Journal of Thermal Analysis and Calorimetry, Vol. 56 (1999) 655–671

RECENT PROGRESS IN LOW TEMPERATURE CALORIMETRY

E. Gmelin

Max-Planck-Institut fuer Festkoerperforschung, Heisenbergstrasse 1, D-70569 Stuttgart Germany

Abstract

The paper gives a review on recent progress on new methods, instrumental innovations and new trends in low temperature calorimetry as reported in the last five years in the literature. The paper refers to establishing strictly adiabatic conditions, improved analysis of quasi-adiabatic experiments, high resolution adiabatic and isoperibol scanning calorimeters and microcalorimeters for the study of μg-samples.

Keywords: calorimetry, low temperature techniques, review

Introduction

Since decades thermoanalytical instruments are based to a great extent on commercial equipment whereas low temperature calorimetry, a particular branch of thermal analysis, today still has to use home-made and individually designed equipment [1–7]. The construction of suitable calorimetric equipment below 100 K remained a domain of a few cryogenic laboratories. Traditionally, low temperature calorimetry (LTC) uses the adiabatic step heating technique introduced by Nernst and Eucken 80 years ago [8]; for an overview [9]. Therefore, from the beginning, and in contrast to thermal analysis (TA), LTC was always concerned with quantitative calorimetry and all the time held a high level of awareness of the inherent problems of 'absolute' caloric values in order to provide high-accuracy data [1, 4–6, 9]. In addition, low temperature calorimetrists have been the source of numerous powerful and ingenious calorimetric methods and innovations which sometimes were later transferred to commercial products but at higher temperatures only [10]. A focal point of the development remained the reduction of the amount of sample mass required for calorimetric measurements. Due to the strong decrease of heat capacity, below ca 100 K by several orders of magnitude, the reduction of mass from the g-range into the mg-range led of necessity away from adiabacy to more isoperibolic conditions. This required new methods and new technologies. So, miniaturisation and calibration have became a permanent subject of innovation for scientists working at low temperatures. The two most accurately measured materials with respect to specific heat below 100 K, namely Al_2O_3 (<0.2%) [11] and Cu (<0.5%) [12], have been initiated from the low temperature community.

1418–2874/99/ $ 5.00

Akadémiai Kiadó, Budapest
Kluwer Academic Publishers, Dordrecht

In the seventies and eighties, LTC enriched the TA-world with the development of new methods which in the meantime can be named 'classical': the non-adiabatic heat step or relaxation time calorimetry [13], the so-called 'ac-calorimetry' performed as temperature or power modulated method [14] (for a review [7]), various scanning methods, e.g. the continuous heating (or cooling) method at constant or variable heating power [15, 16], the 'dual-slope' method [16, 17] or the adiabatic scanning as the most perfect realisation of scanning calorimetry [18–20]. At the same time small-sample Nernst type (quasi-adiabatic) calorimetry (sample mass below 0.5 g) became a routine technique in several laboratories [1, 2, 4, 15, 21, 22]. Several of these methods have found wide-spread application but could never reach the level of commercialisation.

The following decade till now showed a wealth of improvements of the different existing methods and experimental implementations focusing on perfecting the automation of the experiments by the extensive use of more and more powerful computers, application of high-performance electronics, new and better thermometers, better sample and heat shield temperature control by sophisticated electronics, more intelligent and refined 'on-line' and 'post-run' data treatment, compensation of non-adiabacy by hardware or software means, better understanding of dynamic methods by appropriate modelling, considerable progress in small sample experiments and increased accuracy as well as a reduction of the tediously long measuring time, preferentially by application of scanning.

Finally, in the recent five years, in particular in the years 1997/98, new and essentially improved calorimeter constructions have been reported. With respect to accuracy, the difference between strictly adiabatic and isoperibol calorimeters vanishes. Computers enable detailed and refined computational procedures, e.g. post-run data evaluation which at least partially remove non-adiabacy due to thermal loss of any type. Implementation of various methods, for absolute or relative heat capacity determination on the same calorimeter hardware has become customary. The individual methods are then realised by loading the relevant program. Temperature measurement and controlling of sample temperature and that of the surrounding shield approach ± 10 μK so that 'ideal' adiabatic conditions are available. Several measurements with μg-samples have been reported (Sect. 4). The introduction of commercial temperature-modulated instruments [23] as well as the revival of the '3ω' technique [24, 25] that allows to perform heat capacity spectroscopy and encompassing complex heat capacities, constitute new tools for better research. These tools opened new applications for calorimetry. In summary, the recent developments enable more accurate determination of the specific heats, much higher resolution of phase transitions and better determination of critical exponents as well as the investigation of μg samples, rapid (10 h) orienting measurements of heat capacity from 4 to 300 K. However, the classical high-precision calorimetry is still neglected and only a few calorimeters for high-accuracy data have been reported [4, 12, 26, 27] in the last ten years.

In conclusion, the progress in LTC is obvious and it is surprising that always new and fascinating possibilities appear. We note again that most of these developments took and take place exclusively in the few low temperature laboratories.

In this contribution, some of the new and most recent features of low temperature calorimetry are described, the performance of the calorimeters is compared, advantages and disadvantages are pointed out. For reason of limited space, it was not the intention of this paper to explain in detail the various calorimetric methods nor to give a comprehensive literature review, rather than to outline the merits and drawbacks of the methods described recently and to indicate some representative literature, in order to give an orientation to the non-expert reader for the continuously growing number of different calorimetric methods and techniques.

Problems and merits of low temperature calorimetry

Considering low temperature calorimetry (LTC), two questions always rise:

– Do we really need calorimetry at cryogenic temperatures, i.e. below liquid nitrogen?

– Why LTC is not practised at more places and remains restricted to specialised laboratories?

LTC is among the most powerful tools for thermodynamic investigations. The study of the temperature dependent specific heat C_p provides exclusively direct access to define the temperature dependence of the thermodynamic functions, in particular the Gibbs free energy $G(T, p)$. In addition, LTC provides information on enthalpy and entropy changes involved in phase transitions and allows to determine critical phenomena. It indicates (in the range of liquid helium) the electronic density of states of the carriers in a material, characterises spin wave contributions below magnetic transitions, gives the zero-temperature Debye-temperature, indicates defect concentrations and order-disorder phenomena and yields direct entropy information on crystalline electric field effects and two or multi-level thermal excitations, e.g. nuclear spin orientation. The necessity of LTC data is directly demonstrated when the Gibbs function is inspected:

$$G(T, p)=H-TS=\int C_p(T)\mathrm{d}T-T\int(C_p(T)/T)\mathrm{d}T$$

$G(T, p)$ is essentially governed by the difference of the terms of enthalpy and entropy integral (1st and 2nd term). The second term, however, results predominantly from the temperature-dependent entropy and remains of nearly equal size down to the lowest temperatures because of the denominator T. Thermodynamic functions as well as energy of formation are incontestably governed by the low temperature $C_p(T)$ values via $G(T, p)$. This demonstrates clearly the necessity to perform low temperature C_p-experiments in order to define accurately $G(T, p)$. There is indeed a worldwide demand for LTC data.

The special problems of LTC result from

(i) the thermal properties of solids used to built the caloric cell and

(ii) the cryogenic liquid necessary for cooling.

The particular drawbacks of LTC are:

• cryogenic environment, mostly liquid helium with its low heat of evaporation which requires special thermal insulation and transfer-techniques for the cryo-liquids,

• drop-down of the heat capacity of the caloric cell (and all solids) below 100 K by several orders of magnitude which requires that a LTC must be able to detect energies and changes with a resolution of better 10^{-4} in the Joule, mJ and μJ range, simultaneously.

• strong variation of the heat transfer by heat conduction (<ca. 40 K) and heat of radiation (>ca. 40 K) rendering difficult the temperature control of the sample and heat shield,

• strong variation of the values of heat diffusion, i.e. the relaxation times τ_i for the thermal equilibrium between the different parts of the calorimeter: sample, calorimeter-cell including addenda (heater, thermometer) and surrounding heat shield(s). Resulting from the changes of $C_p(T)$ and heat transfer rates with temperature, the different τ_i may vary from minutes to less than msec.

As a consequence, experimentalists who want to start LTC have to learn cryogenics, vacuum technology, low temperature thermometry, ac and dc weak-signal electronics, and will experience a lot of problems related to heat transfer and thermal equilibrium, more than at higher temperatures (>100 K) since in this range the variations of C_p and τ_i seldom exceed one order of magnitude.

We note that in view of the problems and the adjustment of experimental parameters, related with the measurement of small samples, small sample experiments are comparable to low temperature experiments. In both cases, the heat capacity is lowered. Although the measurement with a low sample mass is more difficult (due to smaller C_p-values), it may be advantages because of shorter thermal relaxation times and thus shorter experimental time. In fact low masses are comparable to low temperature in view of the experimental parameters.

Today in many laboratories, LTC experiments are performed as a routine technique. Highly flexible sample holders enable to measure any type of samples, even air or humidity-sensitive ones, without problems [2, 10, 21, 22]. Also experiments in high magnetic fields up to 17 Tesla are made without major problems. Nevertheless, a number of problems remain on the agenda of LTC:

– simplification of cryogenic experiments and commercialisation of LTC,
– high resolution measurements under pressure,
– thermometer calibration in high magnetic fields (B>15 T),
– more caloric standard reference substances,
– still better understanding and modelling of dynamic processes and definition of boundary conditions for the individual calorimetric methods,
– microscopic experiments (Sect. Progress: new calorimeters and improvements).

Methods and classification of low temperature calorimeters

The very basic part of a calorimeter – the caloric measuring device – is always very similar for all calorimeters: The proper calorimeter-cell (of whatever construction) at a temperature $T_C(t)$ is located inside an environment with temperature $T_S(t)$, generally labelled as heat shield (or several shields). The thermal conductance k be-

tween cell and shield rules the thermal coupling. So, the following simple equation describes any calorimeter:

$$Q(T,t)=C(T,t)T_C(t)+k(T)\{T_C(t)-T_S(t)\}=C(T,t)T_C(t)+k(T)\Delta T(T,t)$$

where C denotes the (temperature and eventually time dependent) heat capacity of the cell including the sample and addenda, Q the heat transferred to the cell and ΔT the difference of temperature between cell and heat shield. $C/k=\tau_{ext}$ defines a time constant (external thermal relaxation time) which characterises the temperature equilibrium between the cell (sample/sample-holder/thermometer/heater assembly) and the heat shield as heat sink. The equilibrium of the cell itself occurs with the internal time constant τ_{int}.

For the classification of calorimeters, various schemes exist [28, 29]. Very briefly, a classification is mostly based on the size of k and ΔT and distinguish (i) isothermal, isoperibol and quasi-adiabatic/adiabatic methods, (ii) single or twin cell arrangements, i.e. absolute caloric or comparative (difference or differential) measurements, (iii) step-wise heating or scanning, and (iv) technically, whether the caloric measurement is controlled by Q, T_C or T_S. In view of LTC, however, the most basic distinction refers to the location where the thermometer for the determination of the heat capacity of the calorimeter cell ensemble is placed. The location is either on the calorimeter cell itself (sample and sample support with heater and thermometer), which is the classical arrangement or along the thermal coupling k or even on the thermal shield T_S, usually called heat-flow instruments.

The history of LTC and the experience made show that heat flow instruments are unsuitable for low temperature use due to the drastic lowering of specific heat with decreasing temperature and the related shortening of thermal relaxation times τ_i. Therefore, all methods applied below 100 K own calorimetric cells which include the sample studied and the thermometer to register the sample temperature. The methods – quasi-adiabatic, temperature-modulated, heat-pulse, continuous-heating, differential scanning calorimetry, etc. – are listed in Table 1 giving some characteristic averaged parameter-values and the typical performance of these calorimeters for low temperature use. Also, an abbreviation is given to classify the instruments. Advantages and disadvantages of the methods are readable from this table. The classical adiabatic heat-pulse method (ADC and QAC) [1, 2, 4–6, 9, 11, 12, 21, 26, 27] is still the most precise tool to determine 'absolute' values of heat capacities as well as it allows direct enthalpy measurements, e.g. on first order phase transitions, but the method is less adequate to resolve discontinuities at critical temperatures with high temperature resolution. For that purpose, TMC (or so-called ac-calorimetry) [7, 14] and CHC [15, 18–20, 30–34] are much more powerful. Both methods (TMC, CHC) display excellent temperature resolution, are preferred to detect very small changes of heat capacity, e.g. in comparative arrangements or in magnetic fields, and allow scanning in the heating or cooling mode. A unique advantage of TMC is its ability for repetitive measurement and signal averaging. TMC and PHC are the techniques favoured for small sample calorimetry (<1 mg) whereby PHC [13, 35], due to the step-heating, shows less performance for resolving sharp transitions in $C_p(T)$.

Table 1 Charactristic averaged performance parameters of the differen calorimetric methods for use at low temperatures

Parameter	ADC	QAC	TMC	PHC	CHC	DSC	TMDSC	THC
Inaccuracy, abs.(%)	<0.1–1	0.5–2	2–5	2–5	0.7–5	2–10	2–10	2–10
Inaccuracy, rel.(%)	<0.1–0.5	0.1–1	<0.01	1–3	<0.05	0.5–5	0.5–5	<1–5
Temp.-resolution (%)	+	+	+	+	+	+	+	-
Sample-mass (mg)	>5000	10–500	1–100	50–500	50–1000	10–100	10–100	<0.1–1000
Temp.-range (K)	all	all	0.3–300	all	15–300	>100	>100	all
Measuring time	week	days	days	days	h	h	h	h
Flexibility[xx)]	+	+	+	+	+	+	+	-
Heat transfer[xx)]	+	+	- -	+	-	-	- -	-
Thermal equilib.[xx)]	+	+	+	+	-	- -[x)]	- -[x)]	-

Abbreviations (with comments in parenthesis):
ADC – adiabatic calorimeter (highest absolute accuracy)
QAC – quasi-adiabatic calorimeter
TMC – temperature modulated calorimeter (best relative resolution)
PHC – pulse heat calorimeter (suitable for non-adiabatic conditions)
CHC – continuous heating calorimeter (high resolution, good absolute accuracy, small samples required)
DSC – differential scanning calorimeter (moderate accuracy, small samples)
TMDSC – temperature modulated DSC
MDSC – likewise DSC but additional information on complex heat capacity
[x)] always to be checked.
[xx)] + denotes reasonable good, ++ very good measurement, – and – – means less good and bad performance

The advantages of ADC on one hand and TMC and PHC on the other are best combined in CHC which enable quick experiments with low mass samples with rather good accuracy and excellent temperature resolution. Finally DSC [28, 37] and TMDSC [23, 38] are widely used and reliable for semiquantitative studies. Good quantitative measurements, however, require careful adjustment of the experimental conditions [39, 40]. In view of flexibility, to measure any type of sample, ADC, QAC, CHC and DSC have advantages whereas TMC and PHC are submitted to stringent boundary conditions with regard to internal relaxation time. Heat transfer and thermal equilibrium (relaxation times τ_{int}, τ_{ext}) of sample, sample-support and heat shield are best recorded and controlled in ADC and QAC whereas it is poorly known and difficult to control in DSC experiments.

We mention that ADC, QAC and adiabatic CHC require the most careful and well elaborated constructions and testing for systematic errors once in the beginning. TMC, PHC and isoperibol CHC involve simpler apparatus design but will take considerably more time to optimise the measuring conditions and calibrate the instrument for the individual experiments. For example, TMC and PHC require a properly selected heat link, adjusted to the value of heat capacity under investigation in order to achieve reasonable τ_{ext} and hold the condition: $\tau_{ext} > 10\ \tau_{int}$. Both requirements need time for testing and to gain experience. In PHC, for example, if τ_{ext} becomes too long as to approach adiabatic region, then the underlying zero-line is less known and determination of τ_{ext} would be less good; otherwise if τ_{ext} is too short, the condition $\tau_{ext} >> \tau_{int}$ is not fulfilled and the serious 'τ_2-effect', i.e. superposition of internal and external relaxation times in the thermal equilibrium time, arises [13, 14, 36]. The 'τ_2-effect' arises also from poor thermal conductivity either of the sample or between sample and sample-support. This causes serious problems in TMC, PHC and CHC but not for ADC and QAC. Commercial equipment (DSC, TMDSC) require also a considerable amount of time for calibration and testing to rule out systematic errors, e.g. mass dependence, temperature dependence of calibration factor, etc. [39, 40]. As crude guideline, we say that 'static' methods – ADC, QAC, PHC are less susceptible to unexpected and systematic errors and poor heat conductance in parts of the calorimetric cell, e.g. the sample, allow much better knowledge of the relaxation times involved and show higher flexibility in view of the type of sample to be studied than 'dynamic' methods, i.e. TMC, CHC, DSC. The dynamic methods, however, are favourable for small mass experiments, short-time and high-resolution measurements performed as scanning, but are subjected to serious restrictions on maximum usable sample mass and heat transfer in connection with the admissible τ_{ext} and τ_{int}. The relevant boundary conditions must be held and checked [7, 13, 14, 36, 41].

According to the discussion above, heat pulse techniques (ADC, QAC, PHC) and scanning (TMC, CHC, DSC) are complementary to each other. As mentioned before, many modern calorimeter constructions allow the choice to run various programs, i.e. to perform experiments according to the different methods, with the same calorimeter cell. The focal points of construction calorimetric set-up for LTC remain the approach of adiabatic conditions and, in recent years, the application of scanning for reason of temperature resolution and saving of measuring time.

Table 2 A selection of recently described low temperature calorimeters

Method	Authors (year)		Ref.	Sample mass/ mg	Scanning rate dT/dt/ mK s^{-1}	Temp. range/ K	Accuracies/resolutions				Remarks
							ΔT/ mK	$\Delta C/C$ rel./ %	$\Delta C/C$ abs. %	δP/ mW	
IS	CHC	Cochran (66)	31	5.000	1	1–10	10	0.3	2		
AS	CHC	Asworth (68)	32	30.000	2–5	5–300		0.1	0.3–1		
IS	CHC	Pinet (72)	33	77.000	1–2	2–20		0.5	2		
ASDP	CHC	Lagnier (77)	34	gramms	<5	2–300	20		1		sample follows heat shield
IS	CHC	Junod (79)	15	>500	10–20	20–300	50	0.04	1–2	0.2	heat loss correction every 20 K
ASDP	CHC	Loram (82)	20	2–8.000	<1	20–200	10	0.005			measurement of C_p difference
IS	CHC	Rajeswari (89)	16	1–2.000	20–200	77–300	50	1	5		heat loss correction (natural cooling)
I(SDP)	CHC	Rahm (9?)	30	25–500	1–10	20–300	10	<0.5	2	0.01	two samples or DP
ISDT	CHC	Lysek (92) Barnes (94)	18 66	30.000	0.5	(50–120)	2	0.02		100 pW	atomic force microscope
AS	CHC	Schnelle (95)	19	20–300	2–5	20–300	0.05	0.02	1–2	0.005	sample follows heat shield
ISDT	CHC	Schilling (95)	42	10–20	1–6	50–150		0.02	5	0.002	DTA principle
AS	CHC	Pitsi (97)	53	1.000	0.03	ca. 300					
ASDC	CHC	Lai (97)	67	0.005	30.000	300–400			1–3	0.2	nJ-resolution; microchip
A		Riou (97)	68	0.010		40–160	<0.1	0.01	10		

Table 2 Continued

Method	Authors (year)		Ref.	Sample mass/ mg	Scanning rate dT/dt/ mK s^{-1}	Temp. range/ K	Accuracies/resolutions				Remarks
							ΔT/ mK	$\Delta C/C$ rel./ %	$\Delta C/C$ abs./ %	δP/ mW	
I	TMC	Jurado (97)	45	0.050		8–300		0.5	5		calibration of absolute value needed
AS	TMC	Marone (97)	56	>0.010	10	5–300		<0.1			laser diode heating, relative data
AS	TMC	Garfield (97)	55	ca. 1		30–300		0.2			laser diode heating
A	ADC	Tsukushi (97)	47	>10000		13–375		0.02–0.2			top-loading system
A/I	QAC	Pecharski (97)	59	1000		3–350		0.7	1–2		automatic parameter selection
I	PHC	Hwang (97)	51	250		4–100			1.2–2		total curve fitting for evaluation
IS	PHC/ TMC	Yao (98)	54	20–40	0.3–10	80–400	0.05				(dual slope method)
A	ADC	Takahara (98)	48	>50000		80–380	<10	0.2			simultaneously C_p and V

Abbreviations for the 1st row, indicating the calorimeter classification, are:
A – adiabatic, I – isoperibol
S – scanning mode
DT, DP – twin cell arrangement, with either measurement of temperature difference or power difference, respectively
The abbrevations used for the calorimetric method (2nd row) are identical to those given in Table 1

Progress: new calorimeters and improvements

The following selection of calorimeters for the determination of $C_p(T)$ at low temperatures were essentially published in 'Rev. Sci. Instrum.' and refers to reports from the last two years. Particularly complex, very specific or sophisticated constructions have been excluded. Each of the referenced papers gives quite comprehensive and detailed description of the apparatus. For reason of limited space, we do not describe or discuss details but only judge the performance. The LTC's representing progress, the reference number, an abbreviative description of the calorimetric method applied and some of their characteristic features are listed in Table 2. In addition reference is made to some earlier low temperature scanning calorimeters.

New methods, new calorimeters

A significant improvement and extension of the usable temperature range of the conventional DTA configuration has been reported by Schilling and Jeandupeux [42]. Heat capacities of milligram samples are measured in the range 40 to 300 K with a relative accuracy of $dC/C<0.02\%$ by use of high-precision electronic components. The base temperature (shield) is scanned linearly – with a typical rate of 1–10 mK s^{-1} – and the sample follows isoperibolically. Measuring the temperatures of the base (labelled b) by a platinum resistance thermometer, and the sample (s) and reference (r) by copper-constantan thermocouples yield the difference of the heat capacities between sample and reference:

$$\Delta C=C_s-C_r=(k_s/k_r)\{(dT_s/dt)/(dT_r/dt)\}\{(T_s-T_r)/(T_s-T_b)+1)\}C_s-C_r$$

and hence

$$\Delta C=C_r(T_s-T_r)/(T_s-T_b)$$

if the thermal conductances k_i and scanning rates dT_i/dt for sample and reference are equal: $k_s=k_r$, $dT_s/dt=dT_r/dt$, respectively. Both conditions are quite easy to fulfil. Thus the heat capacity of a sample is determined simply by simultaneously monitoring the temperature differences T_s-T_r and T_r-T_b without calculating any derivative in time or temperature.

Based on the classical TMC technique, Fominaya *et al.* [43, 44] developed a modification that makes the calibration of thermometers obsolete. The particularity of the set-up is the insertion of an additional reference mass with a separate heater between the ensemble sample/sample-support with heater and thermometer, and the heat sink (thermal shield or bath). The method is interesting for applications where the thermometer must often be calibrated, e.g. calorimetric experiments in very high magnetic fields B (B>12 T) or at high pressure. The theoretical treatment results in a simple formula:

$$C_s=C_r(P_s\omega_s/P_r\omega_r)$$

where C_s and C_r, P_s and P_r, ω_s and ω_r denote the respective heat capacities, heating power and modulation frequencies of the sample (s) and reference (r).

In an attempt to simplify cryogenics, Jurado *et al.* [45] developed a TMC that operates on the cold stage of a commercial closed-cycle refrigerator in the temperature range from 8 to 300 K. It uses chromel-alumel thermocouples as thermometers, works at a frequency of 2 Hz and has typical temperature amplitudes of 5–20 mK. Samples as small as 100 μg have been measured and the relative resolution amounts to 0.1%. The absolute heat capacity values were determined by a Perkin Elmer DSC-2. In this context, we note that presumable the mechanical vibrations of a refrigerator do not affect THC and PHC, however may be deteriorating for ADC, QAC and CHC.

No top-loading adiabatic calorimeter has been constructed so far because of the complicated structure. Only Handa [46] reported on a top-loading Tian-Calvet heat-flow instrument. Now, Tsukushi *et al.* [47] describe an adiabatic top-loading calorimeter for the range 20 to 290 K that reduces drastically the time required for changing the sample (ca 10 min) and enables also sample changing at liquid nitrogen temperatures. The Nernst type calorimeter uses rhodium-iron resistance thermometers and is run with a sample cell of 9 cm^3 weighing nearly 100 g. The inaccuracy amounts to 0.2% at 13–30 K and decreases 0.02% above 50 K.

A novel adiabatic calorimeter introduced by Takahara *et al.* [48] enables the simultaneous measurement of enthalpy and volume under high pressure up to 100 MPa in the temperature range 80–380 K using also rhodium iron thermometers. The sample is pressurised hydrostatically and the volume is determined with a new type of dilatometer using bellows installed in the cell. The cell mass is ca 650 g, the inaccuracy ±0.2%.

Scanning

In the last five years, CHC as a particular type of scanning calorimeter became a widely used technology for the wide temperature range 10–300 K. Based on the earlier work by Junod [15] and Pinel and Lebeau [33], a variety of different implementations and modern electronics helped considerably to improve CHC and establish it as an advantageous and flexible type of calorimeter. This type combines (as mentioned above) the merits of ADC/QAC and TMC/PHC. The CHC are built as single stage (without use of a reference) or twin stage caloric cells working with isoperibol or adiabatic surrounding conditions according to whether a temperature difference ΔT between sample and heat shield is accepted or not. The sample (and reference when twin-staged) is heated either with constant power and the heat shield follows the sample temperature, or the shield temperature increases, mostly linearly, and the sample temperature is recorded. In the adiabatic version, the heater power supplied to the sample varies in such a manner that the sample temperature always equals the shield temperature. An advanced adiabatic version of a CHC system, described by Schnelle and Gmelin [19], uses platinum resistance thermometry, needs sample masses of 20–200 mg at a scanning speed of 0.2 to 10 mK s^{-1} (typically 2 mK s^{-1}), gives an absolute accuracy of 1–2%, reaches a relative resolution of nearly $\delta C/C \approx 10^{-4}$

and records ca. 100 data K^{-1}. Temperature deviations between sample and heat shield are detected to ±10 μK and the heat supplied to the sample by a software-type PID temperature controller, to hold the temperature difference between heat shield and sample within the limit of 50 μK, is a direct and absolute measure of heat capacity. CHC systems show equally high performance for calorimetric experiments in high magnetic fields upto 17 Tesla which is needed to study anisotropy effects on single crystals [49–51].

Using extremely slow heating and cooling runs (<100 mK h^{-1}) allows to study rate dependent effects [52, 53], for example the long internal thermal relaxation time, e.g. in polymers, the orientational transition of C_{60} near 260 K in the order 10 h [53] or time-dependent heat capacities.

As a modern example of non-adiabatic scanning, Yao *et al.* [54] installed the 'dual mode' (or slope) method, initially described in [16, 17], in which the losses caused by isoperibolicity during the heating cycle are taken into account by measuring the temperature *vs.* time curve during cooling or with a different small heating power. The calorimeter is used either as CHC, TMC or PHC. We remark that the isoperibolic form of PHC is much easier to construct than the adiabatic type.

Most recent scanning type TMC's work with a laser diode as a heater and optical light guides to determine heat capacities of mg- and μg sample. Commonly, thermocouples serve as thermometer and the absolute heat capacity is taken from other methods [55, 56].

Computational

Computers have simplified considerably the former laborious and time-consuming computation of heat capacity curves. Recently the application of more elaborate evaluation procedures, in order to take into account isoperibolicity, yield data of better quality and thus more efficiency.

Correction of heat leaks can be made either on-line or as post-experimental computation. Such corrections are of particular interest in the 'static' type of calorimetry (QAC). Extrapolation methods for the correction of heat leaks by radiation or conduction were discussed for example in [57]. Ota and Gmelin [58] and Pecharsky *et al.* [59] described methods correcting losses on-line.

Application of a correction for the exponential post-heating temperature drift curve in quasi-adiabatic or isoperibol heat-pulse calorimetry (QAC, PHC) with isothermal heat shield is particularly advantageous for small sample measurements and for experiments above 100 K to correct for radiative heat losses [58]. Instead of using the well known formula for the calculation of the heat capacity $C=(Pt_h/\Delta T)$ (heater power P, heating time t_h and resulting temperature increment ΔT), the following equation is used [58]:

$$C=(Pt_h/\Delta T)[1+(t_h/\tau_{ext})^2/24]$$

where $\tau_{ext}=C/k$. The time τ_{ext} is determined from a fit to the curve temperature *vs.* time of the post-heating curve. The corrective term [...] largely accounts for temperature fluctuations of the heat shield, non-adiabaticity and non-linear heating as well as losses during the heating cycle. The scatter of the C_p data, evaluated by this way, improves by a factor of five compared to those calculated with the usual and simpler formula. The reproducibility of the data increased from 0.7 to 0.2% [58].

Due to the 'τ_2 effects' the exponentials of τ_{int} and τ_{ext} become superposed and may also deviate from the proper form of a single exponential. Then a linear curve fitting of the logarithmic temperature *vs.* time plot (*T vs. t*) of the post-heating driftline becomes questionable. Additional corrective terms may be required to represent the *T vs. t* curve. Such a second order correction to the above equation may be helpful when strong heat leaks are present and yield nevertheless correct C_p results. A parabolic function has been applied as correction for the non-linear logarithmic *T vs. t* curve [60].

The majority of (so-called) automated calorimeters, described in the literature, operate in fact semi-automatically, i.e. they still need human interaction to observe when thermal equilibrium is reached, to adjust manually the appropriate experimental parameters, e.g. for delay time, heating time, time-length of temperature-driftlines, etc.. This parameter setting may be avoided by strict analysis and formalisation of the measuring process and incorporating in a real-time data collecting software [51, 59]. Pecharsky *et al.* [59] report on the analysis, design and operation of a fully automatic quasi-adiabatic calorimeter for sample masses of about 1 g in which via software the measuring paramaters are optimised. The computer handels intelligently the detection of existence of thermal equilibrium, the determination of τ_i and the compensation of the thermal losses according to the given mass and heat conductivity of the sample, thermal conductance in the calorimeter, etc. It is crucial that the losses are minimized, i.e. the temperature difference to the sample remains zero. The application of several heat shield thermometers on several separately controlled shield sections, as usually done [4] does not guarantee zero-loss conditions. The losses, however, are best evaluated by recording the actual fore drift and post driftline of the sample temperature and adjusting the drifts to zero by controlling the heat shield temperature. Thus, the heat shield temperature sensor need not be calibrated, it can even be suppressed [51, 59]. The fore driftline stability amounts to <0.02 mK s^{-1} in quasi-adiabatic calorimetry with isothermal shield during the full cycle of a heat capacity measuring point [51]. In small sample quasi-adiabatic calorimetry, an excellent accuracy and low data scattering results from combining the described compensation of the losses by a software temperature controller (for the heat shield) and the above mentioned procedure to compute isoperibolic post-driftlines [70, 71].

Recently, Jih Shang *et al.* [61] fitted the whole temperature response of a heat-pulse calorimeter (PHC), i.e. heating cycle and thermal relaxation process, in order separate internal and external relaxation times. Thus the τ_2 problem is ravelled.

Often both ways are applied simultaneously, the on-line correction and a post-experiment correction and parameter-optimisation, respectively. Now, it is no problem,

to store all data of the temperature *vs.* time heating and relaxation curves of the sample, and eventually of the shield, also. After terminating the experiment, the $T(t)$ curves for each C_p data point can be inspected with regard to internal and external relaxation, thermal coupling etc., first and second order derivatives of $T(t)$ may reveal discontinuities in the losses as a function of time. Thus, the quality of the measured data can be critically judged, e.g. by evaluating the measured data with various thermal equilibrium times, and reliable correction may be performed [51].

Ultra-small sample measurements and mesoscopic techniques

The increasing trend of further miniaturisation of semiconductor devices into the sub-micrometer scale enhances also activities and requirements of low temperature calorimetry. Calorimetric sensors for µg samples at room temperature have been developed [62], however, we will refer here only to LTC.

Looking on modern sub-micrometer topographical methods, as Scanning Tunneling Microscope and Atomic Force Microscope, the calorimetrist should be aware that these technologies are now also applied in the research of thermal parameters, e.g. SThM, the Scanning Thermal Microscope. The author has recently reviewed the potential of the SThM in view of thermal measurements and calorimetry [63]. A first commercial instrument has come on the market [64]. The SThM technique may provide in future routine data on locally (nano-meter scale) and timely (nano-sec scale) highly resolved thermal parameters and effects, e.g. thermal resistance or heat capacity [65].

The most sensitive calorimeter using the AFM technology and based on the deflection of a bimetallic micromechanical sensor as a function of temperature demonstrated a sensitivity of <100 pW and may be able to detect a minimum energy of <100 fJ (femto-J) [66].

Recently, heat capacity measurements of Sn nanostructures using a thin film DSC with 0.2 nJ sensitivity were described by Lai *et al.* [67]. The authors studied the melting process of Sn films of different thickness down to 1 Å, formed via thermal evaporation, by combining two calorimeters in a differential measurement configuration.

One must be aware that in this mesoscopic range classical physics and chemistry may be no more valid and new phenomena may occur. An extrapolation of the thermal data to macroscopic scale is doubtful [63].

Beside of mesoscopic effects, classical calorimetry presumably ends with µg samples. Then TMC seems to be the best choice. Riou *et al.* [68] describe a very sensitive calorimeter based on TMC for measuring ca 10 µg samples. A polyphenylquinoxaline membrane suspended on a round copper disk offers a usable diameter of 0.6 mm and has an addenda heat capacity of 1.5 µJ K^{-1} at 100 K. The time constant of the sample holder is 5 ms and thus allows to work at 10 Hz with the 'ac-technique' using copper as thermometer. The absolute and relative accuracy are 0.1 and 10%, respectively, with a temperature resolution of a few µK. The micro-sample holder, the membrane stage has been described in detail. Equally, Marone and Payne [56]

built a TMC which uses a diode laser as the heater with frequency 0.2 to 50 Hz. The absence of a contact heater reduces the addenda. The calorimeter works from 5 K to room temperature and samples as small as 4 μg have been measured using a 12.5 μm type-E thermocouple as thermometer.

Summary and conclusions

Classical calorimetry originated more than hundred years ago. Since the time of Walter Nernst more and more sophisticated apparatus have been developed. Although progress seems to be slow, permanently new methods appear and this overview proofs again that in recent years the perfection and refined use of the different types of calorimeters even accelerated. Nevertheless, calorimetric measurements are not as simple as it appears: the removal of systematic errors, the avoidance of experimental artefacts and the careful calibration of the energy and temperature scale remain on top of the problems facing the calorimetrist [6, 39].

Also calorimetry is facing a 'mental' problem. Many of the actual experimentalists presumably do not really know how accurate their results are on the absolute or relative scale of uncertainty or which temperature scale (IPTS-68 or ITS-90) was used for calibration. Many error indications are lower than the accuracy of the calibration substances used. Only few reports talk about calibration whereas often preference is given to the description of comfortable programs and the presentation of coloured curves. It will remain a continuous challenge for calorimetrists to produce well-documented, accurately described data of high quality. It should be a duty to any thermoanalysts/calorimetrist to report his data according to the recommendation given in 'For better Thermal Analysis' [69].

What will the future bring – quo vadis calorimetry?

Still more preference will be given to the dynamic methods. High speed very small sample mass calorimetry, sample heating by laser, still higher resolution, specific heat spectroscopy and extension of sub-micrometer studies may be the next marks in progress for LTC. The commercialisation of LTC has just started and will most probably succeed. In addition, more sophisticated computer programs will compensate more and more the intrinsic imperfections of the different methods. The development should be faster with regard to LTC under extreme conditions, e.g. high pressure, thermometry in high magnetic fields, and the simplification of cryogenic environment of LTC. The most serious problem which will unfortunately continue to exist for some longer time, is the lack of more (beside of sapphire and copper) high-precision certified reference substances for calibration and their commercial distribution. For this reason, the revival of the classical high-precision (<0.2%) calorimetry will move in future more and more into the centre of interest.

* * *

Thanks are given to the technical staff and many scientific co-workers and guest scientists of the Low Temperature Laboratory who contributed by their work to the improvement of our heat capacity installations and who performed many experiments. Particular thank is given to Dr. W. Schnelle and the technical help by K. Ripka.

References

1 E. Gmelin, Thermochim. Acta, 29 (1979) 1.
2 E. Gmelin, Thermochim. Acta, 110 (1987) 183.
3 G. R. Stewart, Rev. Sci. Instrum., 54 (1983) 1.
4 M. Sorai, K. Kaji and Y. Kaneko, J. Chem. Thermodyn., 24 (1992) 167; T. Matsuo and H. Suga, Thermochim. Acta, 88 (1985) 149.
5 F. Gronvold, J. Chem. Thermodyn., 25 (1993) 25.
6 I. Wadsö, Thermochim. Acta, 300 (1997) 1.
7 E. Gmelin, Thermochim. Acta, 304/305 (1997) 1.
8 A. Eucken, Z. Phys., 10 (1909) 586; W. Nernst, Sitzb. Kgl. Preuss. Akad. Wiss., 12 (1910) 261.
9 E. F. Westrum, Jr., G. Furukawa and J. P. McCullough, in Experimental Thermodynamics, Vol. I, ed. J. P. McCullough and D. W. Scott, Butterworths, London 1968, p. 133.
10 The lower temperature limit for the commercially available DSC and TMDSC equipment, offered by the companies well known among thermoanalysts – Linseis, Mettler, Netzsch, Perkin-Elmer, Seiko, Setaram, TA-Instruments – is around 100 K. A commercial low temperature calorimeter working, according to the pulse-heat (relaxation time) method, down to and below 4 K is now offered by Oxford Instruments, Oxon OX8 1TL/England.
11 D. A. Ditmars, S. Ishihara, S. S. Chang, G. Bernstein and E. West, J. Res. Natl. Bur. Stands., 87 (1982) 159.
12 D. L. Martin, Rev. Sci. Instrum., 58 (1987) 639.
13 R. Bachmann, F. J. di Salvo and T. H. Geballe et al., Rev. Sci. Instrum., 43 (1972) 205.
14 P. F. Sullivan and G. Seidel, Phys. Rev., 173 (1968) 679; J. E. Graebner, Rev. Sci. Instrum., 60 (1989) 1123.
15 A. Junod, J. Phys. E: Sci. Instrum., 12 (1979) 945.
16 M. Rajeswari and A. K. Raychaudhuri, Europhys. Lett., 10 (1989) 153.
17 S. Riegel and G. Weber, J. Phys. E: Sci. Instrum., 19 (1986) 790.
18 M. Lysak, P. Day, M. LaMadrid and D. Goostein, Rev. Sci. Instrum., 63 (1992) 5750.
19 W. Schnelle and E. Gmelin, Thermochim. Acta, 269/270 (1995) 27.
20 J. W. Loram, J. Phys. E: Sci. Instrum., 16 (1983) 367.
21 E. Gmelin and P. Rödhammer, J. Phys. E: Sci. Instrum., 14 (1981) 223.
22 E. Gmelin and K. Ripka, Cryogenics, 21 (1981) 117.
23 M. Reading, D. Eliott and V. L. Hill, J. Thermal Anal., 40 (1993) 949.
24 Y. H. Jeong, Thermochim. Acta, 304/305 (1997).
25 I. K. Moon, Y. H. Jeong and S. I. Kwun, Rev. Sci. Instrum., 67 (1996) 29; D. H. Jung, T. W. Kwon, D. J. Base, I. K. Moon and Y. H. Yeong, Meas. Sci. Technol., 3 (1992) 475.
26 J. C. van Miltenburg, G. J. K. van den Berg and M. J. van Bommel, J. Chem. Thermodyn., 19 (1987) 1129.
27 K. Saito, T. Atake and H. Chihara, J. Chem. Thermodyn., 19 (1987) 633.
28 W. Hemminger und G. Höhne, Grundlagen der Kalorimetrie, Verlag Chemie, Weinheim 1979.
29 J. Rouquerol and W. Zielenkiewicz, Thermochim. Acta, 109 (1986) 121.
30 U. Rahm and E. Gmelin, J. Thermal. Anal., 38 (1992) 335.
31 J. F. Cochran, C. A. Schiffman and J. E. Neighbor, Rev. Sci. Instrum., 37 (1966) 499.
32 T. Asworth and H. Steeple, Cryogenics, 8 (1968) 225.
33 J. Pinel and C. Lebau, J. Phys. E.: Sci. Instrum., 5 (1972) 688.
34 R. Lagnier, J. Pierre and M. J. Mortimer, Cryogenics, 17 (1977) 349.
35 M. Regelsberger, R. Wernhardt and M. Rosenberg, J. Phys. E: Sci. Instrum., 19 (1986) 525.
36 J. P. Shepherd, Rev. Sci. Instrum., 54 (1985) 273.
37 G. W. H. Höhne, W. Hemminger and H.-J. Flammersheim, Differential Scanning Calorimetry, Springer, Berlin 1996.

38 B. Wunderlich, Thermochim. Acta, 300 (1997), and further refs therein; B. Wunderlich, J. Thermal Anal., 48 (1997) 207; J. E. K. Schawe, Thermochim. Acta, 271 (1996) 127, and further refs therein
39 E. Gmelin and S. Sarge, J. Appl. Chem., 67 (1995) 1789.
40 S. M. Sarge, W. Hemminger, E. Gmelin et al., J. Thermal Anal., 49 (1997) 1125.
41 I. Hatta, Thermochim. Acta, 300 (1997) 7.
42 A. Schilling and O. Jeandupeux, Phys. Rev. B, 52 (1995) 9514.
43 F. Fominaya, J. Chaussy and P. Gandit, Rev. Sci. Instrum., 69 (1998) 168; and Rev. Sci. Instrum., 68 (1997) 4191.
44 R. Geer, T. Stoebe, T. Pitchford and C.C. Huang, Rev. Sci. Instrum., 62 (1991) 415.
45 J. F. Jurado, E. Ortiz and R. A. Vargas, Meas. Sci. Technol., 8 (1997) 1151.
46 Y. P. Handa, R. E. Hawkins and J. J. Murray, J. Chem. Thermodyn., 16 (1984) 623.
47 I. Tsukushi, O. Yamamuro, K. Sadanami, M. Nishizawa, T. Matsuo and K. Takeda, Rev. Sci. Instrum., 69 (1998) 179.
48 S.Takahara, O. Yamamuro, M. Ishikawa, T. Matsuo and H. Suga, Rev. Sci. Instrum., 69 (1998) 185.
49 A. Junod, E. Bonjour, R. Calemczuk, J. Y. Henry, J. Muller, G. Triscone and J. C. Vallier, Physica C, 211 (1993) 304.
50 J. P. C. Klaase, Rev. Sci. Instrum., 68 (1997) 89.
51 S. Uma, W. Schnelle and E. Gmelin, private communication.
52 J. Thoen, E. Bloemen, H. Marijnissen and W. van Dael, Proc. 8th Sympos. of Thermophys. Properties, ed. J. V. Sengers, ASME, New York 1982; and J. Thoen, Int. J. Mod. Phys. B, 9 (1995) 2157.
53 G. Pitsi, J. Caerels and J. Thoen, Phys. Rev. B, 55 (1997) 915.
54 H. Yao, K. Ema and C. W. Garland, Rev. Sci. Instrum., 69 (1998) 172.
55 N. J. Garfield, M. A. Howson and N. Overend, Rev. Sci. Instrum., 69 (1998) 2045.
56 M. Marone and J. E. Payne, Rev. Sci. Instrum., 68 (1997) 4516.
57 S. Matsuo, Thermochim. Acta, 125 (1988) 307.
58 S. B. Ota and E. Gmelin, Meas. Sci. Technol., 3 (1992) 1047.
59 V. K. Pecharsky, J. O. Moorman and K. A. Gschneidner, Rev. Sci. Instrum., 68 (1997) 4196.
60 Deepak Varandani, A. K. Bandyopadhyay, V. S. Yadav, E. Gmelin and A. V. Narlikar, Meas. Sci. Technol., 7 (1996) 511.
61 J. Shang Hwang, K. Jan Lin and Cheng Tien, Rev. Sci. Instrum., 68 (1997) 94.
62 J. Lerchner, J. Seidel and G. Wolf, Sensors and Actuators B, 32 (1996) 71.
63 E. Gmelin, Thermochim. Acta, 310 (1998) 1.
64 A. Hammiche and H. Pollock, announcement by Topometrix Comp. in Application News Letter, 96-1 (1996) .
65 R. Forster and E. Gmelin, Rev. Sci. Instrum., 67 (1996) 4246.
66 J. R. Barnes, R. J. Stephenson, C. N. Woodburn et al., Rev. Sci. Instrum., 65 (1994) 3793.
67 S. L. Lai, A. G. Ramanath and I. H. Allen, Appl. Phys. Lett., 70 (1997) 43.
68 O. Riou, P. Gandit, M. Charalambous and J. Chaussy, Rev. Sci. Instrum., 68 (1997) 1501.
69 G. Lombardi, For better Thermal Analysis, 2nd ed., ICTA (Int. Confed. for Thermal Analysis), Rome 1980.
70 S. Uma, W. Schnelle, E. Gmelin et al., J. Phys.: Condens. Matter, 10 (1998) L33.
71 M. Foldeaki, W. Schnelle, E. Gmelin et al., J. Appl. Phys. 82 (1997) 309.