

# Study of Calo 2000

## Combined heat flow and heat balance calorimetry for crystallization tests

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## 1 Objective

***In order to obtain further information for the control of a process, it must be possible to display calorimetrically the behaviour of a crystallization on-line.***

It is anything but easy to fulfil this demand and it must be developed step by step: first off-line and then on-line.

The following protocol shows the first part of a road which is fraught with difficulties, and the results obtained.

## 2 Starting position

SYSTAG has been dealing with heat flow calorimetry and especially with isothermal heat flow calorimetry for a long time. This has the benefit that with nearly all reactors extremely good measurement results are obtained, because many of the variable factors cannot change or only change slightly.

This is not the case with crystallization, because this can only be carried out in a *temperature ramp* and the *energies* are still *very small*.

One needs to start with a cylindrical 1 liter jacket reactor with the objective of detecting approx. 0.1 Watt or less with heat flow *and* heat balance measurements. A normal thermostat must be used, so that in practice all possible cases can be covered later.

## 3 Measurement principle

Why should we look for a new procedure, when there are already many calorimeters on the market?

With crystallization, and also with other processes (polymerization), changes in thickness can take place on the wall that displays the 'measurement resistance' for the heat flow, which make the measurement useless. The perfidy in this situation is that this can happen gradually, so that possibly the user is not aware of anything. Incorrect error interpretation can then take place.

The aim therefore is to have ***both measurement methods available in parallel***, in order to significantly increase the accuracy of the evaluation.

Both principles are well known:

1. **Heat flow (or HF):** temperature difference measurement between reactor and jacket output with known wetted surface area and wall thickness with conductivity.

2. **Heat balance (or HB):** temperature difference measurement between jacket inlet and jacket outlet with known volume flow, density and specific heat of heat transfer fluid.

The heat balancing in the jacket offers the greatest advantages, because it is largely independent of the thickness of the wall and its wetted surface. Consequently dosages to the reactor are easier to measure and to calculate. With the heat flow calorimetry however the measurement is directly dependent on the wetted surface and the thickness of the wall, i.e. two parameters which can change from one experiment to the next.

But why both methods, when the heat balancing in the jacket is much safer? This has its basis in the quality of the measurement signal. The heat flow measurement gives signals which are approx. 5..10 times greater and can therefore be evaluated with simpler means. Also, the technical effort for a heat flow calorimeter is much easier for exactly this reason. Even so the disruption influences are markedly less, because the outside jacket to some extent acts as a screen.

Therefore, by knowing both signals the best one can always be selected – or at least on the basis of the heat balance signals the error of the heat flow signal can be estimated reliably.

## 4 Influences with heat balance calorimetry in the jacket

### 4.1 Temperature difference measurement in the jacket

Temperature difference measurements between inlet and outlet - you may think there is nothing simpler! We only need to reduce the rate of flow of the heat carrier in the jacket sufficiently, so that the temperature difference becomes sufficiently large and it can be measured in a sufficiently accurately and stable way. That's right – except that the control of the inner reactor can no longer be carried out sufficiently quickly, so that the system becomes extremely slow and immediately starts to oscillate. The rate of flow is therefore set at specific lower limits.

### 4.2 Control of flow in the jacket

The objective is to know exactly how big the heat balance is. Several approaches are open to you:

- a) Measurement of volume of flow, knowledge of density and cp across the measured temperature range.

- b) Measurement of mass of flow, 'virtually no' knowledge of cp across the measured temperature range.
- c) Maintain stability of rate of flow and calibration through calibration heating at the start and finish of the measurement range of the experiment. Further knowledge is then definitely required.

It is clear that c) represents the simplest, cheapest and in addition also the most accurate one (calibration). This is therefore the route that was selected from the start.

### 4.3 Thermostat deployment

Because a universal thermostat is required the Huber Unistat TANGO was selected in the first instance. With the UNISTAT series model it is later possible to cover practically the entire temperature range.

Firstly a cascade controller was used. The master controller was controlled by TR and the target value ramp. The TANGO was used as external slave controller. It's target value was the master controller's output.

Diagram 78dn\_5chNT shows the first result of such a controller with a 0.7l filling and a mixture of H2O + KNO3. Because of the small rate of flow the control can only be kept stable isothermally (with both calibration impulses of approx. 6.2 Watt). In the ramp and with lower temperatures the controller oscillates because of the previously mentioned reasons and a stable measurement is out of the question.

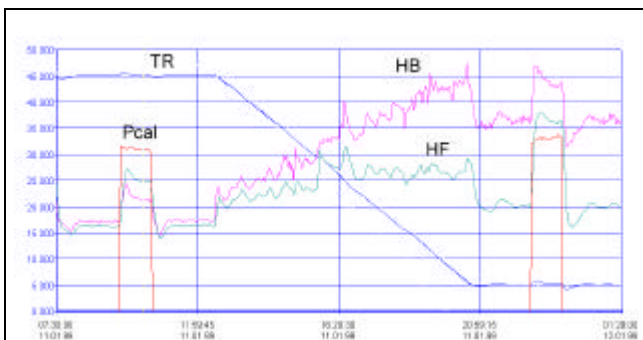


Diagram 78dn\_5chNT

The effective signal of the Heat Balance HB resulting from this was approx. 100 mK. The HF heat flow signal was approx. 700 mK. With low temperatures both measurement signals increase significantly with practically the same calibration power.

Because of this bad starting position the control moves completely to the external (free structure selection) and the UNISTAT from the manufacturer has been converted to an external control as a pure heat/cooling controller device.

The result was decisive. Now the control structure and control characteristics can be carried out externally in such a way that oscillation tendencies can be reduced significantly. Obviously a quick impulse answer can no longer be expected with a smaller rate of flow of the jacket. This somewhat slower control is the price which has to be paid for a combined HF/HB calorimeter.

### 4.4 Further development of the measuring and control

Diagram A12er5dn shows an already significantly better result with very high peaks with spontaneous crystallization of an over saturated solution. Heat balance HB and heat flow HF.

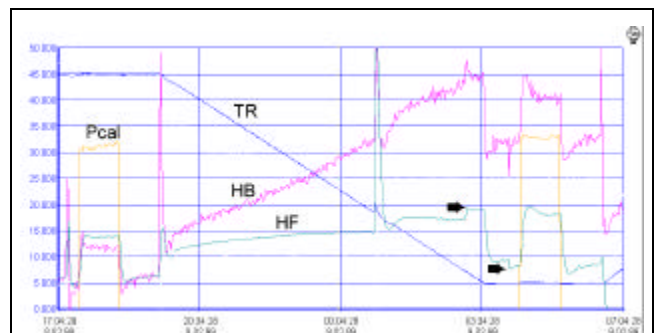


Diagram A12er5dn

Here also the dreaded phenomenon of sudden wall thickening is shown dramatically (see arrows). The heat flow signal increases very suddenly within a range of approx. 8°C and is only brought down again (removed) after a longer time at a constant 5°C. With an – albeit still strongly fading – heat flow only one peak can be seen, which can be compensated for.

It is shown that the measurement resolution and measurement stability must be improved with limited measurement range through precision modules in order to decrease large basic artefacts. The result is impressive, see diagram Nr03dn.

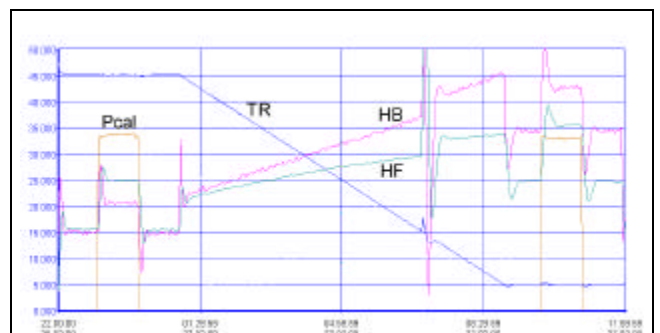


Diagram Nr03dn

With further measures the inlet temperature must now be stabilized at the jacket inlet, so that the

measurement signal becomes quieter. This is successfully demonstrated in the next diagram Nr06dn.

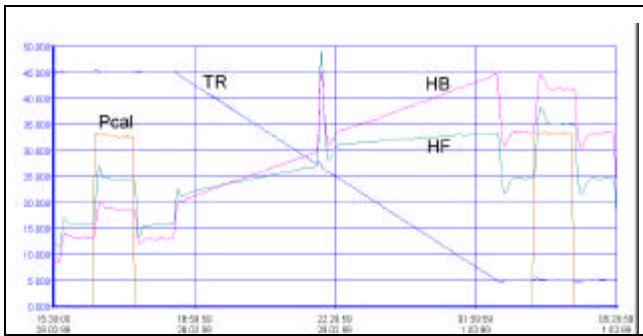


Diagram Nr06dn

In this diagram we see very nicely how the HB heat balance signal changes very strongly with the temperature. The HF heat flow changes also, but this is more curved. Generally for the determination of accurate base lines for evaluation some difficulties can already be foreseen.

#### 4.5 Problems with background temperature on measurement signals

Over time it becomes obvious (see diagram Filt5dn1) that even the smallest change of the background temperature has a big influence on the measurement signal. The experiment with pure water additionally shows quite clearly the extreme curve of the measurement line for the (HF) heat flow calorimetry and also the strongly increasing or decreasing measurement line of the (HB) heat balance calorimetry. Typical experiment demands are: 0.5l water and 5 K/h.

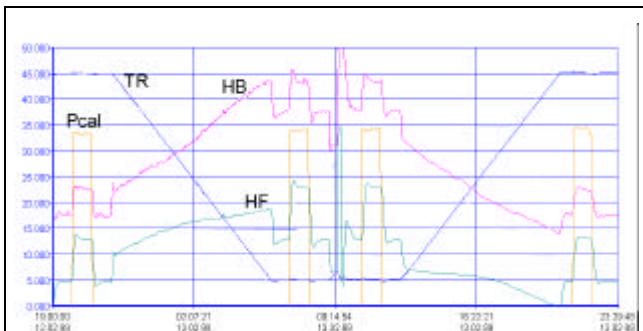


Diagram Filt5du1

For this reason we have no choice but to isolate the system in order to keep control over such influences, so that they can be arithmetically corrected. The system is therefore built in an isolated cabinet. Diagram SR11c\_Part4 shows a step by step calibration with an inner cabinet temperature of around 48 C. The result of the HF zero point signals

is very good, but that of the HB has deviations of up to 1.8 Watt in the middle temperature range. A significant non-linearity is therefore still present. This needs to be eradicated.

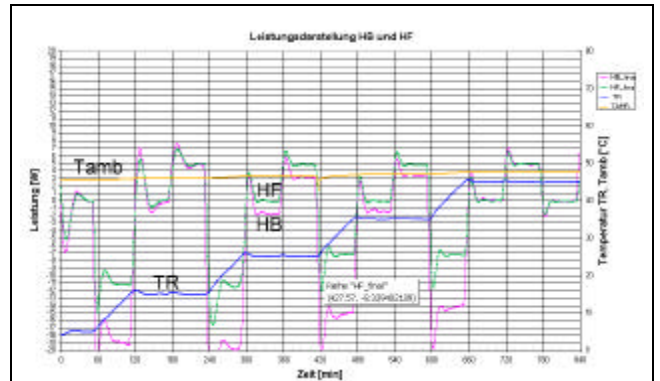


Diagram SR11c\_Teil4

Through heat exchange the cabinet temperature of the reactor temperature was somewhat reduced. See diagram SR21c\_PartWT1. The deviations of the HF and the HB signals are now only marginal and can be compensated away arithmetically.

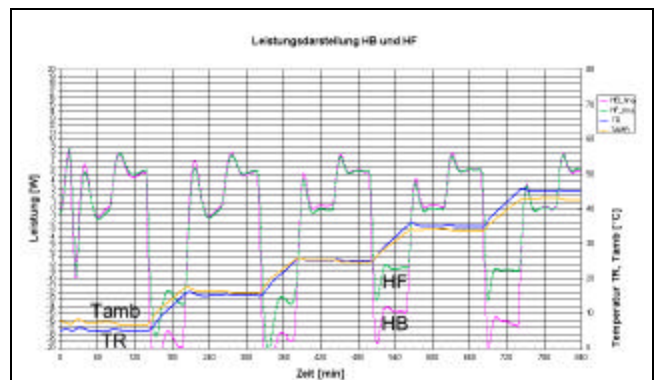


Diagram SR21c\_TeilWT1

Unfortunately a new effect now shows up with accurate evaluation: the evaporation and the continual condensing with inner cabinet temperatures above the outside room temperature strongly distorts the energy balance of the actual reaction. Reason: the inner cabinet temperature always lies somewhat below the reactor temperature. This energy loss cannot be ignored. In addition it is extremely difficult to calculate and for every + 10K increases by approx. double the amount.

We have therefore no choice but to lead the inner cabinet temperature sufficiently above the reactor temperature, so that a continuous condensation of the lid is no longer possible. See diagram FH37cdc\_015.

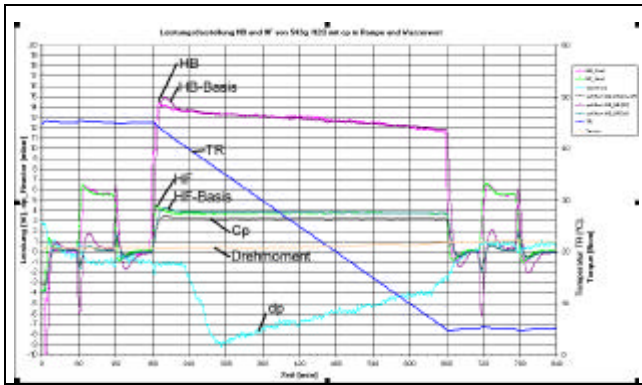


Diagram FH37cdc\_015.tif

It needs to be taken into account that in addition we have covered the system with a balloon, so that the pressure remains somewhat stable and so that above all no solution (in this case water) is lost! At the start of the cooling the pressure however falls (reasons not quite clear, but probably through the shaft thickness of the stirrer, because no magnetic coupling was used). This also manifests itself in a slightly decreased cooling power of the HF signal (approx. 0.1 Watt) and HB signal (approx. 0.2 ... 0.3 Watt) against the calculated base lines.

**4.6 Limits of measurement technique**

The previous diagram FH37cdc\_015 very nicely shows the limits reached currently: overall we can still detect approx. 0.05 to 0.1 Watt, which especially becomes obvious with comparisons. Also, the remaining measurement errors and oscillation (artefacts) can already be determined in this magnitude.

It is possible to move the limits somewhat downward by we expect approx. 10 ... 20 mW. This however again requires a somewhat increased effort. With this magnitude all other peripheral effects now obviously come into play, such as drop forming, torque changes of 1 .. 3 Ncm, the smallest pressure changes of a few mbar, etc. This obviously applies to a really large reactor with a capacity of up to 1 liter (water in our experiments)!

**5 Evaluations**

The first part of SYSTAG's know-how lies in the measurement methods described and the second part in the corresponding mathematical process, which is not publicized.

However in order to be able to calculate for ourselves from the experiment a baseline which is as accurate as possible, we need to know the cp values of the solution. Within small limits it is possible to compensate weak changes across the temperature range with the help of the water equivalents.

**5.1 What do we need in order to calculate accurately?**

- a) A reaction free, isothermal low temperature calibration phase with an extremely stable calibration heating power (approx. 5 Watt).
- b) A similar, isothermal high temperature calibration phase.
- c) Knowledge of the exact feed weight of the solution and all educts with their cp values.
- d) At least one stable reaction free phase within the temperature ramp for a fine alignment of the continuously calculated water equivalent.

→ **Consequently we have successfully reached the target of the original demand!**

**6 Restrictions for realization of any calorimeter**

This highly sensitive measurement system needs some reference data from the reactor and its surroundings. The operating conditions are also subject to certain conditions which are listed briefly below.

- 1) In addition the reactors need to be well isolated, so build them into a temperature controlled cabinet. With glass reactors triple jacket types with evacuated outer jackets are useful. Steel autoclaves must also, additionally be isolated.
- 2) Each reactor must be measured individually and its reference data must be made known to the system in the form of tables. Consequently it also becomes possible of course to exchange reactors, except that measuring is a time consuming event.
- 3) The thermostat must be tuned to the cabinet size, the reactor and the process temperature. Too much or too little power is not conducive to a high accuracy.
- 4) The cabinet must be adjusted to the system's temperature range. Temperatures over 180°C are more difficult to realize. Temperatures in the minus range up to -40°C are possible without problems, but lower temperatures are again somewhat more difficult.
- 5) Because of the heat balance measurement the heat conducting circulation can no longer be as

large as you would like. The reaction times of the reactor system are therefore somewhat longer than for the conventional heat flow calorimetry. It is also possible therefore to calculate with somewhat longer oscillation times.

- 6) The heat conducting fluid must also be measured and known. You can't just fill in anything!
- 7) The user must always work in a closed system (by closing all openings completely). This is necessary as long as evaporation and condensation energies can falsify the measurement result.
- 8) With reaction calorimetry with the smallest results the same applies, i.e. all 'heat pipes' must be 'isolated' in the zone outside the cabinet, for example with leads or siphons, which are filled with liquids
- 9) A reflux itself must also always be measured calorimetrically. Drawing off of a distillate also produces such a 'heat pipe', i.e. as a consequence the measurement errors increase. On the other hand, with distilling we are generally dealing with significantly higher energies, so that this problem retreats somewhat into the background.

## 7 Measurement examples

### 7.1 Test run with water and calibration heating, also in ramps

To make sure that the system measures correctly, a test run with a slow ramp is carried out. Within the ramp you heat twice. See diagram FH15cu3c.

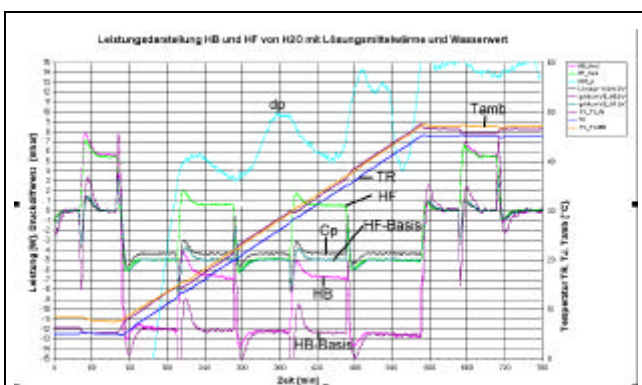


Diagram FH15cu3c

The power measurement between the base value and effective measurement value remains stable and corresponds exactly with the calibration heating power.

### 7.2 Cooling down of a solution from potassium nitrate in water, -5K/h

**Experiment demands:** 240 g KNO3 and 545 g H2O. Reactor closed with balloon but however not closed very tightly (reason not known). Anchor stirrer at 100 rpm. Everything made from glass. See diagram FH39cdck.

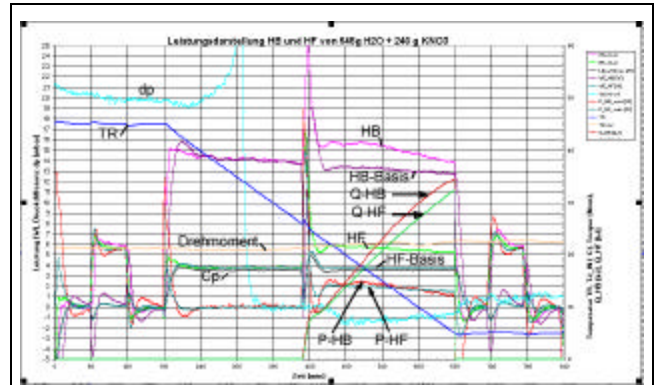


Diagram FH39cdck

The HB and HF power curves from the start of the crystallization up to 5°C below in the heat flow show a less strongly decreasing power than in the heat balance signal.

The integration within the range of the crystallization start up to 5°C is displayed with the Q-HF curve for the heat flow and with the Q-HB one for the heat balance. The measurement shows that the balance shows fractionally more energy. The cause is not quite clear yet. Perhaps small measurement errors can play a part.

### 7.3 Heating up a solution from potassium nitrate in water, +5 K/h

**Experiment demands:** 240 g KNO3 and 545 g H2O. Reactor closed with balloon, which however was not really tight. See diagram FH40cuck.

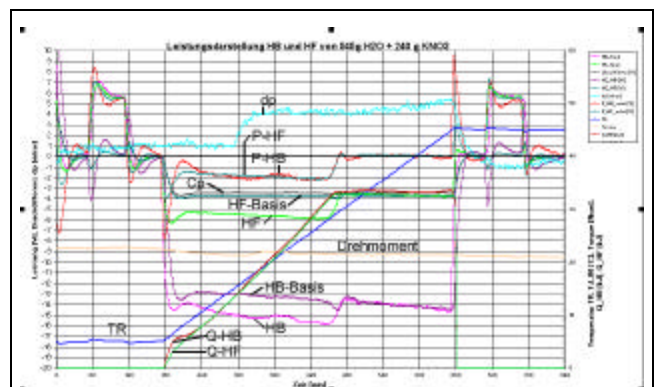


Diagram FH40cuck

The P-HB and P-HF power curve from 5°C up to reaching the full solubility shows the behaviour.

The integration within the range of the ramp start at 5°C up to the end at approx. 30°C is displayed with the Q-HF curve for the heat flow and with the Q-HB curve for the heat balance. The measurement shows that the balance shows fractionally more energy (but less than before).

### 7.4 Cooling down of a unstirred solution of potassium nitrate in water, temperature ramp -5 K/h

**Experiment demands:** 240 g KNO3 and 545 g H2O. Reactor closed with balloon, which again was not tight. Anchor stirrer at 0 rpm, i.e. a **completely quiet solution**. Equipment is glass. For results see diagram FH41dor.

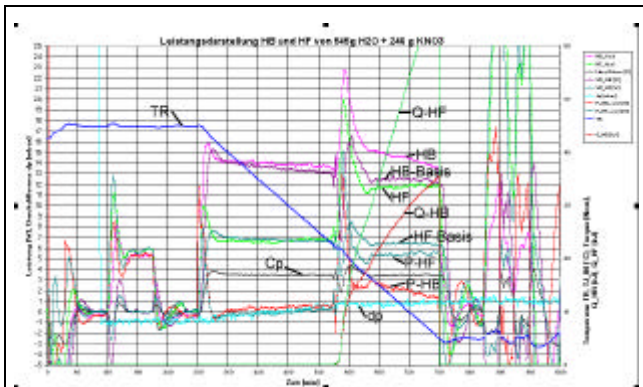


Diagram FH41dor

These curves demonstrate very nicely that something has changed. The water equivalent of both types of experiments has changed: with the heat balance by approx. -22% and with the heat flow by approx. -15%. Apart from this correction nothing has been changed with this evaluation from the previous experiment FH39cdck under 7.2, because even the calibration at 5°C could no longer be used. The controller can no longer work correctly because a complete "KNO3-cake" has formed at the bottom of the reactor.

**Result:**

- ⇒ Significant is that the heat balance measurement, despite different behaviour of the water equivalent, gives rather sensible results, which can no longer be claimed of the water flow!
- ⇒ Even for such critical situations, it must be possible to take the calibration factors of previous experiments and an automatic calibration is therefore no longer necessary!

### 7.5 Heating up of a solution previously cooled without a stirrer with KNO3- "cake" at the bottom around the stirrer (+5 K/h)

**Experiment demands:** 240 g KNO3 and 545 g H2O. Reactor closed slightly and at the bottom there is a whole clump of potassium nitrate around the anchor stirrer. The stirrer is started up carefully with 40 rpm and the calibration is started by heating up. See diagram FH43cusr.

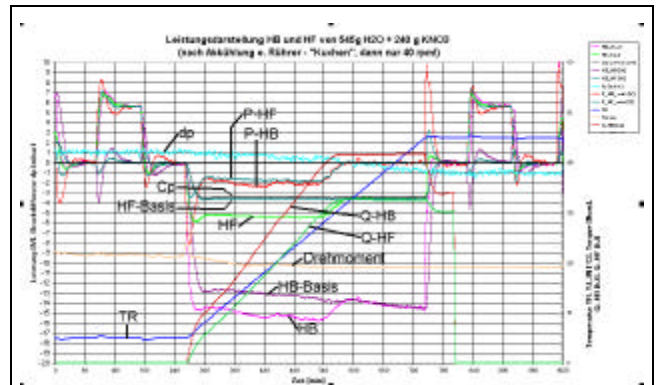


Diagram FH42cusr

The P-HB and P-HF power curves from 5°C up to reaching the full solubility show the behaviour.

The integration within the range of the ramp start at 5°C up to the end at approx. 30°C is displayed with the Q-HF curve for the heat flow and with the Q-HB curve for the heat balance. The measurement shows that the balance shows fractionally more energy when this crystal clump has a special effect (especially at the start of the heating up). On the other hand the heat flow integration gives more or less the same values as before. We have not yet examined the phenomenon further and at present cannot give the answer.

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## 8 Summary of advantages and disadvantages

### 8.1 Heat balance calorimetry against heat flow calorimetry

+/-	Heat balance calorimetry	+/-	Heat flow calorimetry
+	Generated calibration parameters can be pulled down as first approximation information for <b>on-line information</b> without further effort, because the dependency on the level of filling, the thickness of the wall and the zero point shift is extremely small. However, the complete result is always displayed. It is however possible to calculate a directional value for the water equivalent and the reactor contents on-line. The resulting power of the reaction however must be viewed as directional values. Only after an exact calibration and correction are the exact values available.	-	The <b>zero point and the sensitivity fluctuate</b> so strongly that a sensible on-line display is impossible.
-	The water equivalent is very large, because the entire outside jacket wall is added.	+	The water equivalent is really small, because only a part of the inner wall and the cabinets used count.
-	The signal strength is small: in the order of approx. 20 mK/Watt.	+	Large signal (approx. 200 mK/W), which is dependent in the inner wall thickness and the material.
+	Not very dependent on the level of filling, the network (also thermal build up during strong stirring), the stirrer oscillation and the wall thickness.	-	A strong dependency of $U \cdot A$ , the thermal build up (increase of $A$ ) and the stirrer oscillation with higher viscose media (wall film)
+	Ideal for crystallization and higher viscose media.	-	Partly unusable with crystallization and high viscosity.
+	Measurements are also possible in an unstirred condition (for example very slow ramps)	-	In unstirred condition permitted measurements are no longer possible.
-	Very strong dependency on the ambient temperature.	+	Very good protection from the ambient temperature.
-	Because of the reduced heat conducting fluid slightly reduced operating oscillation.	+	Because of the high change over oscillations of the heat conductors, there is a quick impulse answer.
-	Not every thermostat is suitable for the control, because only small fluctuations are permitted at the jacket entry.	+	The thermostat is no longer critical, because it is measured at the jacket outlet, where the signal has already been filtered adequately.

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