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# INTRODUCTION OF A CALIBRATION-FREE REACTION CALORIMETER THAT COMBINES THE BENEFITS OF DSCS AND REACTION CALORIMETERS

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The reaction calorimeter CPA202 (chemical process analyzer) determines thermal effects by measuring the true heat flow (THF) based on unique design principles. In particular, measurements can be performed without requiring any calibration procedures and the obtained results are most reliable and exhibit extremely stable baselines. The benefits in respect of experimental speed, data quality and long term performance are obvious. Due its broad dynamic range the instrument can be employed for measurements ranging from small physical heat to energetic chemical reactions. The CPA allows running experiments seamlessly with reaction volumes between 10 and 180 mL. This volume flexibility simplifies the investigation of multi-step operations and is the basis for various applications employing precious or highly energetic compounds. Due to the fact that calibrations are not required, altering conditions during a single experiment like changes in viscosities, liquid levels or stirring speeds do not affect the results of the measurements.

***Keywords:*** *calibration free, crystallization, reaction calorimeter, reaction kinetics, reflux condenser, true heat flow*

## Introduction

Since almost any physical transitions and chemical processes are accompanied by heat effects, calorimetry is the most universal method to investigate corresponding processes. Especially DSCs have become a routine tool for investigations in solid matter such as glass transitions, crystallization processes or curing reactions [1, 2]. DSCs are also employed for chemical process safety evaluations. However the fact that chemical reactions are frequently performed in liquid solutions is limiting the value of DSC for this type of applications.

Reaction calorimeters (RC), on the other hand, are rather employed for liquid phase reactions, especially, if issues are involved which require more space and scaling-up features. Traditionally, RCs have volumes of one to two litres and allow the accommodation of dosing and sampling devices, additional sensors, stirring and pressurization. Routinely, RC is used for safety investigations [3]. However, nowadays the application range goes beyond and covers areas also in process development and process intensification. More generally, reaction calorimetry can be considered to be a complement to DSC because it can handle liquid phase processes very well and allow the installation of all kind of peripheral devices.

The most obvious reason why reaction calorimeters are not used as frequently for process characterizations as DSCs for materials characterizations is the challenging handling of conventional RCs. They require calibrations before and after each reaction and usually exhibit baseline shifts which make measurements less accurate. In conventional RCs calibrations are necessary because the calculated heat flow from the chemical reactions is only based on the measured temperature differences between the content of the reactor and its surrounding, the jacket. Unfortunately, the heat flow to the surrounding is affected by almost any changing experimental condition like changes in liquid levels, viscosities or stirrer speeds, etc. Consequently, any new experimental situation requires a new calibration. We are introducing in this paper the chemical process analyzer CPA202, a truly calibration-free reaction calorimeter with a stable baseline. The design principle suppresses any un-controlled heat flows to the surrounding and makes the heat flow measurements therefore independent from any changes of the experimental conditions inside the reactor. The measured heat flow is called ‘true heat flow’ (THF). Table 1 summarizes a few characteristics of typical DSCs, conventional heat flow reaction calorimeters and the THF reaction calorimeter CPA202.

## Experimental

### *Instrument*

The principle of the ‘chemical process analyzer’ CPA202 is a reaction calorimeter that was originally

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**Table 1** Comparison of typical characteristics of DSC, conventional heat flow reaction calorimeters (RC) and the true heat flow reaction calorimeter CPA202

| Characteristics | DSC | Conventional RC | CPA202 |
|---|---|---|---|
| Size | milligrams | 1–2 L | 10–180 mL |
| Standard experiment | scanning | isoperibolic | isotherm |
| Handling | easy | challenging | easy |
| Calibration | occasionally | frequently | not required |
| Speed of test | fast | slow | fast |
| Scale-up potential | very limited | high | high |
| Dosing, sensors, etc. | no | yes | yes |
| Main application | solids | liquids | liquids |

developed by the Swedish company ChemiSens for polymer applications and the investigation of polymerisation reactions. For this, a design was required that tolerates dosing of liquids as well of gases and delivers highly reliable results even if viscosities and stirring rates are changing during the experiment.

Two reactors – one is for regular pressure applications and the other one for high pressure applications – are shown in Fig. 1. Both reactors can be filled continuously with volumes from 10 to 180 mL. Materials are typically glass, stainless steel, Hastelloy or Tantalum. The 13 L thermostat represents a thermally stable reactor environment and provides additionally an efficient safety layer. The reactors are made at least partially from metal, a fact that improves the thermal characteristics significantly and allows the connection of peripheral devices by using components that are widely used in fluid systems, e.g. Swagelok fittings. Different from most conventional reactors and also shown in Fig. 2, the reactors are not exposed to a jacket containing circulating thermostat liquid but are submersed completely – including the lid – into a thermostat bath which represents a huge heat capacity. The purpose of this thermostat bath is to act as the thermal reference for the reactor. In order to prohibit any un-controlled heat flows from the reactor to the thermostat bath, the temperature of this is always by active means kept on the same level as the reactor temperature. Even during fast heating or cooling up to 4 and 2 K min$^{-1}$, respectively, the temperature of the thermostat bath follows the reactor temperature. For the transportation of heat between the reactor content and the surrounding bath an active heat pump is required. A Peltier element integrated into the reactor base works as this active heat pump. When a current is supplied to the Peltier element, one side lowers its temperature and absorbs heat from the reactor while the other side increases its temperature and delivers the heat to the surrounding thermostat bath. For the measurement of endothermic effects the current to the Peltier element is reversed and the opposite situation occurs.

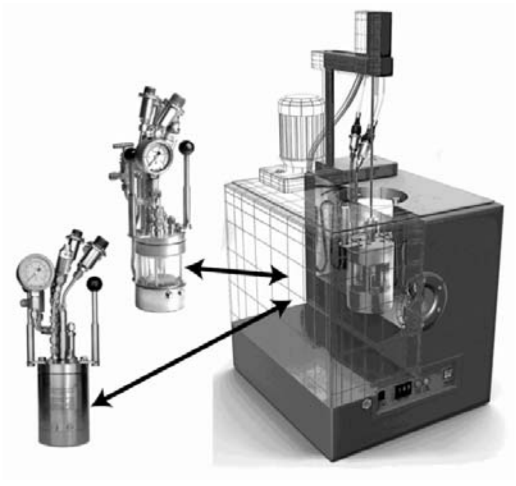

**Fig. 1** Full metal high pressure reactor (left), regular reactor made from glass and metal (behind) and thermostat (right) with stirrer motor and observation window

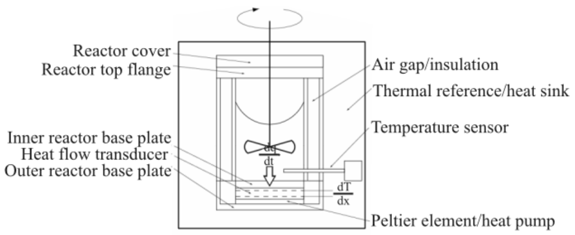

**Fig. 2** True heat flow (THF) principle: heat flows through wall and lid are suppressed. Heat flows are only permitted through the bottom and are measured by a heat flow transducer. A Peltier element is used as a heat pump

The temperature inside the reactor is measured by a Pt-100 sensor. This signal is used to calculate the current, necessary for the Peltier element to keep the reactor temperature on its desired level. The heat flow between the reactor and the thermostat bath, caused by the heat pump effect of the Peltier element, is measured by a separate heat flow transducer. This transducer is also integrated into the reactor base and placed between the inner base plate and the Peltier element as il-

**Table 2** Specifications of the CPA202

| | | | |
|---|---|---|---|
| Dynamic range | 0.003 to 30 W | Thermal modes | Isotherm, isoperibolic, scanning, adiabatic |
| Cooling coil capacity | 200 W | | |
| Temperature range | –50 to 200°C | Power measurements | THF, total power, stirring power, test heater power, condensation power |
| Pressure range | Up to 100 bar | | |
| Baseline stability | 0.001 W | | |
| Number of ports | 8 | Control | Manual and automated |

lustrated in Fig. 2. The careful design of the reactor means that all heat exchange from the reactor to the thermostat bath must pass this heat flow transducer.

The true heat flow transducer utilizes the classical equation for the heat flow in solid material.

$$\mathrm{THF}=\mathrm{d}q/\mathrm{d}t=\lambda A\mathrm{d}T/\mathrm{d}x \quad (1)$$

THF is the calculated true heat flow, $\lambda$ is the specific heat flow conductivity of the transducer, $A$ is the always wetted base plate area equal to the transducer area and $\mathrm{d}T/\mathrm{d}x$ is the temperature gradient across the transducer. From the measured temperature difference $\Delta T$ across the transducer, THF can be calculated since the other parameters have stable and known values. These values are determined by factory calibration once and for all.

The equation illustrates that measurement of the THF is independent from any changes in the experimental conditions. The measurements are not restricted to exothermic processes but are applied to endothermic processes with reversed heat flows as well. Although such a THF reaction calorimeter is frequently run in the described isothermal mode, it can be run in other modes as well: the temperature scanning mode is frequently used for heat capacity measurements, the adiabatic mode can be used for studying of the self-heating processes and the isoperibolic mode is usually employed together with reflux condenser operations.

Table 2 gives an overview of some CPA202 specifications.

Different types of process related power signals are obtained and are available during the measurement. They may be used for calculations and control activities throughout the measurement [4]. The THF is the heat flow through the base plate. Since in the transition regions, i.e. at fast changes in the rate of reaction, significant amount of heat is accumulated in the reacting mass and inert parts, such as reactor base and inserts, an additional quantity, the total power accounts for this:

$$\text{Total power}=\mathrm{THF}+\sum C_{\mathrm{p,\ mass+inert}}\frac{\mathrm{d}T}{\mathrm{d}t} \quad (2)$$

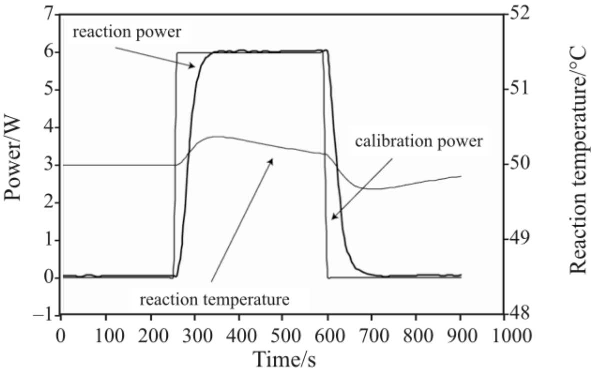

**Fig. 3** On-line total power measurement and calculation according to Eq. (2) when a defined, electrical power pulse is generated

A torque transducer measures directly the stirring power applied to the liquid, representing also a measure for changing viscosities. An electrical power heater allows the introduction of well defined amounts of electrical heat and can be used to verify the performance of the instrument from time to time.

Figure 3 shows such a test. The integration of the introduced electrical power gives 2039 J while the integration of the measured total power graph gives 2032 J. The accuracy is 99.66%. The time constant of the calorimeter can be determined from the declining total power graph and is approximately 20 s. The heat flow through the insulated cylinder wall and the reactor head space is below the instrumental resolution of 0.01 W.

## Results and discussion

The strengths of the CPA202 are the flexibility to deliver most reliable results in various application fields, the broad dynamic range and the relative small volume which makes it most suitable whenever hazardous or precious chemicals are involved. A selection of experiments will demonstrate these capabilities.

### *Two-phase reaction with changing stirring speeds and liquid levels*

The hydrolysis of ethyl acetate with sodium hydroxide is displayed in Fig. 4. Approximately 80 mL of

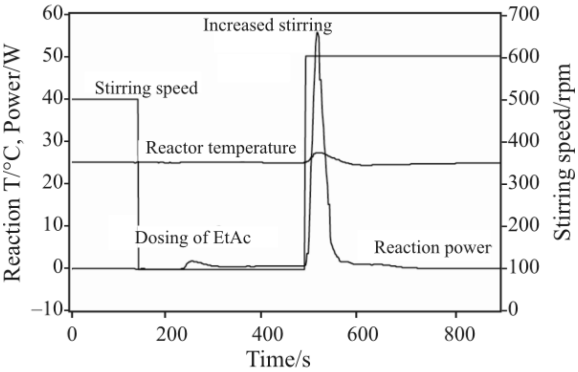

**Fig. 4** Hydrolysis of ethyl acetate in NaOH solution. Displayed are reaction power, reactor temperature (for both, scale on left *y*-axis) and stirring speed

an aqueous NaOH solution is present when the ethyl acetate is added. The dosing is indicated by a small heat effect in the heat flow curve, the reaction power, followed by a relatively small, continuous heat flow. The stirring speed is 100 rpm during dosing and later increased up to 600 rpm. This causes the two phases to mix and the two components eventually react with a maximum heat flow of about 55 W.

As pointed out before, the instrument is absolutely calibration free. Therefore, no calibrations are required throughout the experiment and the highly stable baseline returns to 0 W after the reaction has been finished. The small heat flow in the middle part is due to some reactivity at the phase boundary. The experiment is run in the standard mode of the CPA202, the isothermal mode, and the reaction temperature is constantly 25°C besides a small effect at the relatively exothermic reaction peak. The heat flow of 55 W in a 80 mL solution corresponds to approximately 350 W in a 500 mL solution. This explains why the CPA202 is routinely employed for safety investigations with energetic compounds.

### *Transitions with small heat effects and the requirement of long term stability*

Figure 5 shows the crystallization of a compound at 15°C over a time period of about 5 h. The crystallization as initiated with a seed crystal and the mechanical stirring power was subtracted from the measured signal, the total power, in order to obtain the physical crystallization power. The stable zero-type baseline allows reliable measurements over long time periods.

Figure 6 shows the dissolution of a drug compound with a maximum heat flow of 30 mW and a noise level in the range of 1 mW. Again, the most stable baseline allows a very accurate determination and such small heat effects.

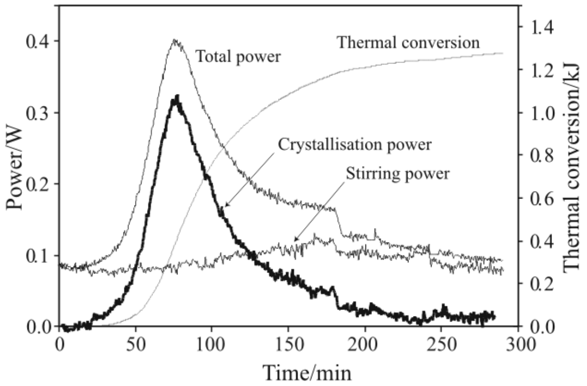

**Fig. 5** Crystallization over a time period of 5 h. The stirring power is subtracted from the originally measured total power. The thermal conversion shows the progress of the transition

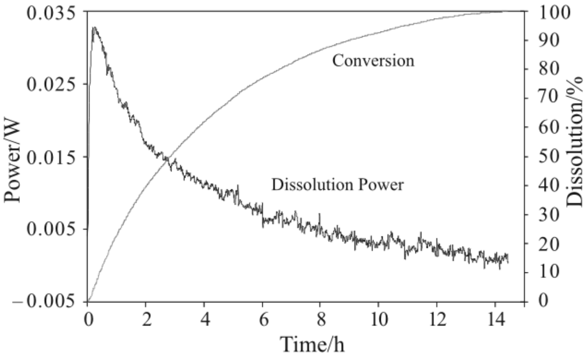

**Fig. 6** Dissolution of a drug compound. The heat flow returns to the baseline after approximately 15 h

These measurements demonstrate that the CPA202 can be used for the measurement of chemical reactions as well as for the determination of subtle physical heat effects.

### *Kinetics*

The CPA202 is used in a number of kinetics experiments, since the accuracy of the results can provide an excellent basis for kinetics calculations [5]. Dosing might be performed with high precision pumps but can also be accomplished by injecting a liquid reactant through a septum in one of the reactor ports just by using a syringe. Such an example is shown in

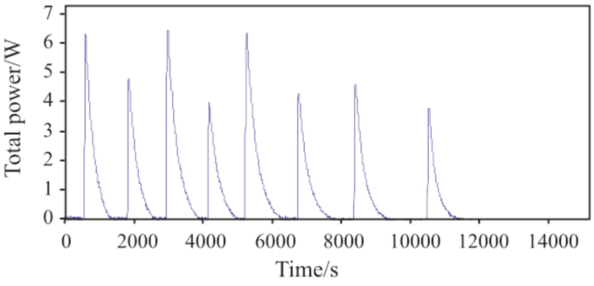

**Fig. 7** Polymerization reactions initiated by syringe injections of hydroperoxide solutions

Fig. 7. The studied process is the polymerization of vinyl acetate at room temperature in a redox-system containing a vanadium catalyst and a hydro-peroxide compound that was added as aqueous solution from a syringe [5]. Since the reaction is a pseudo first-order reaction, the rate constant can be calculated from the logarithmic value of the declining heat flow slopes. The rate constant of 3173±336 L $\text{mol}^{-1}$ $\text{s}^{-1}$ at 25°C could be immediately determined from the logarithmic values of the declining heat flow slopes.

An average time constant of $t_{1/2}$=176±12 s was determined. An additional error comes from the time constant of the system which, however, can be widely compensated by further calculations. In a similar way the CPA202 may be used for quick checks of the quality of catalysts or other compounds.

### *Measurements with reflux condenser and solid batch injector*

Measurements with reflux condensers are very important for process and safety related investigations, since reflux cooling provides the most efficient cooling in industrial processes. The careful design of the employed reflux condenser allows the accurate determination of heats of condensations. As shown in Fig. 8, in a first step the solvent methanol is heated up to its evaporation temperature accompanied by a corresponding increase in condensation power. In a steady state situation the heat applied at the bottom as true heat flow is dissipated as the condensation heat at the top of the reactor in the condenser. The reaction power is the corresponding net effect and equals zero in the first part of the experiment. The reactor temperature equals the boiling point of methanol.

Experiments with reflux condensers are run in the isoperibolic mode, where a certain temperature, which is higher than the one in the reactor, is maintained at the reactor bottom and provides the true heat flow into the reactor.

In the second part of the reaction acetic anhydride is added which leads to the formation of an ester. During dosing the reaction starts and the temperature of the reaction mixture increases due to the fact that the boiling temperature of the methanol/anhydride mixture is higher than the one of pure methanol. Simultaneously, the true heat flow from the reactor bottom decreases due to the fact that there is less difference between the reactor content temperature and the set base temperature. The condenser power corresponds to the sum of the heat generated by the chemical reaction and the heat supplied from the reactor base as true heat flow. From accurate measurements of THF and condenser power the correct reaction power is determined.

In a third and final part of the reaction the reaction slows down after dosing has been completed and comes eventually to an end. This process is accompanied by a decrease of the reaction temperature because the boiling point of the formed methanol/ester mixture is lower than the one of the anhydride mixture. From the reaction power curve the accurate heat flow generated by the chemical reaction can be studied during reflux operation. The curve returns eventually to its baseline.

In another experiment the heats of absorption of natural textile fibres were measured with the help of a so-called batch injector [7]. The batch injector allowed the preparation of the fibres in dry nitrogen atmosphere and at elevated temperatures. After the adsorption temperature was reached in the reactor containing the batch injector and water, the batch injector was opened and the fibres became immersed and wetted immediately. This is shown in Fig. 9 for two different types of fibres.

As this example shows, THF calorimeters can be used for the testing of solid materials and therefore for applications that are typically performed with DSCs.

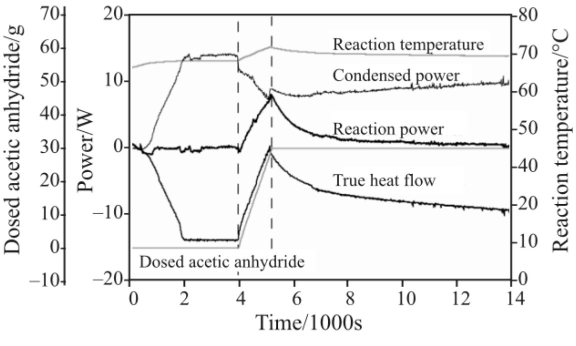

**Fig. 8** Ester formation in methanol with a reflux condenser employed. First, methanol is heated up to its boiling point. Then acetic anhydride is dosed (between dashed lines) and the reaction process continues until the reaction power reaches the zero type baseline again

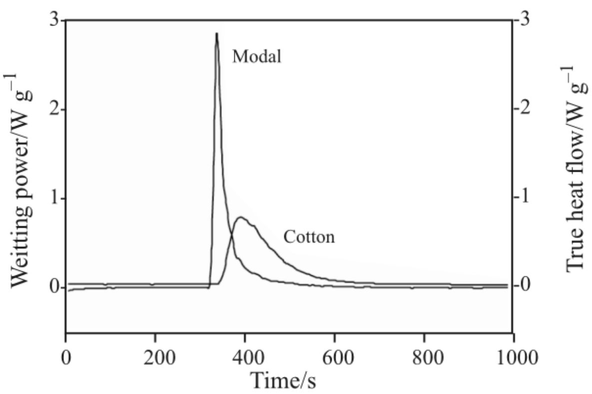

**Fig. 9** The heats of wetting were determined for cotton and modal, a modified natural fibre. The heats of adsorptions were determined to be 41.9 and 87.7 J $\text{g}^{-1}$

## Conclusions

Besides their traditional application areas in the safety and process development fields, true heat flow (THF) reaction calorimeters like the CPA202 have the potential to cover new application areas. Moreover, and as shown in more recent publications, THF calorimeters deliver heat flow figures instantaneously during experiments. Therefore, the THF can be used to control process parameters directly.

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