contribution establishes the magnetic field vs. temperature phase diagram [25]. The unique logarithmic second-order phase transition from the paramagnetic to the antiferromagnetic state below ca. 10 K is shown in Fig. 8. The measurement indicates the preciseness (10-mK steps or better) of the resolution of the heat capacity.

As may be seen from Fig. 9, a large Schottky anomaly is observed in Tb_2O_3 [26]. The anomaly is caused by excitation of the terbium ions in the crystal field. The continuous line displays the lattice term which is proportional to T^3 at low temperatures and has been estimated from the specific heat results for RE oxides, Gd_2O_3 and Yb_2O_3. The energies of the low excitation states of the Schottky anomaly were determined with great accuracy as $E_0 = 0$ meV, $E_1 = 0.95$ meV (12 K), and $E_2 = 1.5$ meV (22 K). They agree with the result of Mössbauer experiments.

A systematic investigation of a series of magnetic (Fe_3O_4) crystals as a function of their vacancy content produced the uncontestable proof that the
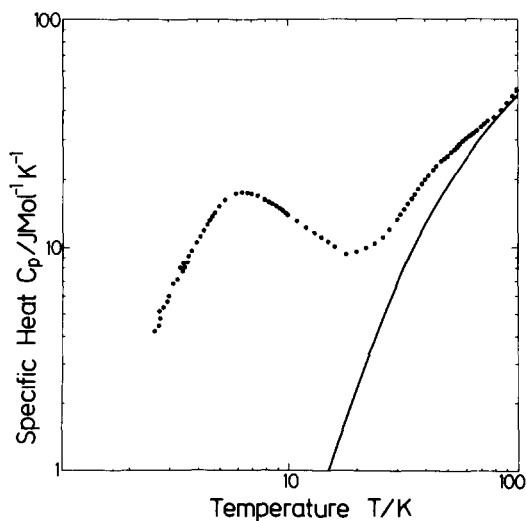

Fig. 9. Specific heat of Tb_2O_3 [26]: (———) contribution of the lattice, (······) experimental values: lattice heat capacity and the contribution of the Schottky anomalies.
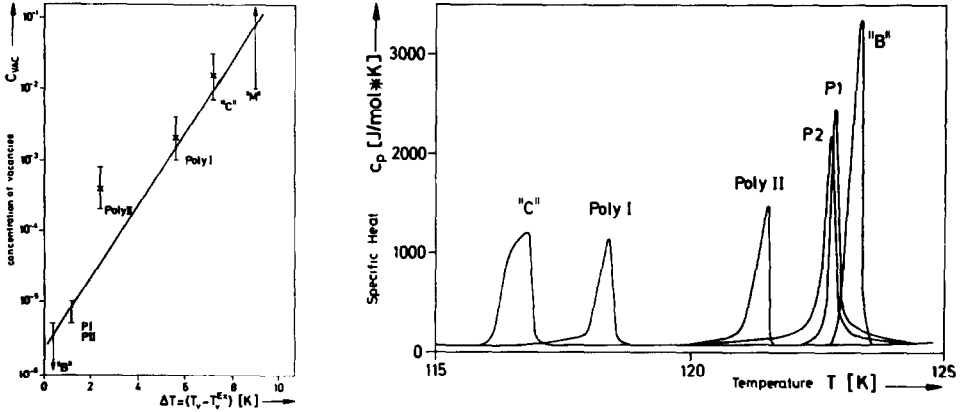
Fig. 10. Specific heat of Fe_3O_4 near the Verwey transition for samples containing a various amount of vacancies [27]. The left-hand side of the figure displays the interplay of vacancy-concentration and decrease of Verwey phase transition at T_v; the right-hand side shows the specific heat of different samples.

immense amount of controversial publications (about 40 papers on $c_p(T)$ in the last 50 years) on the electronic and structural transitions near 120 K are predominantly related to the "structural" purity of the samples: the concentration of vacancies. This result is shown in Fig. 10 [27].

Finally, an investigation of the $c_p(T)$ behavior of a series of $Cr_xMn_{1-x}As$ and $MnAs_{1-x}P_x$ compounds contributed to the understanding of the very complicated magnetic effects in those crystals [28]. Only one example is shown in Fig. 11. The $c_p(T)$ curve is a unique demonstration of which
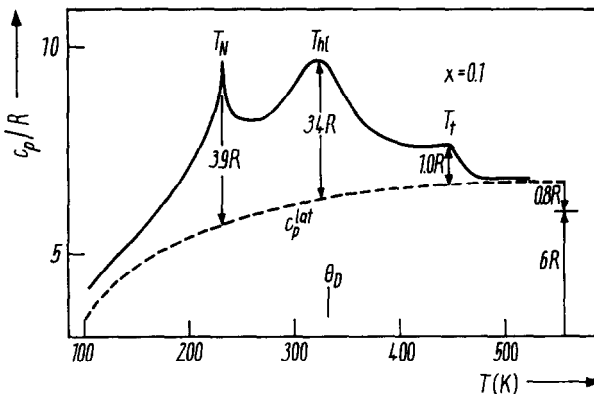

Fig. 11. Specific heat $MnAs_{1-x}P_x$ ($x = 0.10$), showing different contributions [28]: (– – – –) lattice heat capacity; T_N, second-order antiferromagnetic ordering at the Néel point; T_{hl}, two-level, low-spin to high-spin transition (Schottky anomaly); T_t, crystallographic (first-order displacive) phase transition from low-temperature B81 phase to B31 phase.

different energetic excitations in a solid (or liquid) contribute to the heat capacity: lattice vibrations, magnetic contributions which are displayed by the antiferromagnetic ordering near 240 K, high spin–low spin transitions of localized spins leading to a Schottky anomaly, and finally the first-order displacive phase transition at 460 K from B81 to B31 structure [28].

One should recall that this collection of recent results is completely arbitrary. The author would like to emphasize that the physical and chemical understanding of the enumerated phenomena has not only been realized in terms of specific heat values, but the comprehension resulted from many types of experiments, especially measurements of susceptibility and structure analyses using X-rays along with the specific heat determination.

2.2. Basic problems of LTC

In spite of such an extraordinary variety of interesting phenomena to be studied, the question arises: why is LTC (4 K $< T <$ 120 K) so poorly practiced? Indeed two significant problems arise due to the dramatic change of physical properties of solids below 100 K:

(i) a tremendous reduction of thermal energy (i.e. c_p) by a factor of 10^3–10^6 occurs on cooling any material from 150 K to liquid helium temperature;

(ii) this strong variation of $c_p(T)$ which can be seen from Fig. 7, for example, is accompanied by a similar intensive change of the thermal interaction between the sample and its surroundings (shield). This interaction, however, is different in its temperature dependence from that of c_p. Whereas below 10 K the heat transfer from sample to shield is governed by the thermal conduction proportional to the temperature difference ΔT along the electrical connections, the radiational heat exchange is the dominant part above 40–60 K; that heat exchange is proportional to $T^3\Delta T$.

In consequence the thermal relaxation time of the heat transfer between sample and environment is shortened considerably, being, for example, 120 s at 100 K and $<$ 1 s near 4 K, respectively. Table 2 gives representative values of c_p and the different heat transfer contributions at different temperatures.

It must be recalled in this context that calorimetry above 120 K — the range of commercial calorimetric equipment — is essentially dealing with one order of magnitude in c_p (Dulong–Petit law). In addition, the instruments are strongly connected to the surrounding conditions and influenced by the exchange gas flow. The instruments have a poor sensitivity which does not allow energy ranges to be 6 or 7 orders of magnitude smaller than those handled in calorimetry at room temperature. Last but not least, they suffer from an inflexibility to respond to the dramatic variations of physical parameters, especially the relaxation time τ.

TABLE 2

Thermal exchange

	4 K	20 K	100 K	300 K
Radiation $Q \approx S \, [T_2^4 - T_1^4]$	0	$1 \times \Delta T$	$85 \times \Delta T$	$2100 \times \Delta T$
Heat conduction $Q \approx A \Delta T$	$2 \times \Delta T$	$14 \times \Delta T$	$25 \times \Delta T$	$20 \times \Delta T$
Residual gas vibrations, self heating	0	~ 0	~ 0	~ 0
Heat capacity (erg g^{-1})	500	20 000	1 800 000	2 500 000
Transferred heat for $\Delta T = 1$ K during 1 min (% of total heat capacity)	25	5	0.3	4

These problems multiplied as LTC progressed from the 100 g measuring scale to the 10 g and 1 g scales. Hopefully, the next step to the 0.1 and 10 mg scales in sample mass will soon be carried out and will prove that routinely performed LTC is able to cover not only 6 decades or more in the energy scale due to variation of temperature, but also 4 further decades due to reduction in mass. Indeed, it is an obvious progress from measuring 100 g at 300 K, $c_p \approx 50$ J K^{-1} to 10 mg at 1 K, $c_p \approx 10^{-7}$ J K^{-1} = 1 erg K^{-1} which requires for a precision of 1% for an energetic resolution of 1/1000 of an erg!

3. EXPERIMENTAL

The heat capacities given in Section 2.1 were measured with a fully automated, "quasi-adiabatic" calorimeter working either in the temperature range 0.3–4.2 K, 1.7–90 K, or 40–180 K according to the coolant in the cryostat and the appropriate thermometer on the sample holder. These calorimeters have now been used successfully for many years. The calorimeter has not been designed to give ultra-high accuracy (i.e. 0.1%), rather it provides medium accuracy (0.5–1.5%), but high flexibility, simplicity of handling, extremely high reproducibility of the sample holder, and the possibility to determine heat capacities of samples weighing only 100 mg to 1 g.

As the installation was described in detail some years ago [5] and the most significant features have been outlined and discussed very recently [3], the reader is referred to these references *. A significant alteration, however, has

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* In the conference talk the author explained the essential components of the calorimetric set-up, electronics, calorimeter, shields, and sample holder by showing a series of slides.
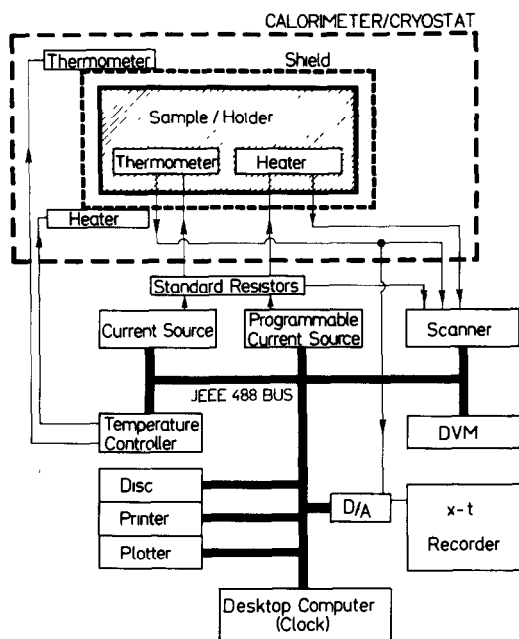
Fig. 12. Schematic arrangement of the electronic hardware for an automatic Nernst step-heating calorimeter; the layout is similar to that shown in fig. 11 of ref. 5 which was replaced 5 years ago by the presently shown, more precise electronic components.

been made since 1981: although the measuring principle and process control parameter of the single heat steps of the quasi-adiabatic experiments have remained unchanged, the hardware and the computer were modernized. The calorimeter is now controlled by a Hewlett Packard 9825A (or 9816) microcomputer including HP floppy disc, printer, and plotter. The entire hardware is connected via an IEE-488 data bus. The voltages of heater and thermometers are switched by an HP3495A scanner and measured by a DATRON 1071 ($7\frac{1}{2}$ digit) voltmeter. The shield temperature control is performed by a CRYOVAC temperature controller. The programmable current d.c. source consists of a KNICK IS3000 current calibrator. The modified hardware is represented schematically in Fig. 12 in a self-explanatory manner.

The heart of the calorimeter is the "platform-type" sample holder, developed in recent years. It is a rigid installation in the calorimeter and its heat capacity need not be measured separately for each unknown sample. The holder is shown in Fig. 13 and explained briefly in the figure caption; details were given in ref. 3. This construction has fulfilled all requirements of a nearly perfect sample holder for (quasi)-adiabatic calorimetry:
(i)   low heat capacity which can be reduced again by a factor of about 10 by use of smaller sized germanium thermometers;
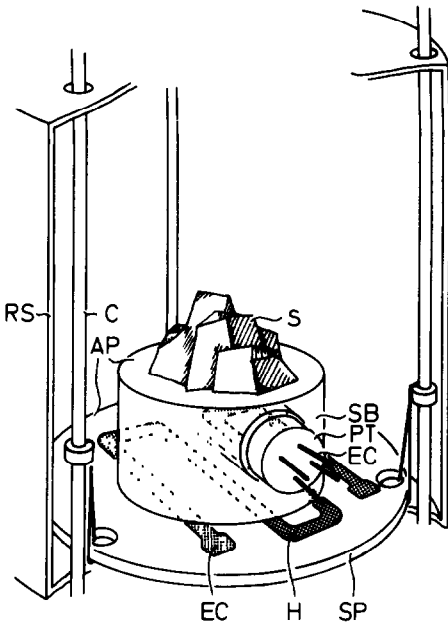
Fig. 13. Platform-type sample holder [3]: C, support for sample holder; SP, sapphire plate, $d = 0.1$ mm, diameter $= 12$ mm; SB, sapphire block, diameter $= 8$ mm, $h = 5$ mm; S, sample; PT, germanium or platinum resistance thermometer; H, NiCr heater of 1.5 kΩ; RS, radiation shield; EC, electrical connections.

(ii) high reproducibility, guaranteed by the rigid installation: the change in heat capacity within 5 years during more than 100 experiments and 11 gauge measurements of its heat capacity was less than 0.35%, that being the accuracy limit of the present installation due to the precision of standard resistors, thermometer calibration, etc.;

(iii) easy handling: the samples are simply placed onto the Al_2O_3 block;

(iv) excellent thermal contact guaranteed by a small amount of APIEZON N grease (0.15 mg) applied by a special, reproducible procedure.

The measurement of copper standard samples in the temperature range 1.5–30 K and pure Al_2O_3 between 80 and 200 K proved the precision of the installation; the achieved accuracies were ± 0.35 and $\pm 0.3\%$, respectively.

In a further attempt to reduce the sample mass needed for an investigation, the heat capacity of the sample holder had to be decreased. However, the use of a simple sapphire plate (0.1 mm thickness, 8 mm diameter) with an evaporated 2 kΩ heater and a small germanium thermometer (of the "exposed elements" type), which was glued to one side of the Al_2O_3 plate only, did not meet our requirements. The project was scrapped after the first tests because of the necessity to calibrate the tiny Ge resistors individually, the uncertainty about its reproducibility, and mainly because of the fact that with the very low heat capacity ($C = 0.3T + 2.3T^3$ erg K^{-1} for $T < 7$ K)

only measurements with the heat leak (relaxation time) method could be performed. These conditions did not meet our intention to continue in the direction of constructing simple and easy-to-handle calorimeters. This requirement ruled out complicated thermometer calibrations and sophisticated tests that are obligatory for absolute caloric measurements with the heat leak method. The only alternative was the application of the differential technique as used successfully above 120 K.

4. DISC: DIFFERENTIAL ISOPERIBOL SCANNING CALORIMETER

This new type of calorimetric method which is described here for the first time meets all the requirements needed to determine heat capacities of samples in the 10-mg range between 4 and 300 K. The essential components of this method are:

(i)   Isoperibol conditions: the experience and knowledge of calorimetry at very low temperatures, which has been mentioned as equivalent to calorimetry with very small samples at higher temperatures, are transferred to the present design.

(ii) Differential arrangement was chosen in order to take into account the strongly temperature-dependent thermal heat transfer to the surrounding at any temperature and to avoid systematic errors.

(iii) Continuous (step-heating) arrangement to shorten the measuring time well known from DSC instruments.

(iv) "Calibration-independent" thermometers.

(v)   Automation and platform-type sample holder are employed as well-known and reliable techniques.

(vi) Cryogenic equipment: simplicity and easy handling.

Isoperibol conditions (the heat leak methods) have rarely been used at temperatures above 4 K [29]. Only a few differential calorimeters have been described: a "dynamic differential calorimeter" by Lagnier et al. [30] which works under adiabatic conditions with energy compensation, continuous heating, and large samples; the differential technique of Jones et al. [31], where samples are connected by a thermal (weak) link and the ratio of heat capacities is measured according to $(C_1/C_2) \approx (\Delta T_2/\Delta T_1)$; and a slightly modified method in which the opposite heat fluxes across the "weak" link are measured by thermometers if the two samples alternately receive a heat pulse [32]. None of the three methods are well adapted to measurements on small samples and partially require good thermal conducting specimens, i.e. metals.

The new principle of caloric measurement * has worked well in the range
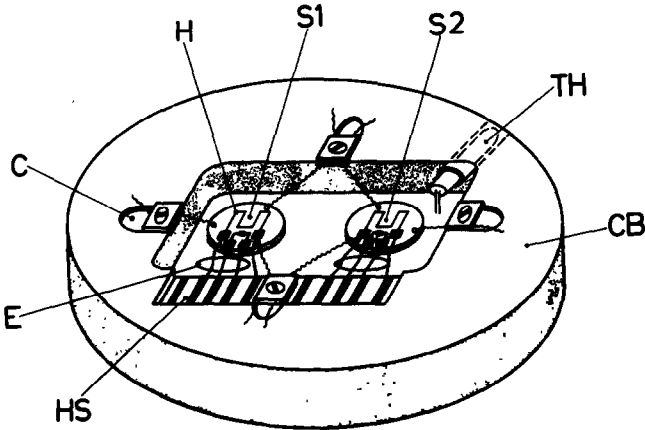
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* Patents pending.

Fig. 14. Support plate with two symmetric sample holders: S1,2, sample holders; CB, thermal bath/shield at temperature T_0; C, cotton wires for supporting S; E, electrical connection by gold wires (thermo-elements) and leads; HS, thermal anchoring; H, heater; TH, thermometer to control T_0.

20–200 K. It consists of a twin arrangement as shown schematically in Fig. 4c. Two sample holders of the platform-type are symmetrically arranged in the middle of a copper plate: two sapphire discs (diameter $\approx$ 8 mm, thickness $\approx$ 0.15 mm) suspended by cotton threads are provided, each with a 2 kΩ heater and a difference thermocouple (Au, 0.07% iron vs. chromel). Each sample holder behaves as described in the heat leak method (see Fig. 4b). The heat leak is provided essentially by the 5 μm thick copper wires bonded to the sample holder on one side and to the copper support on the other side. The copper support, at the same time, serves as the surrounding T_0 bath and as a thermal shield. Figure 14 shows the sample holders and the supporting plate. The temperature–time behavior of the arrangement is as follows: if a heating current is supplied simultaneously to both sample holders the subsequent decay of both temperature increments ΔT_j ($j = 1.2$ in the following) occurs according to the different heat capacities C_j and unequal thermal links K_j with two separate relaxation times τ_j (see Fig. 4b) ("external" relaxation time is now denoted as τ_j):

$$\Delta T_j(t) = T_0 + \Delta T_j^{\max}\left[\exp\left(-t/\tau_j\right)\right]$$

In order to avoid the waiting time for a new temperature equilibrium at a higher $T_0'(> T_0)$, the shield/surrounding temperature is continuously swept at a speed S (K s^{-1}) and successive heat pulses are applied to both samples, the reference with known heat capacity and the unknown sample. The resulting temperature–time diagrams for the heating curves are shown in Fig. 15. The mathematical description of one heating curve is given by the
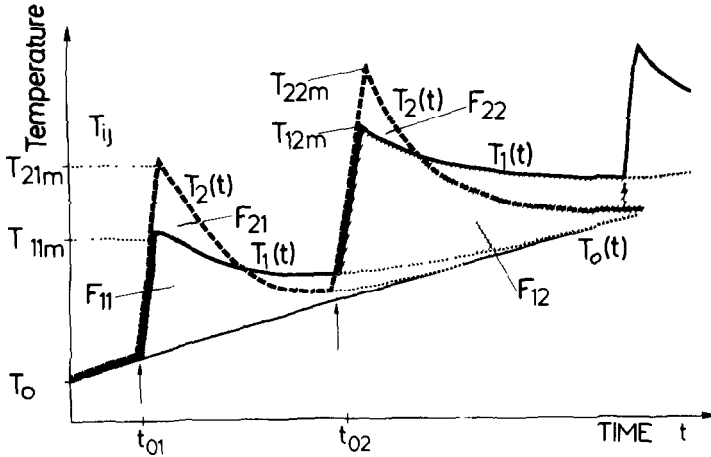
Fig. 15. Temperature–time behavior of the differential, non-adiabatic heating curves: $T_0(t)$, background-shield temperature which linearly increases; t_{01}, t_{02}, start of heating for first and second heating cycles; T_{jk}, temperatures, $j = 1,2$ number of sample holder, $k = 1 \ldots n$ number of heating cycle; F_{jk}, surface area of $\int_0^\infty \Delta T_{jk}\, \mathrm{d}t$ from which τ_{jk} are calculated.

formula

$$\Delta T_{jk}(t) = \left(\Delta T_{jk}^{\max} + S\tau_{jk}\right)\left[\exp\left(-t/\tau_{jk}\right)\right] + S\tau_{jk}\left(t/\tau_{jk} - 1\right)$$

from which τ_{jk} is determined by iteration ($j = 1$, 2 right- or left-hand side sample holder; $k = 1$ to n denotes the number of the non-adiabatic heating cycle).

During an automatic measurement the heating curves are computed in a first-order approximation by logarithmic fitting in order to obtain τ_j. From that quantity the approximate heat capacity is calculated. After having performed a complete experiment, the k_j values are smoothly fitted and a new determination of the c_p data by three methods is made: (i) evaluation of $\tau_j \rightarrow c_j = \tau_j k_j$; (ii) computation of the temperature increment $\Delta T_j^{\max}$ of the short heating times (~ 1 s); (iii) calculation of the surface area of the integral $\int_0^\infty \Delta T_j(t)\mathrm{d}t$.

The flat sample support (Fig. 14) is placed on top of an inverted, continuous flow cryostat which is directly positioned on top of a liquid helium vessel. The sample support is covered with a radiation shield of copper and enclosed in a vacuum can. There is no cold indium seal. The evaporator–sample support assembly acts as a shield and provides a reference temperature T_0 simultaneously. The temperature is computer controlled by an IEE-488 interfaced, computer-controlled valve for the liquid helium throughput in connection with an IEE-488 interfaced commercial temperature controller/indicator (CRYOVAC type TIC 303 M). The temperature T_0 is measured by a calibrated, commercially available germanium resistor; the

two temperature differences $\Delta T_1(t)$ and $\Delta T_2(t)$ are recorded by Keithley Nanovolt-Nullmeters (Type 140) which amplify the very small thermo-voltages (± 10 nV $= 10^{-8}$ V). Then the amplification is measured with an HP 4545 digital voltameter.

The remaining electronics contain similar components as described in ref. 5 and Section 3, Fig. 12, respectively, and are organized using the IEE-488 standard, exclusively. The set-up is nearly identical to that of our adiabatic calorimeter shown in Fig. 13.

The DISC set-up has proven to give reliable data. Measurements of a 20 mg piece of aluminum were in agreement with literature data within 5%, although the sample holders were not tested seriously and were not characterized with respect to their heat capacity; neither of the thermocouples has so far been submitted to a precise examination. In addition, the temperature sweep is not yet an accurate constant. Nevertheless, the overall behavior of the calorimeter with respect to the relaxation times, τ_l, is very promising. The calorimeter seems adapted to handling by non-scientific personnel and requires rather limited cryogenic knowledge.

CONCLUSION

A review of the history, the methods most commonly used, and of recent trends in low-temperature calorimetry has been given. Emphasis was placed on unsophisticated and easy-to-handle calorimetric cells and the scaling-down of the sample masses employed in calorimetry from the 100 g scale in the seventies to now 1 g scale and 10 mg range in the near future. The principle, essential components, and preliminary results of a new type of differential isoperibol-scanning calorimeter (DISC) were described for the first time. When looking to the future, the community of thermoanalysists can regard the actual trends optimistically. There is a strong belief that very soon calorimetric studies in a further decade of temperature, namely 10–100 K, can be performed as routinely and reliably as it is done today with DTA/DSC instruments above 120 K.

However, it is a challenge to every calorimetrist, especially those from low-temperature laboratories, to pursue the elaboration of higher precision (1%) of commonly feasible calorimeters, and the development of electronic components and calibration procedures. At present still too much attention is paid to the fascinating field of automating experiments, whereas the uncontested necessity of progress in developing new and better-elaborated thermoanalytical methods and measuring devices is clearly neglected in research laboratories as well as in industry.

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