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Temperature oscillation calorimetry for the determination of the heat capacity in a small-scale reactor

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ABSTRACT

This contribution describes a method for heat capacity determination in a small-scale reaction calorimeter under quasi-isothermal conditions ($\pm 0.16\,^\circ$C to $\pm 0.77\,^\circ$C). The heat capacity of the reactor content is calculated from the amplitudes and the phase shifts of the reactor temperature, of the electrical heater and of the cooling rate when forced temperature oscillations are applied. The heat capacities of eight solvents (water, ethanol, methanol, acetone, 1-octanol, diethylenglycol, toluene, and 1-butanol) covering a wide range of viscosity were calculated for various experimental conditions, including reactor volume and stirrer speed. Systematic deviations were detected when compared to the corresponding literature values. Straight line calibration with the total heat transfer coefficient and two modern multivariate calibration techniques (partial least squares and neural network) were applied to correct for these deviations. The different calibrations show similar precision and allow for an online determination of the heat capacity with an accuracy comparable to other published methods. Successful applications include the determination of the heat capacities for *n*-heptane, for various homogenous ethanol/water mixtures, and during the course of the hydrolysis of concentrated sulfuric acid.

1. Introduction

During early stages of process development chemical industry needs flexible and versatile tools to assess information about chemical reaction systems. Over the years, reaction calorimeters have become essential devices for data oriented research and development in chemical engineering. They are commonly used for the optimisation of a chemical process considering economic factors and safety assessment (Westerterp and Molga, 2006). They are also applied to elucidate reaction mechanisms and associated activation energies, rate constants, and heat of reaction (Puxty et al., 2006).

Laboratory reaction calorimeters typically consist of a double-wall reaction vessel with a volume ranging from 0.1 to 10 l, and a circulating cooling medium that removes the heat from the reactor. Three different operational modes can be distinguished by their way controlling the reaction temperature: the *adiabatic mode* where heat flux to the surrounding is prevented, the *isoperibolic mode* where the surrounding is kept at a constant temperature, and the *isothermal mode* where the reactor temperature is kept constant. Several publications are dedicated to the principles and the development of different reaction calorimeters that are commercially available (Landau, 1996; Regenass, 1997).

The classical equation in reaction calorimetry is the global heat balance of the reactor and its perfectly mixed content,

$$\dot{q}_{\mathrm{acc}} = \dot{q}_{\mathrm{react}} + \dot{q}_{\mathrm{heater}} + \dot{q}_{\mathrm{stirr}} + \dot{q}_{\mathrm{dos}} - \dot{q}_{\mathrm{cool}} - \dot{q}_{\mathrm{loss}} \quad (1)$$

where $\dot{q}_{\mathrm{acc}}$ is the total heat accumulation in the reactor [W], $\dot{q}_{\mathrm{heater}}$ is the power provided by the electrical heater [W], and $\dot{q}_{\mathrm{cool}}$ is the heat flow out of the reactor due to cooling [W]. The heat, $\dot{q}_{\mathrm{stirr}}$, dissipated from the stirrer is calculated online with a torque measurement. The heat, $\dot{q}_{\mathrm{dos}}$, due to the dosing of the reactant is a function of the feed rate, the specific heat capacity of the dosed liquid and the temperature difference between the dosed liquid and the reactor. The heat loss from the reactor to the environment, $\dot{q}_{\mathrm{loss}}$, is calibrated at steady-state. The heat liberated during the course of the chemical reaction, $\dot{q}_{\mathrm{react}}$, contains information related to the reaction rate and the reaction enthalpy. Depending on operational mode and measurement principle, e.g. in heat-flow, heat-balance, or power-compensation calorimetry, some terms in Eq. (1) can be neglected (Zogg et al., 2004).

The temperature rise and the corresponding accumulated heat in the reactor are directly related to the specific heat capacity of the reactor content.

$$\dot{q}_{\mathrm{acc}} = m \cdot c_p \frac{\mathrm{d}T}{\mathrm{d}t} \quad (2)$$

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Table 1
Overview of common calorimeters used to determine heat capacities[a]

	Sample size, ml	Dosing	Stirring	Working principle	Applications	Accuracy in c_p, %
Picker	30[b]	n.a.	n.a.	Fluid flow, differential	c_p of liquids	<0.5[b,c], <2[d]
ADC	60[e], 0.6[f]	Yes	Yes	Adiabatic, heat accumulation	c_p of solids and liquids, heat of reaction and mixing	<1[g], 0.3[e], 0.5[f]
DSC	0.05[h,i]	No	No	Heat-flow, differential	Thermal behavior and c_p of solids, heat of reaction and decomposition	3–10[g], 1–5[j]
TM-DSC	0.05[h,i]	No	No	Heat-flow, power compensation, differential	Thermal behavior and c_p of solids, thermal diffusivity	0.5–5[j]
DRC	100–500[h]	Yes	Yes	Isoperibolic, heat accumulation, differential	simulation of industrial reaction, heat of reaction and mixing, heat transfer coefficient	7[k]
DC	5[h], 1[l]	n.a.	Yes	Heat accumulation, differential	c_p of liquids and solids, heat of mixing	3–5[g], 0.1[l]
Calvet	12.5[h], 1[m]	Yes[n]	Yes[n]	Heat conduction, differential	c_p of solids and liquids, heat of reaction, mixing, and decomposition	0.5[o], <0.2[m,p]
RC	200–2000[q]	Yes	Yes	Heat-flow	Simulation of industrial reaction, heat of reaction and mixing, heat transfer coefficient	10[r]

ADC, adiabatic calorimeter; DSC, differential scanning calorimeter; TM-DSC, temperature-modulated differential scanning calorimeter; DRC, differential reaction calorimeter; DC, drop calorimeter; RC, reaction calorimeter; n.a., not applicable.

[a] The values reported here correspond to the actual specifications given by the manufacturers and from relevant literature.

[b] Picker et al. (1971).

[c] Fortier et al. (1976).

[d] Hovorka et al. (1999).

[e] Messerly et al. (1990).

[f] van Miltenburg et al. (2002).

[g] Warrington and Höhne (2007).

[h] www.setaram.com.

[i] www.perkinelmer.com.

[j] Gmelin (1997).

[k] André et al. (2003).

[l] Suurkuus and Wadso (1974).

[m] Cerdeiriña et al. (2000).

[n] Special cells are needed. Dosing and stirring at the same time is not possible.

[o] Becker et al. (2000).

[p] Gonzalez-Salgado et al. (2007).

[q] www.mettlertoledo.com.

[r] Nogent and Le Tacon (2003).

The specific heat capacity c_p, or in short, specific heat, is a thermo-physical property defined by the heat per unit mass required to increase the temperature of a material by one degree celsius, as shown in Eq. (2). Knowledge of c_p is required for the scale-up, reactor design and safety assessment of many chemical engineering and pharmaceutical processes (Pastré et al., 2000). Specific heat capacities have been determined experimentally by calorimetry for decades with numerous techniques (Maglic et al., 1984; Marsh and O'Hare, 1994; Warrington and Höhne, 2007). A classical procedure involves raising the temperature of a sample at a defined rate. The most common instruments used are the Picker fluid flow calorimeter, the drop calorimeter, the differential scanning calorimeter and the adiabatic calorimeter. An overview is given in Table 1.

In reaction calorimeters, temperature oscillation calorimetry (TOC) allows the simultaneous determination of the global heat transfer coefficient UA and the heat capacity c_p throughout a reaction without any mathematical interpolation (Tietze, 1998). Only few studies focused on the c_p determination by TOC because reactions are usually performed under isothermal conditions. Moreover, the use of a pre-calibrated value of c_p is often preferred because the algorithms for UA determination with TOC are more robust and less sensitive to noise when compared to the simultaneous calculation of c_p and UA (Guerrini De Luca and Scali, 2002). Nevertheless, Tietze (1998) observed a systematic error in the determination of the c_p for water and for acetic acid ester compared to literature values. Also, Bou-Diab et al. (2001) found that the viscosity had an influence on the determination of c_p. The determination of c_p by TOC was extensively studied with MT-DSC (modulated-temperature differential scanning calorimetry). Among others applications, it is used for the investigation of glass transition in polymers that leads to slight changes in heat capacity (Kraftmakher, 2004). The problem of a systematic deviation in c_p was also recognized with MT-DSC (Lacey et al., 2006). Hatta and Katayama (1998) suggested a linear calibration based on the thermo-physical properties of the MT-DSC apparatus. Also, a frequency-corrected heat capacity with a calibration function was proposed that accounts for the dynamic behaviour of the sample (Androsch, 2000).

To our knowledge, no systematic calibration procedure has been suggested for the determination of c_p by TOC within a reaction calorimeter. The aim of the present work is the development of a method for the c_p determination by oscillation reaction calorimetry. First, the possibility to run a small-scale reaction calorimeter under temperature oscillation conditions is demonstrated. Then, the influence of various experimental conditions, including medium, stirrer speed or volume, on the determination of c_p are investigated. Three calibration techniques are tested to improve the prediction of c_p. Finally, the technique is applied to determine c_p of homogenous mixtures and reactive media. In this work, the TOC method was developed for a small-scale reaction calorimeter that combined the principles of power-compensation and heat-balance (Visentin et al., 2004).