

# **THE DEVELOPMENT OF HEAT FLOW CALORIMETRY\* AS A TOOL FOR PROCESS OPTIMIZATION AND PROCESS SAFETY**

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## **Abstract**

Classical thermo-analytical micro methods (DTA, DSC) are still very useful for process work, but medium scale instruments based on heat flow measurement are attaining an increasingly important role in this domain.

As in many areas, development of reaction calorimetry for industrial applications was driven by needs and by available means (technical capabilities).

The needs have been fairly constant over the past decades. There are data needs:

- Reaction rates
- Heat release rates
- Heat of desired reactions and decompositions
- Heat capacities and heat transfer capacities

It took the specialists of calorimetry a long time to recognize and to accept the operational needs, namely:

- Working under controlled temperature conditions (constant temperature, temperature ramps)
- Adding components during runs (continuously or in portions)
- Simulation of industrial mixing conditions

The main driving force for the development of process oriented calorimetric instruments was the evolution of electronic hardware which made the control of heat flow on a (non micro) laboratory scale easy.

The paper gives an overview on the principles of heat flow control and reviews the developments of the fifties and sixties, when the matching of heat flow with heat release by reactions was the goal.

With the advent of fast and powerful laptop computers, the focus has shifted. Now, the deduction of true heat release rates from signals which may be badly distorted, is the goal.

Some recent developments are reviewed and the hope is expressed that calorimetric equipment, inexpensive enough to be affordable for every laboratory engaged in process work, will be available soon.

**Keywords:** calorimetry, heat transfer, process development, process safety, reaction kinetics, thermal hazards

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\* In the English literature, the two expressions "heat flux" and "heat flow" are used. As we are generally not interested in flux (=flow per unit area), "heat flow" is preferred here.

## Needs for process optimization and process safety

The aim to eliminate thermal hazards from chemical production processes has helped to advance the development of calorimetric instruments, particularly for use in process development, as it is now generally accepted that process safety problems are to be solved by appropriate process design rather than by added on safety devices.

There are clearly two classes of needs:

- Results
- Means to get the results reliably and efficiently

In early phases of process development, desired results are mostly qualitative:

- Can I work with normal precaution, or are there particular hazards? e.g.:
  - Is there a potential for a high temperature rise (caused by the desired reaction or a decomposition)?
  - Can material involved deflagrate or detonate?
- At which temperatures, concentrations, and in which reaction media does a reaction proceed, and how fast?
- How do reactants and catalysts affect the reaction rate?

Later, when processes are to be established and equipment must be designed or adapted, the required results become more quantitative, e.g.:

- heat release rates
- heat removal capacities and their dependence of the transport properties of the reaction medium.

All these results we want to get effectively and efficiently.

## Available calorimetric principles/classification of calorimetric instruments

There is no generally satisfactory classification of calorimeters, because there are so many characteristic features.

Hemminger and Höhne [1] distinguish in their often cited book:

- Calorimeters compensating the thermal effects (by phase transition, electric effect or chemical reaction)
- Calorimeters measuring temperature differences
  - in time (adiabatic or isoperibol instruments)
  - in space (some heat flow calorimeters and the flow calorimeters)

When the focus is on heat flow calorimetry, a different classification (Fig. 1) is preferable [2], distinguishing mainly between:

- Heat accumulation methods (adiabatic and most isoperibol instruments)
- Heat flow methods

Heat flow methods may be further classified with respect to their various ways of:

- a) Heat flow control:
  - passive (heat flow driven by partial heat accumulation, Fig. 2a)
  - active (heat flow forced by a control system, Fig. 2b and Fig. 3), e.g.

- compensation heating
  - Peltier heat transfer
  - temperature adjustment in the "heat sink"
- b) Heat transfer measurement:
- electric current (Peltier or Joule effect)
  - heat balance in the heat sink
  - temperature difference over heat transfer resistance
  - and for systematic completeness (but not used for kinetic work):  
amount of phase transfer caused by heat flow (e.g. ice calorimeter)

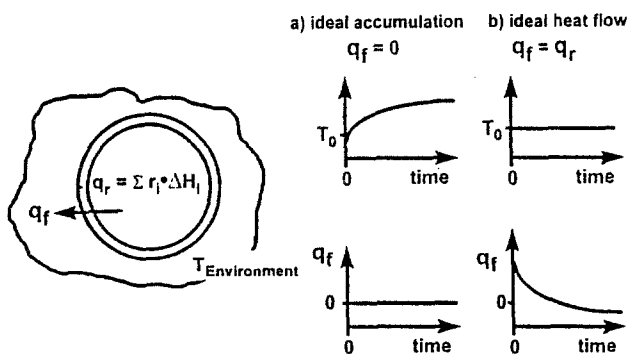


Fig. 1 The limiting cases of calorimetry

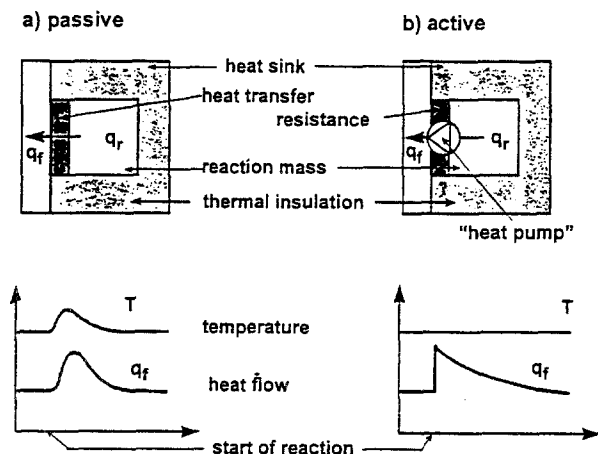


Fig. 2 Heat flow calorimeters

*Some comments*

- Passive heat flow calorimeters are useful only for small samples and good heat transfer between reactor and heat sink; otherwise dynamics will be poor and deviations of the reactor temperature from the desired value will be large.

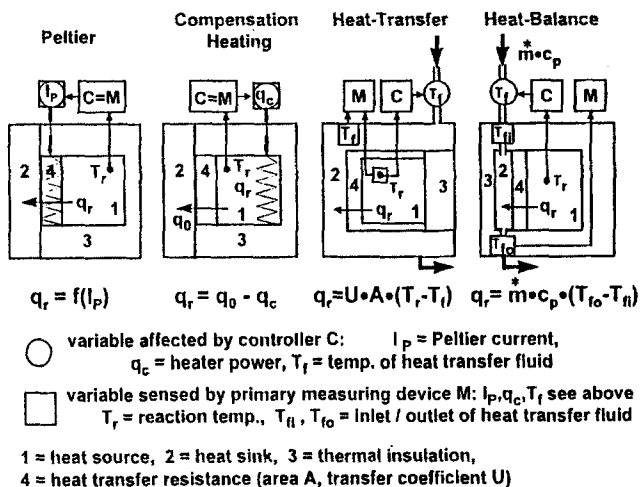


Fig. 3 Combinations of heat flow control and measurement used in active heat flow calorimeters (from Ref. [33])

– Among active heat flow calorimeters, compensation heater types are by far the easiest to build; they also have excellent dynamics.

– Both, compensation heater heat flow calorimeters and heat flow calorimeters with jacket temperature adjustment, (the latter when combined with heat flow measurement via temperature difference) suffer from varying sensitivity when the heat transfer properties of the reaction medium changes. The former show more-over a serious baseline drift in this case [3].

– Heat flow calorimeters with jacket temperature adjustment have relatively poor dynamics, particularly when heat flow is measured by heat balance on the jacket.

– Peltier types have excellent dynamics. However, until recently, there were serious restrictions in their application range (temperature range, materials and geometry of reactor).

## Short history of heat flow calorimetry and overview of past and present designs

Calorimetry is old, probably the oldest non-trivial physical discipline (if we call weighing trivial). History reviews tell us that famous Lavoisier investigated the heat release from a living mouse in an ice calorimeter shortly after the introduction of the concept of heat by Black.

Calorimetry developed slowly, but is still progressing. Presently new momentum has come from Atomic Force Microscopy with a design detecting nanocalories with time constants of a few milliseconds [4].

Heat flow calorimetry (Table 1) has its roots in DTA. It was systematically developed in the second quarter of this century by Tian [5] and Calvet [6].

**Table 1** Heat flow calorimetry

1923	Tian [5]	thermopile-calorimeter
1948	Calvet [6]	twin cell thermopile-calorimeter
1956	Borchardt + Daniels [7]	
1957	Kissinger [8]	DTA for kinetics
1969	Rogers + Smith [9]	
1965	Becker + Walisch [10]	Peltier controlled heat flow calorimeter
1966-83	various authors in industry	heat flow calorimeters for safety and process design
1982	Nilsson + Silvegren [27]	model supported Peltier controlled heat flow calorimeter
1991	Eigenberger + coworkers [28]	laboratory fermenter calorimeter
1992	Moritz and coworkers [29]	model supported compensation heater heat flow calorimeter
1993	Reichert and coworkers [30]	calorimetry with a model supported standard laboratory reactor

Kinetic evaluation of heat flow data was discussed in the fifties by Borchard and Daniels [7], by Kissinger [8], and by Rogers and Smith [9] (to quote some of the most cited papers).

Important systematic work towards modern active heat flow calorimetry was done in the sixties by Becker and coworkers [10] in Germany.

Heat flow calorimeters designed for the investigation of the kinetics of industrial reactions were built in almost every major chemical company (Table 2).

**Table 2** Heat flow calorimeters from the Chemical Industry

Year	Type		Author	Affiliation
1960	passive	"Thermokinegraph"	Baumgartner + Duhaut [11]	Inst. Français du Pétrole
1966	active	compensation heater	Andersen [12]	Monsanto
1966/81	active	adjustment of jacket temp.	Regenass + coworkers [19-22]	Ciba-CH
1969	active	adjustment of jacket temp.	Meeks [18]	Dow
1973	active	compensation heater	Koehler + al. [13]	BASF
1975	active	adjustment of jacket temp.	Hub [23, 24]	Sandoz
1976	active	compensation heater	Chandler [14]	Ciba-UK
1977	active	wall compensation heater	Schildknecht [16]	Roche
1979	active	compensation heater	Hentschel [15]	Hüls
1980/83	active	compensation heater + heat balance on jacket	Litz [17]	Bayer

– The first of these instruments known to the author, came from the Institut Français du Pétrole [11]: a passive heat flow calorimeter which was available commercially in the early sixties, but seems to have disappeared soon.

– The most frequently used method of heat flow control is compensation heating (used by authors from Monsanto [12], BASF [13], Ciba-UK [14], Hüls [15], Roche [16] and Bayer [17]), sometimes with sophisticated features to cope with the inherent flaws of this method.

– Adjustment of the temperature of a heat exchanger coil (and heat balance over this coil) was used at Dow [18].

– Jacket temperature adjustment was used at Ciba Basel [19–22] (deriving heat flow from the temperature difference over the reactor wall) and at Sandoz [23, 24] (determining heat flow by a heat balance on the jacket). The Sandoz design was commercialized by Contraves, the Ciba design by Mettler [25].

– A noteworthy isoperibol heat flow calorimeter was developed at BASF [26].

The list is necessarily incomplete. Many successful efforts were probably never published. That is the reason of the mention of the work by Chandler [14] who built with essentially no money a compensation heater heat flow calorimeter which worked perfectly in its range of application.

The development of heat flow calorimetry is ongoing. To mention examples of this: The Peltier based instrument developed by Silvegren and coworkers [27] (now available commercially by Chemisens), and a fermenter calorimeter, developed by Eigenberger and coworkers [28] also available commercially (by Berghof), and model-based designs by Moritz and coworkers [29] and Reichert and coworkers [30]. The latter designs [29, 30] are important for the following discussion.

Reviews on heat flow calorimetry were given by Becker [31], Regenass [32,33], Karlsen and Villadsen [34], Moritz [35] and Steinbach [36].

## The development within Ciba

Calorimetric work in the Chemical Engineering Section of Ciba started 1965 with the task to keep a Skraup Reaction\* under control. There had been a run away in the plant and process safety had to be improved [37].

At that time, temperature control on industrial stirred tanks was improved by “cascaded control”: The heat flow from or to the reactor (steam/cooling water) is controlled not only by the temperature of the reactor contents, but the temperature of the jacket is also sensed and adjusted according to the deviation of the reactor temperature from its set point: e.g. when  $T_R$  is 1°C too high, the jacket is set 5°C below the reactor temperature set point. This greatly improves temperature control stability.

A. Mauerhofer, an electronic engineer at Ciba, designed a little box which made this type of temperature control available for the laboratory. Plotting the tempera-

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\* The highly exothermic formation of a quinoline by condensing an aniline with glycerol in sulfuric acid.

tures of reactor and jacket vs. time (on an automatic recorder), we obtained heat release data which immediately led us to a kinetic model of the reaction, from which we could predict safe and time efficient temperature programs for the industrial reactor. This fascinated us and gave us recognition and freedom to do some methods development.

When we want to measure heat release rates by transferring the involved heat to a heat transfer fluid, the temperature of this fluid must be adjusted very fast (at least, we thought so at the time).

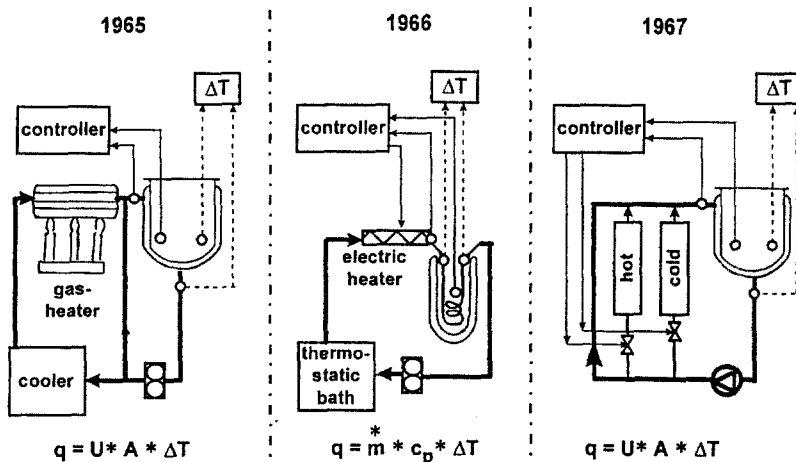


Fig. 4 Early heat flow calorimeters at Ciba

Our first attempt (Fig. 4, left) was a jacket circuit with cooler and a gas heater switched on and off by a controller. Heat release rate was determined from the temperature difference between reactor and jacket. It worked, but it was an energy wasting machine, and the big fire was not exactly what we needed in the lab.

Next (1966) we tried a fast temperature controlled electric heater on a coil circuit in a Dewar type of reactor (Fig. 4, middle). We used constant fluid flow and measured the temperature between the inlet and outlet of the reactor. The result was a typical lab calorimeter, useful for data, but awkward to operate.

Third (1967), we went back to jacket temperature control (Fig. 4, right), now with temperature adjustment by mixing (injection of precooled or preheated fluid).

With this design, we could solve many process problems. It was used on a service basis for customers in various areas of Ciba. Figure 5 shows 3 application examples from this time period.

Besides applications, we could also look into the basics. Several colleagues did their Ph.D. thesis work on performance evaluation and on applications of the Ciba heat flow calorimeters [38-42].

In the early seventies, we came to the conclusion that we should have "Bench Scale Calorimeters" (BSC) in the various process development departments, for two reasons:

– After a few serious thermal run aways in the plants, there was a long queue of work orders.

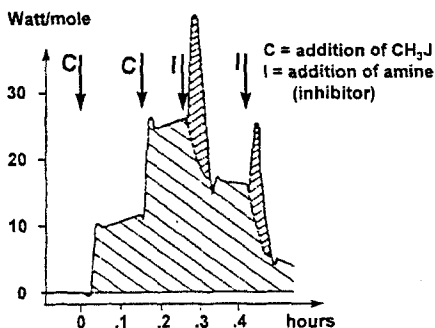
– We had noticed that it was very difficult to convey insight on process improvement opportunities to those responsible for the processes.

After a failed attempt to convince an established supplier of thermal instruments to provide calorimeters for us, we started a redesign.

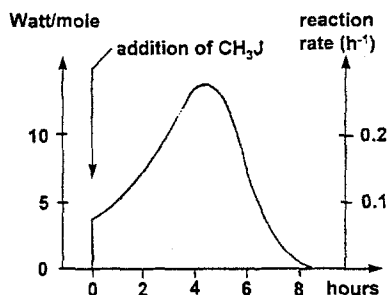
It was fortunate that W. Kanert, a chemist with a professional education as a draftsman, had just obtained his chemistry diploma and was looking for a Ph.D. thesis opportunity. He implemented the “BSC-75” [21, 40], a design which was much more compact than its predecessor (Fig. 6). 18 units were built; some are still in use. A wide range of options were available:

a) The highly exothermic isomerisation of trimethyl-phosphite [38]

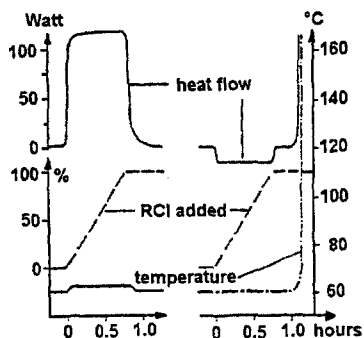
Catalysis and inhibition  
(catalyst:  $\text{CH}_3\text{J}$ , inhibitor: amine)



Acceleration of reaction rate, caused by increasing polarity of the reaction mixture



b) The check of the reaction initiation in an industrial manufacture of Grignard Reagent ( $\text{RCl} + \text{Mg} \rightarrow \text{RMgCl}$ )



c) The oxidation of chlorotoluene in solution with molecular  $\text{O}_2$ , catalyzed by  $\text{Co}^{2+}$  and  $\text{Br}^-$  [42] ( $\text{RCH}_2 \rightarrow \text{RCHO} \rightarrow \text{RCOOH}$ )

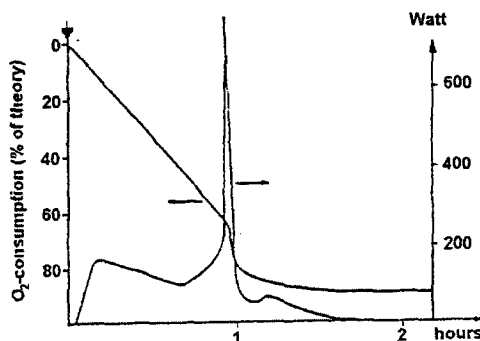


Fig. 5 Early application examples:

a) The highly exothermic isomerisation of trimethyl-phosphite [38].

b) The check of the reaction initiation in an industrial manufacture of Grignard reagent ( $\text{RCl} + \text{Mg} \rightarrow \text{RMgCl}$ );

c) The oxidation of chlorotoluene in solution with molecular  $\text{O}_2$ , catalyzed by  $\text{Co}^{2+}$  and  $\text{Br}^-$  [42] ( $\text{RCH}_2 \rightarrow \text{RCHO} \rightarrow \text{RCOOH}$ )



- pressure reactors up to 150 bar
- heaters, coolers and heat transfer fluids for a temperature range of  $-70$  to  $250^{\circ}\text{C}$
- various construction materials for reactors (glass, glass-lined steel, titanium).

In 1975, Mettler acquired a license on this calorimeter. Unfortunately, the project was abandoned.

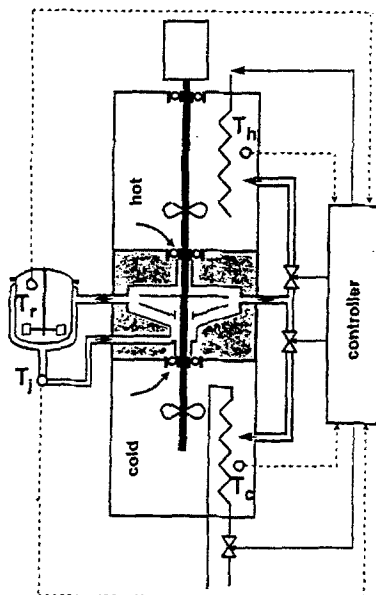


Fig. 6 BSC-75

In 1979, we were faced with problems of instrument supply again. We improved the mechanical design (based on the cooperation with Mettler) and used a computer based control system supplied by the same manufacturer [43] who had supplied the electronic equipment of the BSC-75.

This "BSC-81" [22] could be accommodated in a standard fume cupboard and could do automatic experiments, data acquisition and evaluation. However, it was far less successful than the BSC-75 as it required "experts" to operate it and there were more computer failures than acceptable for a safety calorimeter.

When 1981 Mettler became a Division of Ciba-Geigy, the project of a Mettler Bench Reaction Calorimeter was restarted. The "RC1" became commercially available in 1985, first mechanically identical with the later version of the BSC-81, but with an appropriate and reliable control and evaluation system; however, with quite restricted application accessories. Only recently, important features of our BSC-75 (pressure, temperature range) were added to the RC1.

## Recent and future developments

When we look at the calorimetric information needs in chemical process design work, namely:

- (a) Safety data for lab work
- (b) Qualitative kinetic information
- (c) More rigorous data for process optimization and equipment design

only (b) is a problem area. Safety data for lab work is well served by a large choice of commercial instruments for micro samples (DTA, etc.), and for process optimization suitable heat flow calorimeters are commercially available.

Heat flow calorimetry might be as much a standard method of monitoring reactions as all the forms of spectrometry and chromatography presently in use. Not as specific, but much more convenient. However, there is still little application of calorimetry by people dealing with synthetic chemistry, since the method was never made attractive enough for the common potential user.

The needs of the users of calorimeters are:

- Measuring qualities (sensitive, accurate, representative of process under question)
- Handling qualities
  - variety of standard operations (stirring, adding components, ramping temperatures, etc.)
  - time requirement for preparation, calorimetric run and evaluation
  - space requirement in the laboratory
- Availability to user (cost of acquisition and cost operation)

When we try to translate these needs into instrument specifications, we see that the problem of presently available calorimeters is not with sensitivity or with accuracy, but with handling properties and with cost.

The specifications with respect to handling and cost are set by conventional laboratory reactor systems (i.e. container of reaction mass, heat transfer equipment, control equipment, etc.). Such systems are of course no calorimeters, but they have many components in common with calorimeters, up to computers for data acquisition and/or automatic running procedures.

This leads to the question, whether it is feasible to turn conventional laboratory equipment into a simple calorimeter by modeling and data treatment and if so, what accuracy and sensitivity of heat release should one aim for?

An accuracy of  $\pm 10\%$  of the released heat is probably sufficient and achievable.

Sensitivity requirements are more stringent and much more difficult to achieve. Probably, the detection of a change in heat release rate (5 min mean) which corresponds to 5% of the maximum heat release rate of the investigated reaction, would be quite helpful.

How is it possible to implement low cost, easy to use heat flow calorimeters? Two attempts were made recently:

Moritz and coworkers [29] put an isoperibol calorimeter into a compensation heater type heat flow device (thus eliminating influences by the reaction on the heat

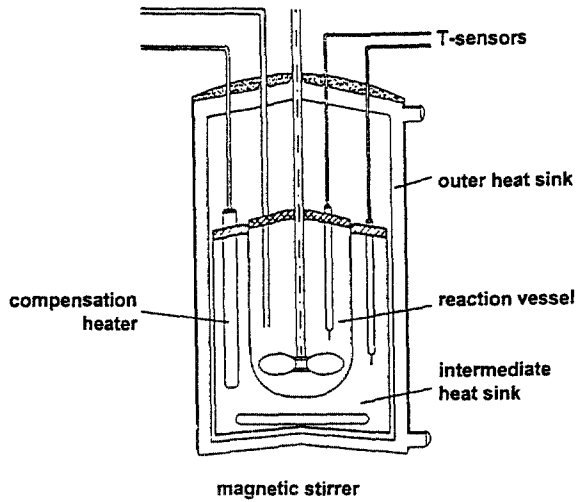


Fig. 7 Compensation heating isoperibol calorimeter (Moritz + coworkers)

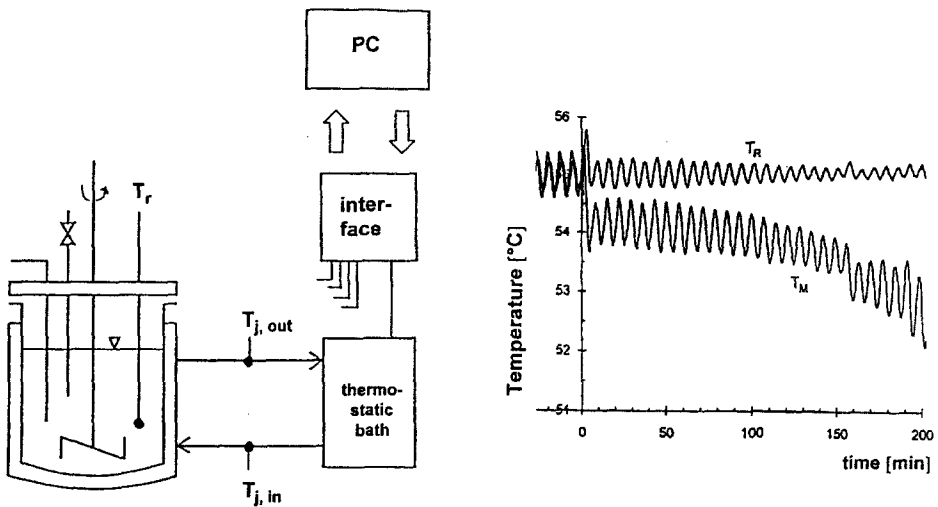


Fig. 8 Temperature modulated heat flow calorimeter

transfer resistance) and corrected for heat accumulation in the isoperibol reactor by modeling. The calorimeter provides heat release rates and heat transfer data simultaneously (Fig. 7).

Reichert and coworkers [30] attached a fast commercial thermostat to a commercial autoclave and modulated the set temperature of the reactor within narrow limits (Figs 8 and 9).

Possibly one can get the desired results even simpler (Fig. 10):

When we know the heat transfer characteristics of the reactor wall and of the film heat transfer resistance on the jacket side (they are not affected by the reaction, but will depend on temperature), we can, by solving the partial differential equations which describe the temperature profiles in the reactor wall as a function of time and location, estimate the wall inside temperature which determines heat transfer from or to the reactor contents. If we know the inside film heat transfer coefficient (it can be estimated from transients caused by temperature changes in the jacket if the heat capacity of the reactor contents is known), we can separate heat release and heat transfer effects on the temperature of the reaction mass.

Karlsen, Søbørg and Villadsen [44, 45], did this with a BSC-81 in 1984 by heating and cooling the reactor contents from the jacket (Fig. 11). The heat release calculated by the estimator (true value = 0) was within 0.2% of the heat transferred and

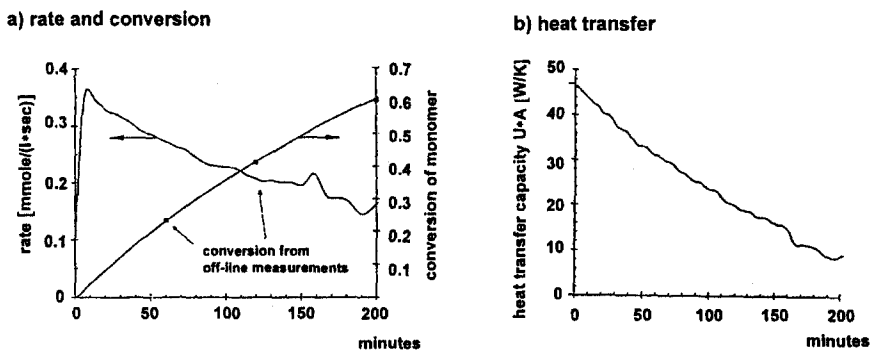


Fig. 9 The temperature modulated heat flow calorimeter provides heat release and heat transfer data without a secondary heat transfer resistance (polymerisation of methylmethacrylate)

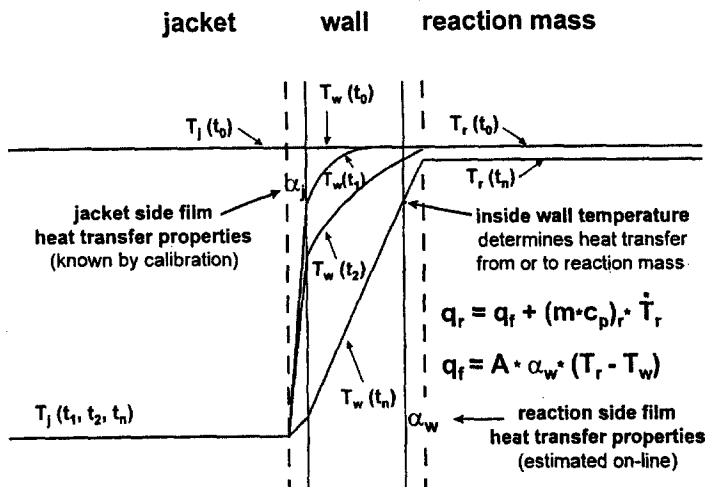


Fig. 10 Temperature transients at the reactor wall

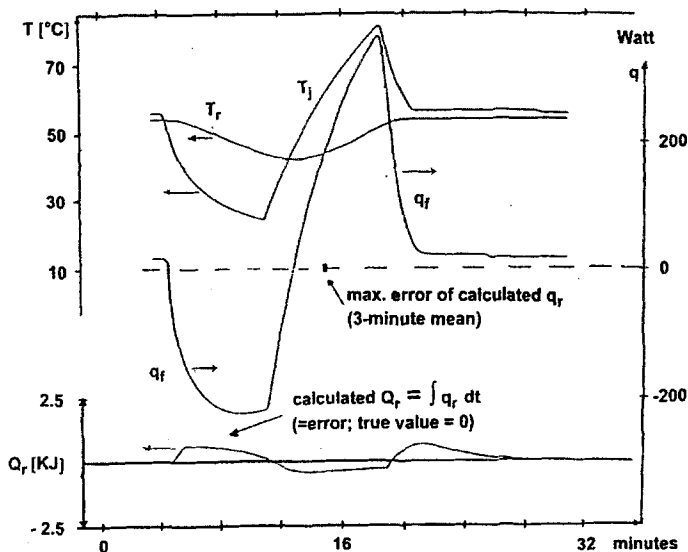


Fig. 11 Separation of heat release effects and heat transfer effects by mechanistic modeling (Karlson, Søberg and Villadsen, 1984/87); (cooling, then heating of reactor contents)

the estimated heat release rates (true value=0) were (as a 3 min mean) less than 4% of the mean heat transfer rates during the experiment (pages 1170–71 of Ref. [45]). These results were obtained with a computer which was a hundred times “weaker” than present laptop computers.

From Karlson’s experiments one may conclude:

- When a computer based estimator is available, there is no need for very fast and highly accurate jacket temperature control
- The only necessary accessories additional to those of a conventional automated lab reactor are
  - a temperature sensor in the jacket,
  - a high resolution of the reactor temperature,
  - a calibration heater,\*
 and, of course, algorithms for control, self-tuning and evaluation.

In other words, it may be possible to build a calorimeter from inexpensive components, but the development effort will be high.

\* A calibration heater is indispensable for calibrating specific calorimeter reactors (once and for all) and for determining the heat capacity of the reactor contents (from transients, only the ratio of heat transfer capacity to heat capacity  $U \cdot A / m \cdot c$  can be obtained). As a calibration heater is an alien element in synthesis equipment, it is probably preferable to use the heater for calibration only, and to calculate the heat capacity of the contents from the batch recipe by means of a physical property estimator.

A calorimeter for general use in synthetic work will become a commercial success only if

- it is as easy or easier to use than a conventional laboratory reactor,
- it does not require substantially more space,
- its additional costs are clearly outweighed by the value of additional information,

and, last but not least, if the potential users are aware of the opportunities and willing to buy.

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