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Which calorimeter is best? A guide for choosing the best calorimeter for a given task

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Abstract

Most scientists are not knowledgeable about calorimetry. The purpose of this paper is to assist the novice in calorimetry to select the best calorimeter commercially available for their task. The primary literature is a poor guide for instrument selection. Instrument developments in calorimetry are usually not reported in primary literature and calorimetric measurements are usually done with the calorimeter that is available, not the best instrument for the measurement. A procedure for choosing the best calorimeter for a given task is described.

Keywords: Calorimetry; Calorimeter; Heat measurement; Enthalpy

1. Introduction

The purpose of this paper is to assist the novice in calorimetry to select the best calorimeter commercially available for their task. The community of calorimetrists has not communicated their science in a way that people from outside the field can appreciate and use the information. People outside the calorimetry community are largely unaware of the many applications of calorimetry besides determination of enthalpy changes. No single source adequately describes the many applications or current capabilities of calorimeters. A basic oxygen bomb calorimeter and a Styrofoam™ cup with a thermometer are the icons of calorimetry in the minds of most people. Applications of calorimetry to kinetics, metabolism, determination of equilibrium constants, stability and compatibility of materials, electrochemistry, chemical analyses, reaction identification, and hazard analysis are not widely known or appreciated. Nor is the detection limit of a few nanowatts which makes possible the prediction of shelf-lives of centuries from a few hours of measurements or the detection of reactions of micrograms of material.

Because instrument development is nearly all done by manufacturers, these developments are often not reported in the primary literature. And, if they are published, it is often in journals that are not commonly read by potential users. Recent books on calorimetry are either too basic or too specific and physical chemistry textbooks include only the basics of traditional applications. Recent years have seen a decline in the US Calorimetry Conference because the organization remains focused on the use of calorimetry to determine thermodynamic properties of clean, chemically well-defined systems whereas current uses of calorimetry are primarily on complex, often poorly defined, systems, and the most common use is probably kinetics, not thermodynamics.

Given the lack of knowledge of calorimetry by most scientists, another problem becomes apparent when a novice in calorimetry decides they need to use calorimetry in a particular application. When calorimeters were individually constructed and used in the laboratory where the calorimeter was built, the calorimeter was usually built for a specific purpose and the users thoroughly understood the capabilities and limitations of their instrument. Now, nearly all calorimeters are built and sold commercially, and users rarely have much knowledge of the instrumentation. People who want to do calorimetry typically can define the problem or system they want to study, but find it difficult to identify the best calorimeter for their task if it even occurs to them that they need to do so.

The literature is a poor guide for selecting the optimum calorimeter for a given task. Instead of using the optimum instrument, people use the calorimeter that is available, the one they have previously used or heard others have used, or they duplicate what was previously reported in the literature. Lack of a mean-

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ingful, consistent nomenclature for calorimeters and calorimetry compounds the problem. Books are often outdated by instrument developments made subsequent to the training of the authors and the authors are not knowledgeable about instruments other than the one they have used. The web is of little use to a novice, searching on key words such as calorimetry or calorimeter brings a long list of beginning chemistry experiments done with a thermometer and a coffee cup, not a particularly useful result. The problem is illustrated by questions frequently asked by potential customers of Calorimetry Sciences Corp: what is the best calorimeter for measuring *X* (where *X* may be a binding constant, reaction rate, enthalpy change, heat capacity, or some other property)? Calorimeter *Y* was used to measure *X*, is that the best calorimeter for that? Can you send me papers or references were a CSC calorimeter was used to measure *X*? These questions demonstrate that manufacturers are the de facto key to solving the problems of educating people about calorimetry and instrument selection.

2. Procedure

How should a person who is not an expert in calorimetry and not knowledgeable about the many different calorimeters that are commercially available select the best calorimeter for their task? The answer is given in the following as a four step process, written in the second person, and thus addressed, not to the expert in calorimetry, but to the person whose job it is to select the calorimeter.

First, specify as exactly as possible what it is you want to measure. This may seem to be obvious, but calorimetry has a multitude of uses. Calorimetry can be used to determine most thermodynamic properties; e.g. enthalpy changes for reactions (ΔH), for phase changes, for mixing, etc.; equilibrium constants and thus free energy changes for many reactions; heat capacities and coefficients of thermal expansion and compressibility; entropy and entropy changes. Calorimetry can also be used for qualitative and quantitative analyses. ΔH can often be determined for an unknown reaction in a complex system, and the value of ΔH can then be used to assist in identifying the reaction. Quantitative analyses is done by two methods, either by calorimetric titration or from the ratio of measured heat to ΔH for the reaction. In the analytical literature, the former method is called thermometric titration and the latter method, direct injection enthalpimetry. The same principle used in enthalpimetry is used in thermal analysis with temperature-scanning calorimeters, i.e. where ΔH is the enthalpy change of the process initiated by the temperature change. Because calorimetry directly measures the instantaneous rate of the process, calorimetry is a particularly advantageous method for determination of the kinetics of slow processes, i.e. with half-life of minutes to centuries. Calorimetry eliminates the difficulty of measuring the slow accumulation of products.

Table 1
Variables of calorimetric measurements

Property to be measured
Isothermal or temperature-scanning
Temperature range
Pressure range
Reactant and product phases, i.e. solid, liquid, or gas and vapor pressure
Estimated total heat per unit of reaction, i.e. ΔH for the reaction
Estimated rate of heat production, i.e. reaction rate times ΔH. Maximum and minimum. (This may depend on rate of reaction, or on the rate of addition of reagents, and may limit the temperature scan rate.)
Sample availability (μg, mg, g, or kg)
Desired sample size (because of inhomogeneity or cost)
Sample properties, e.g. viscosity, hygroscopicity, toxicity, pathogenicity, live cells or tissue, etc.
Expected number of experiments per day

Second, determine how you are going to use this property of the system. Analysis of thermodynamic and kinetic data from calorimetry always involves a model for the system, e.g. a set of chemical reactions, kinetic equations, or a theoretical model for the property as a function of temperature, pressure, or composition. Calorimetric data will be fitted to the model to obtain model parameters, and thus provide a description of the system as a function of the experimental variables. Calorimetric data can also be used to test the predictive power of such models, and thus to gain fundamental insight into a process or property of a material, or to predict failure or hazardous conditions. Such models may require collection of ancillary data simultaneously with the calorimetric measurements. Probes may be available to make the ancillary measurements in the calorimetric vessel simultaneously with the calorimetric measurement.

Third, you need to specify the list of parameters in Table 1 as completely and exactly as possible.

Lastly, communicate a summary of the above three items to several calorimeter manufacturers, and ask for their recommendation of an instrument, including a price. The scientists at these companies can often be very helpful. For example, the policy of Calorimetry Sciences Corporation is to help the customer find the best calorimeter for their task, even if it is made by another company. But, keep in mind that the people at a company may not be knowledgeable about all instruments and that they do represent the interests of a particular company and viewpoint. Thus, it is advisable to contact as many companies as possible. Companies appreciate such enquiries. Following the above procedure will increase your knowledge about calorimetry and should lead you to the calorimeter best suited for your application and budget.