ELSEVIER

Thermochimica Acta 371 (2001) 19–22

thermochimica acta

www.elsevier.com/locate/tca

Toward a standard nomenclature for calorimetry

Lee D. Hansen*

Department of Chemistry and Biochemistry, Brigham Young University, Provo, UT 84602, USA

Received 22 August 2000; accepted 18 December 2000

Abstract

A systematic nomenclature for describing calorimeters is proposed. The instrument name and description must include four parts: the method of heat measurement, a description of the temperature control of the surroundings, a description of the means of initiating the heat effect, and a description of the operation of the calorimeter including data analysis. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Calorimeter; Calorimetry; Heat measurement; Nomenclature

1. Introduction

The nomenclature of calorimetry is sorely in need of being standardized and better defined. The proliferation of commercially available calorimeters over the last 30+ years has spawned a list of names and acronyms that are imprecise, uninformative, and often misleading. A particularly egregious example is the use of "isothermal differential scanning calorimeter (DSC)" to describe isothermal operation of an instrument more commonly used in a temperature scanning mode. Common names are often based on application rather than a description of the calorimeter, e.g., "bioactivity monitor" and "ITC, isothermal titration calorimeter". Authors have frequently used names based on the method of initiation (e.g., titration calorimetry, scanning calorimetry) or on the surroundings (e.g., isoperibol) or means for correcting for extraneous heat effects (e.g., twin, differential, adiabatic). Least common are names based on the method of heat measurement. As an illustration of the problem posed by current nomenclature practice, the following list of names for calorimeters was obtained from the contents page of Thermochimica Acta 337 (1999) v–vi, a special issue on developments in calorimetry: levitation melting calorimetry, IC-calorimeter, flow-calorimetry, water absorbed dose calorimeter, microcalorimetry, DSC analysis, TMDSC, high temperature calorimetry, and nanocalorimetry. No one person could be expected to make sense of all of these terms and acronyms. Names based on features other than the method of heat measurement give little insight into how the instrument functions as a calorimeter. The nomenclature appearing in current literature will likely have no meaning to readers 20 or 30 years from now. Just as common names for chemicals, which were based on source, properties, or applications have been displaced by IUPAC sanctioned names that provide structural information, common names for calorimeters and calorimetric procedures and applications need to be replaced or supplemented by a systematic nomenclature that provides precise, clear information about a calorimetric instrument and its operation. Just as with chemical nomenclature, common names for calorimeters will probably never

---

* Tel.: +1-801-378-2040; fax: +1-801-378-5474.
E-mail address: lee_hansen@byu.edu (L.D. Hansen).

PII: S0040-6031(01)00422-1

disappear, but authors should be required to supply a description constructed with standardized nomenclature.

2. Method of heat measurement

The foremost function of a calorimeter is the measurement of heat energy, and thus the means for heat measurement must be part of the description, probably the first part of the description. Only two principles upon which heat measurement can be based are known, i.e. (a) the law of conservation of energy and (b) Newton's law for the rate of heat transfer. The law of conservation of energy is the basis for heat measurement in two distinct types of calorimeters, i.e., compensation and temperature change. In the compensation type, the heat from the test process is exactly balanced by heat from a phase change or electrical circuit, with the amount of phase change or electrical power being the actual measured variable. The suggested names for such calorimeters are, respectively, "phase change compensation" and "power compensation" calorimeters. The second type of calorimetry derived from the law of conservation of energy uses temperature change as the measured variable, usually in a near-adiabatic system. To a first approximation the amount of heat is then calculated as the product of the temperature change and an apparent heat capacity of the system. Thereafter various corrections are applied to correct for non-adiabaticity. The name suggested by the method is temperature-change calorimetry. Calorimeters based on Newton's law of heat transfer should be designated as "heat conduction" calorimeters. The use of the terms "micro-" and "nano-" calorimeter to designate instruments that, respectively, measure heat effects in the microwatt and nanowatt range should be discouraged because the terminology is misleading [1] and often misunderstood as referring to the sample volume. Further, it is not clear how the terms should be applied to calorimeters that measure a total heat effect.

3. Surroundings

The second item that must be considered to understand the operation of a calorimeter is the surroundings, i.e., the reaction vessel and contents constitute the system and everything outside the reaction vessel constitutes the surroundings in the thermodynamic meaning of the terms. The surroundings are always temperature controlled in some fashion, either at a constant temperature, at a variable temperature referenced to the sample temperature, or so as to minimize the temperature difference between the system and surroundings, otherwise the calorimetric measurement cannot be reproduced. "Isothermal" and "adiabatic" have been used to refer to the first and last of these control modes. While the terms are accurate, they have frequently been misused, i.e., power compensation calorimeters are commonly referred to as isothermal (meaning the method of heat measurement) calorimeters, while the term adiabatic calorimeter has been used to describe the mode of temperature control of the surroundings. The term isoperibol, which literally means constant surroundings and includes both temperature and pressure, has been used to describe the surroundings of both temperature change and heat conduction calorimeters. The term pseudo-adiabatic has been used to describe the operation of temperature-change calorimeters in isothermal surroundings because such calorimeters are usually designed to minimize heat transfer between the system and surroundings. However, the terms "isothermal surroundings" or "adiabatic surroundings" are suggested as being more accurate and descriptive. Other modes of control need to be described in sufficient detail to allow someone skilled in the art to reproduce the conditions.

4. Initiation of the effect to be measured

The third item to be specified in a calorimeter description or name is the means by which the measured effect is initiated. There are only three fundamental and independent ways of initiating the effect to be measured, i.e., by changing the temperature, by changing pressure or volume, or by changing the composition of the system. Changing temperature continuously gives rise to the methods commonly known by their acronyms DSC and DTA. Changing temperature in small increments is the basis for other methods for determination of heats of phase changes and heat capacities. Changing the volume of a system by changing the pressure exerted on the sample is the basis of a method developed by Randzio [2] for calorimetric determination of pVT and thermodynamic properties of materials. Changing the composition of the system can be done by changing the pressure of a reactive gas in contact with the sample (e.g., changing the water vapor pressure over a hygroscopic material or by changing the vapor pressure of a volatile component of the system), by injection of a reactant from outside the system or by moving or removing a boundary between reactants (e.g., by continuous or incremental titration, or by injection of a solid into a solution), by the introduction of light or a catalyst, or simply by inserting the sample into the measuring vessel. This list is certainly not complete, but illustrative.

The names suggested for these various initiation methods are ‘‘temperature scanning (continuous or incremental)’’, ‘‘pressure/volume scanning (continuous or incremental)’’ to refer to methods in which the pressure on the system is changed to induce a volume change, ‘‘pressure scanning (continuous or incremental)’’ to refer to methods in which the pressure of a reactant is changed, ‘‘titration (continuous or incremental) from inside or outside the system’’, ‘‘flow’’ for calorimeters in which both reactants or one material (in the case of heat capacity determinations) enters and exits the reaction vessel continuously, ‘‘photochemical calorimetry’’, and ‘‘sample insertion’’, for the above examples of methods, respectively.

5. Operation

How the calorimeter was actually operated can be included as a fourth item in the name or may be given as additional descriptive material, but must be included. Descriptive terms such as ‘‘twin’’ or ‘‘differential’’ are appropriate to use because they assist in understanding how corrections for extraneous heat effects and instrument baseline are made. Many current instruments can be operated in more than one way [3], e.g., operation of a temperature scanning instrument at constant temperature. Readers should not be assumed to know what either the ‘‘normal’’ mode or the alternative mode is without being told what was actually done. Pressure and volume conditions must also be specified. If no volume change occurs in the system, the measured heat is equal to the total energy change. If the system operates at constant pressure either because the reaction vessel is open to the atmosphere or because the pressure is controlled by a back-pressure regulator or some other device, then the heat measured is equal to the enthalpy change. The description of the calorimeter should clearly state whether it operates at constant pressure or constant volume, and thus measures H and C_p or U and C_V.

6. Summary

The terminology listed above and summarized in Table 1 is a practical means for describing a calori-

Table 1
Standard nomenclature for calorimeters

Heat measurement method
- Phase change compensation
- Power compensation
- Temperature change
- Heat conduction

Surroundings

Temperature control
- Isothermal surroundings
- Adiabatic surroundings
- Other

Initiation of measured effect

By changing the temperature
- Continuous temperature scanning
- Incremental temperature scanning

By changing the pressure or volume of the system
- Continuous pressure/volume scanning
- Incremental pressure/volume scanning

By changing the composition of the system
- Continuous pressure scanning
- Incremental pressure scanning
- Continuous titration
- Incremental titration
- Solid, liquid, or gas injection
- Flow
- Photochemical
- Catalyst injection
- Sample insertion
- Other

Operation
- Constant pressure
- Constant volume
- Twin or differential
- Mode of operation
- Data analysis

meter and its operation. The use of these terms will increase understanding for authors, reviewers, and readers. Current manuscripts too frequently contain too little descriptive information about a calorimeter to judge whether or not data analysis has been done appropriately. Authors too often depend on canned programs supplied with a commercial instrument without the necessary depth of understanding required to judge the results from and limitations of these programs. Requiring authors to describe a calorimeter beyond just giving the manufacturer and model number would at least ensure a minimal understanding of the instrument. This requirement would also solve the problem of readers who wish to use the literature after the manufacturer no longer supplies data for a particular instrument.

Continuing efforts by IUPAC committees to establish an acceptable nomenclature for calorimeters should include equal numbers of committee members drawn from the fields of thermal analysis and calorimetry. Temperature scanning methods should not be overemphasized simply because they have the largest number of practitioners. Instead, committee composition should reflect the wide range of instruments and techniques that must be considered in developing a standard nomenclature. In this light, the present paper is an attempt to reflect and expand on earlier papers on calorimetric nomenclature ([3,4] and references therein) which, like this paper, are admittedly still works in progress.

The recommendation of this paper is that authors are required to describe all four aspects of any calorimeter used in a study in the terms listed in Table 1 in addition to giving manufacturer and model. Data analysis procedures are also need to be described, not just referenced to a canned program. These descriptions need to add only three or four sentences to a manuscript, but will greatly increase the value of the work, both short and long term. To quote an informal review of an early draft of this paper "it is absolutely necessary that there should be sufficient detail in a paper to allow for possible reinterpretation in the light of future developments, to understand how to repeat an experiment, to understand how to extend an approach and, crucially to know how reliable a measurement is. All these demand clarity of expression and precise information. I wonder who, and on what grounds, could object to this" [5].

References

[1] L.D. Hansen, Pharmaceutical Technol. 20 (1996) 64–74.

[2] S.L. Randzio, Recent developments in calorimetry, Section C, Vol. 94, The Royal Society of Chemistry Annual Reports, 1998, pp. 433–504.

[3] W. Hemminger, S.M. Sarge, in: M.E. Brown (Ed.), Handbook of Thermal Analysis and Calorimetry — Definitions, Classifications and Nomenclature, Vol. 1, Elsevier, Amsterdam, 1998.

[4] W. Hemminger, F.W. Wilburn, P.C. Gravelle, B.O. Haglund, P.J. Hianes, G. Hakvoort, M. Odlyha, J. Simon, S.M. Sarge, Recommendations for names and definitions in thermal analysis and calorimetry, ICTAC News, December 1998, pp. 107–122.

[5] A.E. Beezer, Personal communication 1999.