Using the Transfer Function of an Isoperibolic Reaction Calorimeter for Thermo-kinetic Analysis

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Summary: It is an aim of the present work to determine the chemical heat flow rate of a reaction without explicitly solving the heat balance equations. Therefore, it is necessary to calculate the heat flow rate directly from the temperature course of an experimentally determined reaction. For this transformation the transfer function of the calorimeter is needed[1]. An isoperibol reaction calorimeter was used for the experiments. With different calibrations and gained transfer functions, it is shown that the chemical heat flow rate can be determined from the temperature course of a reaction. The evaluation is fast and easy to use, which improves automation and prevents possible input errors.

Keywords: calorimetry; convolution; deconvolution; evaluation; isoperibol; reaction calorimeter; transfer function

Introduction

The intention in calorimetric measurements is to determine the heat of reaction and its gross heat flow rate in order to describe quantitatively the course of the chemical reaction. For the purpose of thermo-kinetic measurements different types of calorimeters can be used. However, non-isothermal operation mode requires an adequate kinetic model of the chemical reaction for proper thermo-kinetic analysis. Consequently, isothermal reaction conditions are preferred, because mass and heat balances are decoupled and can be solved separately.

An isoperibolic calorimeter (*CalWin*[2]) was constructed in which polymerization reactions can be carried out in 1 L laboratory scale, under realistic reaction conditions. Isoperibolic operation means that the jacket temperature of the calorimeter is held at a constant level. In order to reduce the increase of reaction temperature during exothermal reactions, the calorimeter has a ballast vessel as thermal storage. In case of moderate reaction rates temperature typically shifts of 1 to 2 K[1]. Therefore, the isoperibolic reaction calorimeter described in the present work is a passive calorimeter, which can be run under quasi-isothermal conditions.

So far, data evaluation was only done on the assumption of stationary temperature profiles and heat transfer terms. Solving the heat balance equations of the calorimeter, was accomplished by determining the different necessary parameters, e.g. the cooling constant according to Newton's cooling law, the heat transfer coefficient, the effective area of heat transfer from the ballast vessel to the jacket and the total heat capacity of the calorimeter (classical method). This evaluation is complicated, needs time-consuming calibration, and finally is afflicted with some error, particularly when reactions are running faster.

The purpose of the present work is to determine the chemical heat flow rate without an explicit solution of the heat balance equations. Therefore, it is necessary to calculate the heat flow rate directly from the temperature curves measured during the course of a reaction run. For

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this transformation the transfer function of the calorimeter is needed.

The transfer function of a calorimeter describes the altering of an input signal into an output signal. The heat flow rate of an electric heater (heating-cartridge) is the input signal. The output signals are the temperature curves in the ballast vessel and the reactor. The purpose of this method is the calculation of the heat flow rate curve directly from the measured temperature curves.

If the calorimeter corresponds with an ideal adiabatic model, the heat evolution rate from an exothermal reaction produces a temperature rise in the calorimeter that is proportional to the released amount of heat. The proportionality factor is the total heat capacity C_K of the calorimeter.

$$\dot{Q}(t) = \frac{dQ}{dt} = C_K \frac{dT_R}{dt},$$

where C_K can be obtained by calibration, and the heat flow rate from measurement of reactor temperature.

In contrast, it is not possible to directly conclude the corresponding heat flow rate curve from a measured temperature curve with an isoperibolic calorimeter (Figure 1).

The shape of the measured temperature curves in Figure 1 differs widely from the true event $\dot{Q}(t)$ in the system. However, there are two ways to reconstruct the heat production rate $\dot{Q}(t)$: the solution of the heat balance equations and the application of the transfer function of the calorimeter. In the second case, the transfer function of the calorimeter must be known in order to calculate the heat flow rate curve. The procedure for calculating and principle application of the transfer function is described elsewhere[1,3–11].

From different calibrations (and the transfer functions gained from those), it can be shown, that the heat flow rate can be determined from the measured temperature curves of a reaction and from the transfer function of the calorimeter by deconvolution. The determination of the heat flow rate via the transfer function offers the following advantages compared to the explicit solution of the heat balance equations:

- The evaluation – in contrast to the classical procedure – is fast and easy to use, simplifying the automation and preventing possible input errors.
- The total heat capacity and the overall heat transfer coefficients have not to be explicitly known or definable for the evaluation.
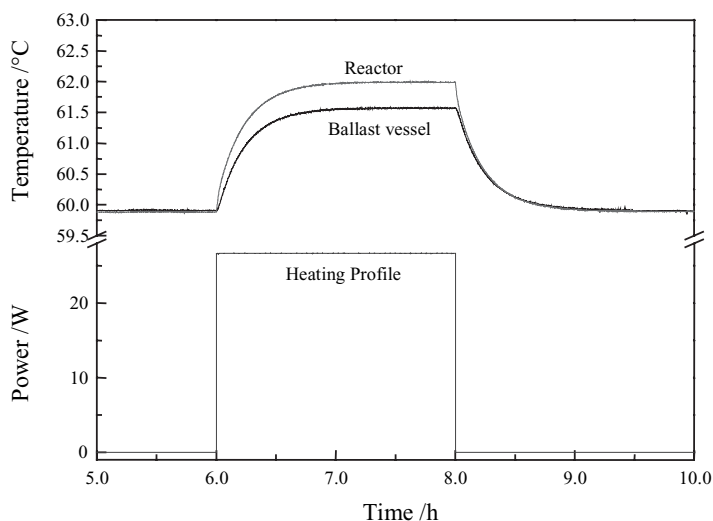

Figure 1.
Power input profile by electric heating and resulting temperatures in ballast vessel and reactor.

- The transfer function can be calculated once and applied under comparable conditions continually.
- The total amount of heat of reaction is obtained with a relative error of less than 3 %.

Experimental

Configuration of the Isoperibolic Pressure Calorimeter

The isoperibolic pressure calorimeter *CalWin* used in this work (Figure 2) is based on investigations by *Stockhausen*[2] and was developed continuously. The measuring and evaluation principles are based on earlier works by *Küssner*[12,13].

The calorimeter (A) includes a 1.1 L reactor, which can be used up to a maximum pressure of 50 bar and a maximum temperature of 200 °C. The autoclave is screwed centrically into a ballast vessel filled with up to 2.0 L of water and closed with a high-grade steel lid. Pt-100 resistance temperature sensors (B) are deployed into the reactor and the ballast vessel. The lid allows screwing the electric heating-cartridge into the reactor or ballast vessel as needed. An Intermig[TM] stirrer (C) is used for mixing the reaction mass. The water in the ballast vessel is mixed by a magnetic stirring stick (D).

The unit consisting of ballast vessel and reactor is placed into a size-accurate double jacket vessel. In this case, the ballast vessel fits very closely into the double jacket. The double jacket is rinsed thoroughly with water, which is held at constant temperature by a thermostat. This ensures a constant operating temperature.

The design of the isoperibolic calorimeter is optimized to achieve a gradual flow of heat, which is generated by the exothermal reaction, into the ballast vessel in the first step and into the jacket in the second step. The overall heat transfer value $(UA)_R$ of the conductive heat flow rate from the autoclave to ballast vessel is significantly higher than the overall heat transfer value $(UA)_B$ for the second step. Subsequently, the increase in reactor temperature can be controlled by the total heat capacity of both the reactor and the ballast vessel. Heat losses to the surroundings by free convection are considered by calibration.

The calorimeter is fitted on a magnetic stirrer (E). The heating cartridge (F) and the Pt-100 temperature sensors are controlled by the measuring unit *PP2* from the company *Remü* (G). Data acquisition, storage and evaluation are carried out with the aid of a PC (H).

Realization of the Simulation Measurements

For the simulation runs both reactor and ballast vessel were filled with water (900 mL in the reactor and 1900 mL in the ballast vessel, respectively) and heated to a constant temperature (60 °C). After reaching
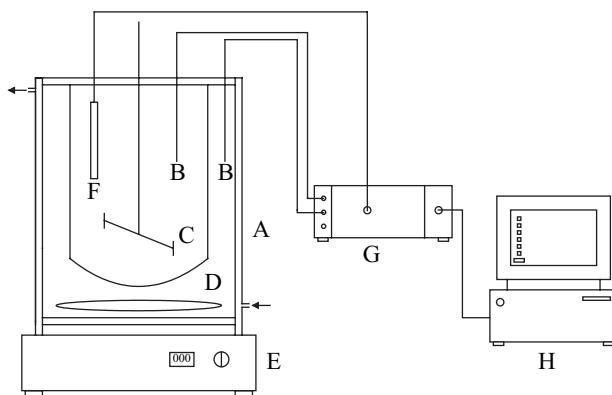

Figure 2.
Scheme of the isoperibolic calorimeter *CalWin* and connected peripheral units.

stationary conditions, the electric heater in the reactor or ballast vessel was switched on for 2 or 3 hours dissipating a constant power input of 10 to 35 W. The amount of heat dissipated into the reactor in this way served for calibration. Simultaneously the temperature was measured by two Pt-100 temperature sensors, one in the ballast vessel (T_B) and the other in the reactor (T_R). After shutdown of the heater temperature data are continuously recorded until the temperatures in the reactor and ballast vessel came up to equilibrium again and remained constant over a period of time (∼1 h). In the same way chemical reactions were simulated by the electric heating-cartridge through variation of the power input. The temperatures T_R and T_B as well as the electric power input were recorded.

Evaluation of the Measuring Data

Evaluation of the experimental data is done with aid of the program Mathematica^{TM} 5.0. Measured data are subject to a three-stage filtering and so received with a small noise level. In the first step all values, which are outside the relevant range are regarded as artifact and replaced by the directly preceding value. In a further step every measured point is compared with the one preceding. If the absolute gradient from one point to the next is bigger than a defined value, e.g. 0.1 K/s, this value is also replaced by the preceding one.

In order to obtain the heat flow rate $\dot{Q}$ and the overall heat transfer coefficient from the ballast vessel to the double jacket $(UA)_B$, the first derivatives of the measured and noisy values of T_R and T_B are needed. This noise would be intensified by common differentiation methods. Through the filter function

$$f_a(t) = \int\limits_{-\infty}^{+\infty} f(t - \phi) h_a(\phi) d\phi$$

and the first derivative of this function

$$\dot{f}_a(t) = \int\limits_{-\infty}^{+\infty} f(t - \phi) \dot{h}_a(\phi) d\phi$$

$\dot{T}_R$ and $\dot{T}_B$ are calculated with a low noise level. This is done by selecting the first derivative of the weighting function $h(\phi)$ instead of the measured function $f(t)$. The weighting function is selected as follows:

$$h(\phi) = \frac{1}{2}(1 + \cos(\pi\phi)) \quad \text{for } |\phi| \leq 1$$

This is a so-called Hanning window function. If $|\phi| > 1$ the weighting function goes $h(\phi) = 0$. Also:

$$h_a(\phi) = \frac{1}{a} h\left(\frac{\phi}{a}\right),$$

where a is half the width of the filter window. The signal-noise ratio of the measured signal is improved by a wide filter window. However, the dynamics of the signal are worsened. The result of this filtering is shown exemplary in Figure 3.

Definition of the Transfer Function

The transfer function of a calorimeter can be gained by calibration by means of an electric heater. Therefore a certain heating profile is brought into the calorimeter. The resulting temperature course and the electric power input are recorded and both curves are Fourier transformed. The Fourier transformed temperature curve is divided by the Fourier transformed electric power input curve (deconvolution). Afterwards the resulting function is retransformed into time domain. This deconvolution provides the transfer function of the calorimeter.

It is not urgently necessary to transform the transfer function back into the time domain in order to use it. For convolution or deconvolution it must be in the frequency domain anyway. Figure 4 details the transfer functions of one experiment.

When calculating the transfer functions, it is important not to use any further filtering after the preparation of the measured values.

Application of the Transfer Function

In the reactions simulated in this work via an electrical heater the amount of heat dissipated into the system is known
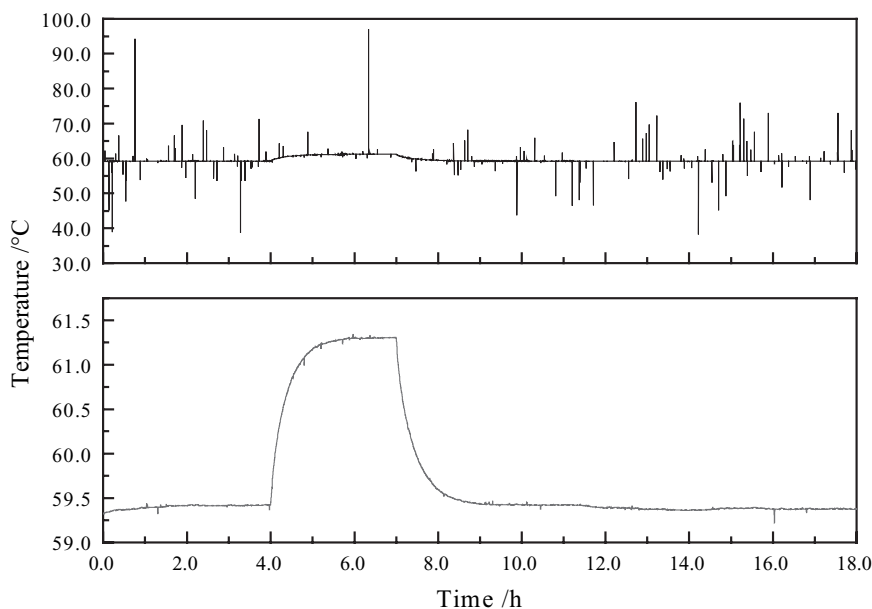
Figure 3.
Temperature graphs before (above) and after (below) the described filtering.

precisely. Through that it is possible to calculate the corresponding heat flow rate from a measured temperature curve and to compare this result with the heat flow rate actually feed into the system. The calcula-

tion of the transfer function takes place as described above. After this, the temperature curve of the examined measurement is Fourier transformed and deconvoluted with the transfer function in the frequency
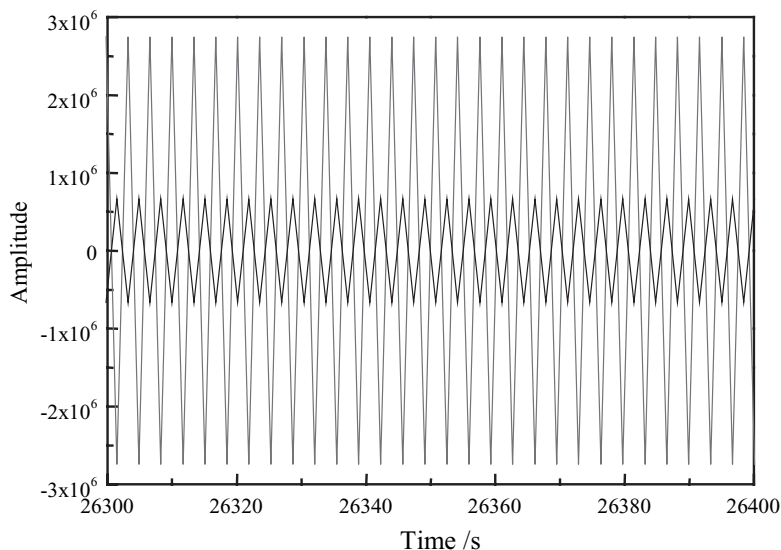

Figure 4.
Part of the transfer functions.

domain. The obtained Fourier transformed heat flow rate curve is filtered with a window function (see above) and is transformed back into the time domain. As a result the "real" heat flow rate of the electric heater is attained.

Results and Discussion

In order to prove the applicability of this method three heating cycles were produced in one experiment, all under the same conditions (Figure 5).

Subsequently, the transfer function of the calorimeter was calculated on the basis of the temperature measurements during the first heating cycle. With this function the respective heat flow rate curves were calculated from the temperature curves of the second and third heating cycles and compared with the power input by the electric heater. The areas under both curves were calculated and compared to each other. Figure 6 shows the result of the deconvolution of the second heating cycle with the transfer function which was determined from the first heating cycle.

For the third heating cycle a similar result was obtained. The comparison of the areas under the heat flow rate curves (calculated and measured) shows a relative error of 0.05 ± 0.01 % based on the area under the measured heat flow rate curve. Consequently, the amount of heat (Q) can be calculated quite precisely within the same experimental run using the transfer function of the calorimeter, which was obtained during calibration.

Applying the Method on a Simulated Reaction

In any experiment a heat flow rate curve can be determined with a transfer function gained from another identical heat flow cycle. In order to ascertain whether the same procedure is applicable on two different heat flow cycles, a further experiment was carried out. The calibration was done in the ballast vessel and then an identical heating-profile was used in the reactor. Indeed, with the transfer function determined by calibration in the ballast vessel the heat flow rate in the reactor can be determined from the temperature curve
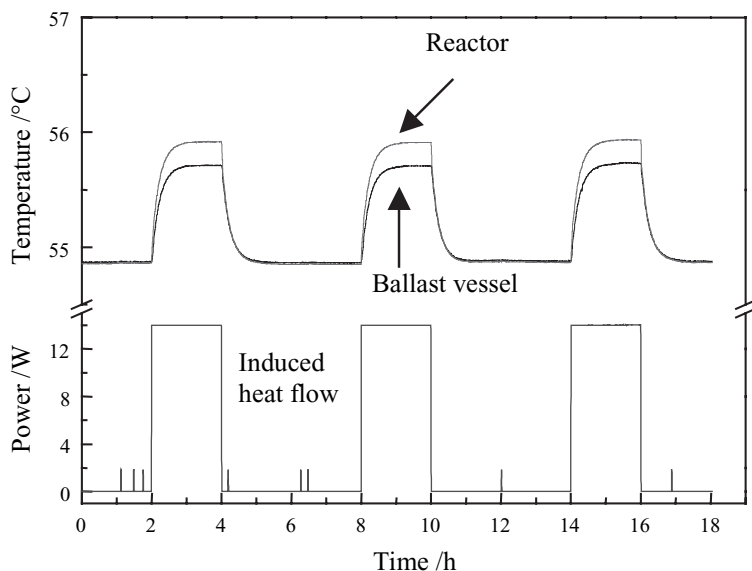

Figure 5.
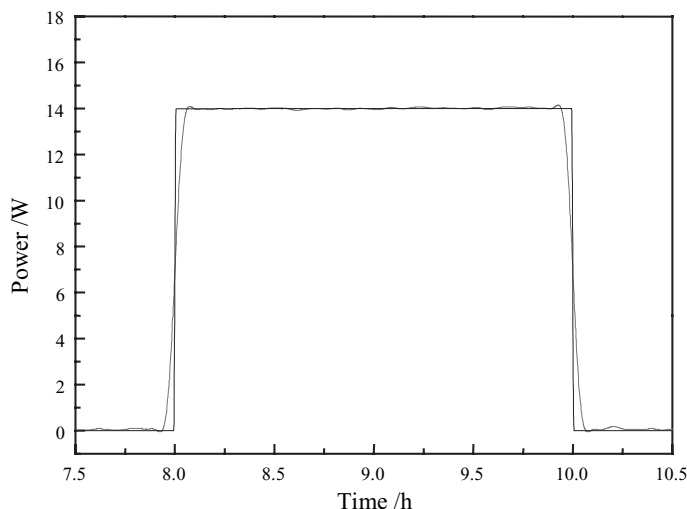Power input by the electric heater and resulting temperatures in reactor and ballast vessel.

Figure 6.
Comparison of the calculated and actual heat flow rate of the second heating cycle (electrical heater placed in the reactor; T_R was used to determine the transfer function).

in the ballast vessel of the second heating period (Figure 7).

Comparison of the areas under the curves shows a difference of 0.3 % based on the measured heat flow rate curve. With a calibration in the ballast vessel a similar heating cycle in the reactor can be obtained.

Until now, only identical heating cycles were compared. That is the heating cartridge was always on for a set period of time. This procedure is still a far call from a real reaction where the reaction heat is unknown. In order to come closer to a real reaction, a reaction was simulated in the
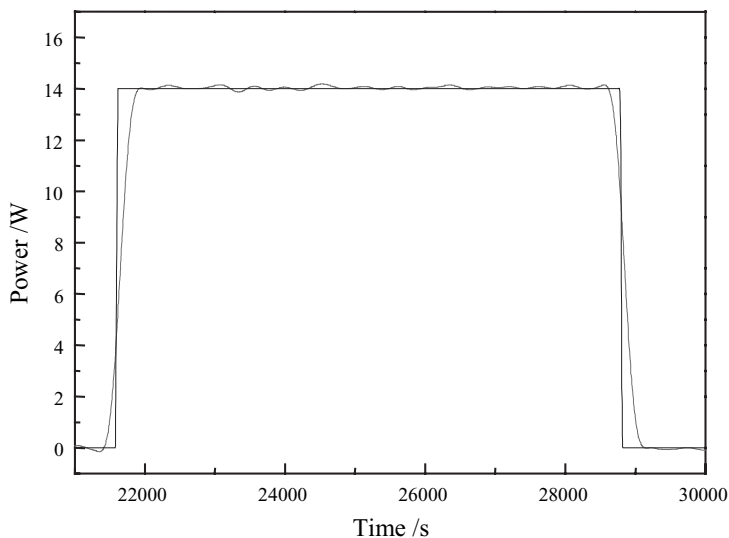

Figure 7.
Calculated and measured heat flow rate of the second heating cycle (electrical heater placed in the ballast vessel; T_B was used to determine the transfer function and the power input into the reactor).

reactor, applying different heating power levels. A calibration in the reactor and later also in the ballast vessel, with reduced heating capacity compared to the first, had to be carried out (Figure 8).

With the transfer function obtained from the first calibration the heat flow rate of the simulated reaction was obtained. The areas deviate around 3 % from each other (Figure 9).

With calibration in the ballast vessel, the result of the area comparison shows a difference of 0.3 % (Figure 10). It is possible to calculate the heat flow rate of a simulated reaction with a calibration in the ballast vessel or reactor.

Application to Real Reactions

So far, the calculated transfer functions were always used to gain heat flow rates from other temperature curves within an experiment. It would be of great advantage, if transfer functions that were determined independently of the current experiment could be used for evaluation. In order to answer this question, a transfer function from one experiment was used to calculate the heat flow rate from a temperature curve of another one (Figure 11).

Again, the areas under the curves were compared. The deviation is 0.5 % based on the area of the measured heat flow curve. This shows that heat flow rate curves from various experiments can be calculated with the transfer function from other experiments. However, the conditions under which the experiments were carried out were still very similar.

In order to check the transferability of the results to ''real'' reactions, some copolymerization runs were carried out. The results of applying a transfer function from a previous experiment to a copolymerization are shown in Figure 12.

The total calculated heat flow using the new method is 136 kJ. The classical calculated heat flow is 134 kJ. That is a deviation of only 1.5 % based on the calculated heat, using the classical method. The respective reaction courses can be reconstructed from the temperature curve of a copolymerization.

Obviously, the classical method and the method of the transfer functions do not supply exactly matching heat flow rate curves because the parameters for calculating the classical heat flow rate curve are not gained by calibration, but from estimation.
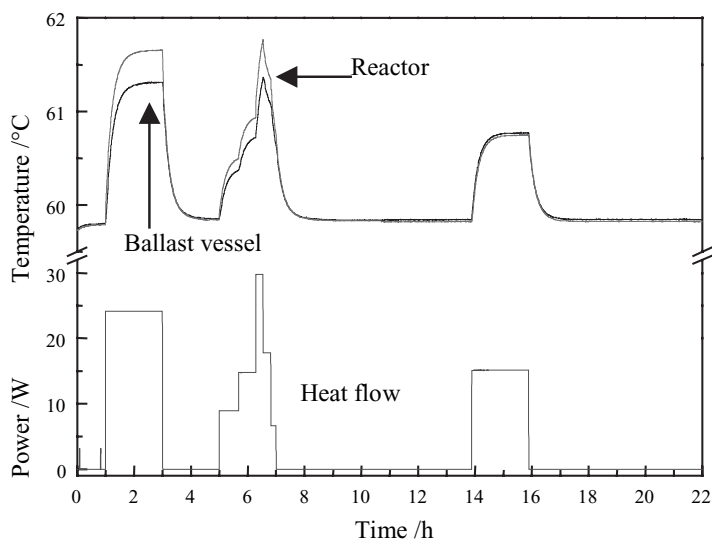

Figure 8.
Temperature graphs in the ballast vessel and reactor as well as heat flow graph of the simulated reaction.
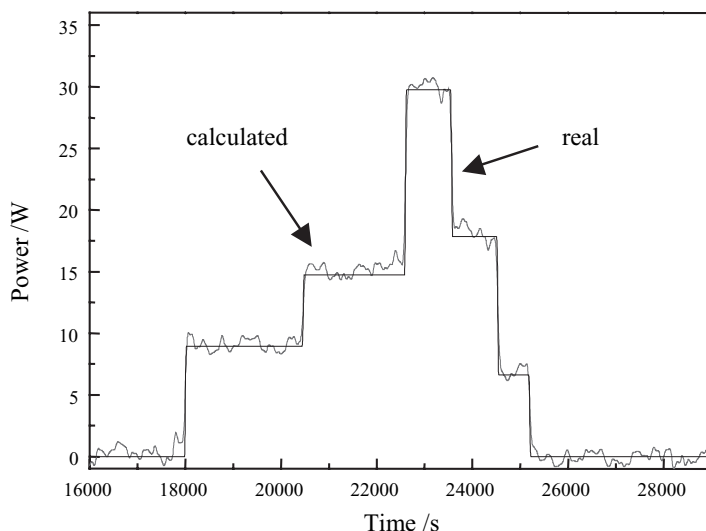
Figure 9.
Calculated heat flow rate from the simulated reaction and the real heat flow rate, using the transfer function from the first calibration (electrical heater placed in the reactor; T_R is used for calculations).

Comparison with the Classical Evaluation

With the classical evaluation method the total heat capacity of the calorimeter is determined first via calibration. Thereby, the heat transfer value $(UA)_B$ is calculated, which is needed for determination of the heat flow rate. In order to calculate the total heat capacity, the adiabatic temperature rise and the temperature in the stationary state have to be known. In all calculations errors are possible and may propagate through the whole evaluation. A further
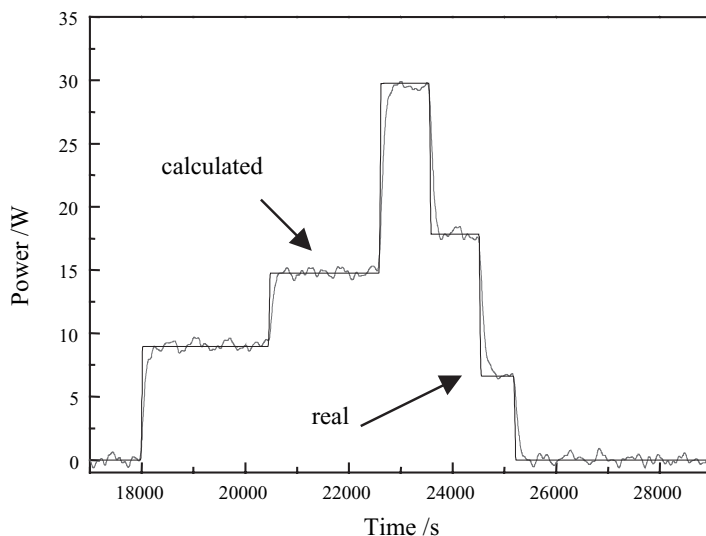

Figure 10.
Calculated heat flow rate from the simulated reaction and the real heat flow rate, using the transfer function from the second calibration (electrical heater placed in the ballast vessel; T_B is used for calculations).
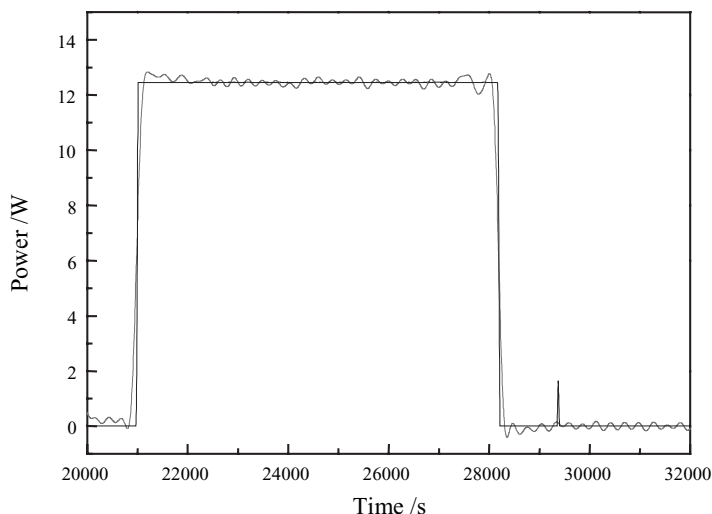
Figure 11.

Heat flow rate calculated with the transfer function from the temperature curve in the ballast vessel of an other experiment and the actual measured heat flow rate (electrical heater placed in the reactor; T_B is used for calculations).

problem of the classical evaluation is the first derivative of the temperature. This leads to a very noisy heat flow rate curve, which must be filtered before results can be received.

In contrast, the heat flow rate curve of a reaction is quickly and easily to be found by a suitable transfer function. Therefore, it is only necessary to calculate the transfer function of a calibration and to use it for the measured temperature curve. Neither the total heat capacity of the system nor the overall heat transfer value are important. Also no differentiation of temperatures has to be calculated, thus avoiding associated problems.
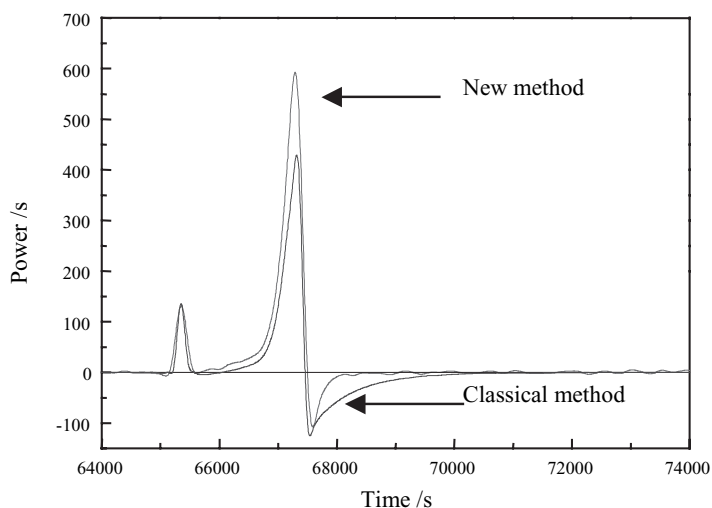

Figure 12.

Heat flow rate of a copolymerization calculated with the classical method and with the transfer function from a previous experiment.

Conclusion

With the method presented in this paper, heat flow rates from temperature curves can be calculated. A great advantage is the simplicity of this evaluation. For the classical evaluation six different parameters have to be entered, in the transfer function only two: the start and ending points of calibration. Thus, less mistakes are expected and the sought-after heat flow rate is quickly received.

Besides the adiabatic temperature rise, the heat transfer value and the total heat capacity of the system can still be calculated with the classical evaluation.

By combination of the two methods a powerful tool is received. In addition, the classical method can be checked quickly and simply by the presented method, comparing both results of the heat flow rate.

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