



# Calo 2000

## CLIENT asks, SYSTAG answers

### Frequently Asked Questions about Calo 2000

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## Common questions most frequently asked about the Calo 2000 system

### Original questions from clients about the Calo 2000 system

*The following original questions have been asked by clients and will certainly give you answers to your own questions. The blue titles have been inserted by us in order to better classify your questions.*

#### Questions from the engineering viewpoint

**To get the perfect isothermal condition, that means constant temperature even if very big heat arises, how does your system design behave in terms of**

- a) **The circulation system and the circulation media, its volume**
- b) **The connection between the circulation system and the reactor**
- c) **The temperature control and other control systems**
- d) **The design of the reactor vessel**
- e) **Other parts related to this point**

We are also cooking only with water as are all our competitors! Therefore no miracle is possible.

We do not get a perfect isothermal condition at all! This is the case if you have a system without any masses and with infinite heating and cooling power possibilities. As soon as some masses are included together with finite heat transfer resistance we always get some exponential functions approaching an end temperature, and therefore there is a limited stability imposed for a physically controlled system. You can never reach an ideal control as long your system is not very accurately known. This is always the case because you are adding components and so on. The situation also changes by evaporation and chemical reactions... Therefore we have to forget the ideal isothermal control.

First we have to ask for what do we require an ideal isothermal control?!

The answer is simple: if an ideal isothermal control is achieved, we can neglect the cp of the content as well as the water equivalent value (WE) of the reactor and all probes inside. On the other hand, in a plant you can never reach such an ideal situation. Therefore you must learn to live with a non ideal situation in any case.

The main goal of a heat balance calorimeter (HBC) is to obtain a "very controlled" control situation without any oscillation (this would be the end of heat balance (HB) determination). The result of such a poor control is that a real isothermal condition cannot be reached. How to proceed?

During reactor temperature (TR) changes, the cp of the content as well as the WE (water equivalent value) must be calculated continuously. This is the case with Calo 2000. The resulting advantage: you can also work without cascade (reactor) control, you can change to the opposite, the jacket control mode with much larger temperature changes of TR and also get a very good result.

The limits of the system are comparable with other systems. The temperature difference for cooling depends mostly on the heat flow resistance of the wall between jacket and content, and also from the stirrer speed and circulation flow. Because of a reduced circulation we have to use a novel idea to get a good circulation around the inner reactor: we use a jet stream which is injected by high pressure. We have a good rotation and a slower speed from inlet to outlet to increase the sensitivity for heat balance measurement. To get an idea about the ratio: The temperature difference from reactor to jacket is about 5..10 times larger than the inlet to outlet of the jacket. If you require a temperature difference of about 15 °C for 100 Watt for HFC, the difference for HBC is only about 2 °C. In fact the total difference is about 1 °C larger (slower flow in the jacket) than with a heat flow calorimeter, like RC1. That means the thermostat must be able to cool 1 °C lower as in a normal HFC.

The reactor vessel is designed as a triple wall reactor in a temperature controlled cabinet. A cylindrical reactor is better than a conical one, but conical reactors are also possible. The reason is the stirrer inside and it's efficiency, a good stirrer is half the calorimetry! The second reason is the different rotation speed at the outside of the heat transfer fluid.

#### Dynamic behavior

**I suppose that in any of the current reaction calorimeter systems the dynamics are not considered fully. But in any elements or units, some kind of dynamics exist like the delay. The temperature sensor, the circulation system, the control devices, and the reactor wall all have dynamic characteristics, and they respond to the input signal with some delay or dead time.**

**Why does the current system have the perfect dynamic compensation for the calorie calculation? Or how do you design around the dynamics you consider?**

You are right, dynamics and time lags are important. We do not claim that we have considered everything (a „perfect“ dynamic compensation) but at most we have used some simplified models, otherwise you can no longer handle it. We also have limits to the complexity of such systems like a calorimeter. The difficult act is to find a

balance between sensitivity and speed. We have done it with some compromises. To get a sensitivity of about 50 mW we are forced to filter some signals. This limits our speed of a step response (time used from 10% to 90%) to about 150 s. This is also reached if you see some time lags from raw measured temperature values of about 10..20 minutes!

The correct time behaviour is not given in all situations: if the system comes close to boiling temperature, it changes strongly because the cover is significantly thermally connected to the content, this is similar to a change of A as well as of WE.

Only by reduction of such filtering can the response time be reduced, but it's not in discussion at the moment.

### Experimental technique

**To get accurate data, is there anything to consider in the experiments using your system? I want to know if there is any experimental technique difficult to inexperienced researchers. For example, connection between the reactor and other units and experimental conditions.**

Yes, some restrictions are necessary! One point is the tightness of the reactor. For calorimetric measurements you must avoid evaporation otherwise it will mask your chemical energy in any non-isothermal condition. In isothermal condition, it can be calibrated by the calibration heater. But if you are tight, also without any calibration you get rough information directly in Watt about your process because you have calibrated the system earlier. To be sure if the system is nearly (not absolutely) tight, you have pressure indication. Also we solved the problem of working in a glass reactor under large temperature ranges with large changes of pressure. The system has a security valve and is also controlled by short venting, if pressure goes up. If you vent once instead of continuously you lose only a few Joule instead of kJoule!

If you are using dangerous solvents, you must use N<sub>2</sub> for the cabinet, normally 1 l/min. During cooling down it will be increased automatically (by control) up to 8 l/min to compensate for the contracting gas volume in the cabinet. Otherwise air would be sucked from the outside into the cabinet.

If you are working below room temperature in any situation you should use dry N<sub>2</sub> to prevent any humidity condensation inside the cabinet which also leads to errors, and vice versa to avoid any ice melting thereafter.

### Multi purpose use possible?

**I am dissatisfied with the current calorimeter system, that is, as the system is too customized for this purpose only, the working rate in terms of time is very low. If this system can be used for other purpose like sample purification, or batch distillation, the system can be utilized much more.**

**Do you have any idea to increase the working time of the calorimeter?**

You are speaking from my heart! Most people are doing development and sometimes they require more or less accurate calorimetric information. At any time a calorimeter must be a good automate for daily lab business.

Our concept is - since we are producing calorimeters anew - to help customers with process development (repetitive tasks). All our systems are automated laboratory reactors with a very good recipe system combined with a very good manual control. If a recipe is running the chemist can intervene manually at any time and immediately. All these actions, by recipe or manually, are written in a report and alarm file. You can therefore reconstruct your process later with all details.

### Computer and operating systems change so fast, what about that?

**Computer technology changes rapidly. Every two or three years, the personal computer operating system or the CPU type and other devices change. For these circumstances, how do you design for the calorimeter system?**

We have seen this development. Our first automation development was the PC-COMBILAB in 1985, for which we used QNX (like the RC1). In 1990 we developed (no, we only started) the QNX-Windows for the PC-COMBILAB, but after half a year we saw that this was the wrong direction. We therefore stopped any further QNX applications and changed to Windows 3.1. Together with this change we saw that the development of process control systems was too big for us. We evaluated the market and found FIX which was on the market since the PDP-11 era (1975) and was always up to date for new operating systems!

Since 1993 we have used two operating systems: the 3.11 (one system was for a pharmaceutical production plant which was validated by the FDA!!) and now the NT 4.0. Maybe in one or two years it will be Windows 2000. Also FIX has developed permanently from version 4 to version 7. We will always be in this mainstream.

### If less costly, more would use it, what do you feel?

**It is said that the lower the cost of the calorimeter system is, the more chemists and chemical engineers are trying to have and to use the calorimeter. What kind of comments do you have about this?**

This is also correct. But calorimetry is a very sophisticated part of chemical engineering and not many people have sufficient knowledge, it's bitter to say that but it's the reality. Therefore we see the market as follows:

- 1) Most users like to get a cheap automation with some simple calorimetry, if any calorimetry is necessary. Most

of them are happy if they know that it would be possible to upgrade it later to a calorimeter. Our answer: Use one of the laboratory reactors LR-M up to LR-XL or the SYSTAG HF calorimeters SC2 - SC4 (see our homepage). Isothermal HFC is and will be the most used calorimeter method because it's simple and cheap. As an upgrade with Calo 2900 you can expand all these calorimeters to a non-isothermal HFC.

- 2) For professional people a real and dependable calorimeter is necessary, which can be one of the Calo 2000 series. But working and understanding require much higher skill, also a lot of experience is necessary for such good work.

**Conclusion:** both user groups will get the best fitting system for their needs from SYSTAG.

### What about all influences like heat loss, cp and dT of addition, level changes etc.

To measure the accurate reaction heat, many items listed below might be considered. We would like to have your comments about it.

- 1) Heat loss from the reactor sidewall or the top of the vessel
- 2) Heat capacity and temperature of the titration liquid
- 3) Heat from the agitator rotation
- 4) Liquid level deviation or pressure deviation
- 5) Heat loss from the condenser

You mention here nearly all the influencing factors we have also learnt! My comment:

#### 1. Heat loss from the wall and top of the reactor:

For HFC this is not as evident as for HBC. In HFC the jacket is a very good insulator from the outside.

But for HBC and HFC the cover has two different problems: As long as the solvent is at low temperature there is not a big problem, because you can measure the heat flow through the cover as well as all probes inside to the reactor content.

As soon as the temperature approaches the boiling point however the vapor acts as a heat transfer medium and "switches" the cover to the content. During this it depends on the cover temperature what happens:

- \* If the cover temperature is higher than the reactor temperature, the cover acts as an additional water equivalent value and as a heat transfer bridge to the outside, energy is put into the system.
- \* If the cover temperature is below reactor temperature you not only have the increase of WE and the heat flow bridge (in the opposite direction), you also get a reflux system which is taking energy from the reactor content!

This heat pipe is well known and has to be compensated for during evaluation. What should be done? We have solved the problem by a small temperature increase of the outside to the inside which is following the working temperature of the system. That's the reason for the temperature controlled cabinet!

#### 2. Titration liquid heat capacity and temperature

We must know these values for a good compensation. You can decide how accurate the knowledge must be: If you have a very slow reaction energy, it's critical. If the reaction energy is large, for the same percent error you can have less quality of knowledge for cp and dT. In any case, we measure the temperature of the addition immediately at the inlet to the reactor and calculate with a given cp. The compensation is accurate enough for most applications.

#### 3. Heat from the agitator rotation

The same applies to the agitator. We have knowledge over the whole temperature range of the "empty torque" changes by viscosity of the flexible shaft (about 6..9 Ncm). We compensate it by calculation. The remaining error is approx. 0.5...1 Ncm. If the speed is high, the error may be in a range of 0.25 up to 0.5 Watt.

#### 4. Liquid level deviation or pressure deviation

We must distinguish between HFC and HBC:

- A) HFC level deviation: for changing levels we calculate the A by all filling masses, (knowledge of density) and the vortex from the stirrer (must be manually "measured" and entered). As long we are far away from boiling point it works well, but near boiling point the same situation as mentioned before happens and can lead to an overcompensation, because of calibration.
- B) HBC level deviation: nearly independent, only near the boiling point some small deviation is possible.
- C) Pressure deviation is also a chapter! As mentioned before a high vapor pressure leads to a high heat transfer but is dependent on the gas. As soon as we are in a steady reflux state there are no problems because of the stable situation.

As long as we are about 10..15°C below the boiling point and have a tight system, there are no big problems. The change in WE can be tuned (not on-line) but during evaluation by a square equation which leads to a very accurate base line. We have done this with Ethanol and Water, both used for crystallization with about 0.5 to 3 Watts of crystallization energy and got very good results over a range of about 60°C.

## 5. Heat loss from the condenser

This is under investigation. The vacuum insulated reflux separator and condenser are very well insulated. We can see that with the TH (head temperature probe inside the reflux separator) which is very stable and stays at the old temperature for a long time if we change the cabinet temperature. Also the temperature difference to the reflux condenser is constant by our cabinet temperature control and can therefore be calculated.

### Comparison with other calorimeters

**To select the calorimeter and its supplier, a customer must know the true capability and the comparison with other systems supplied from other suppliers. Regarding this point, please let me know the comparison between your system and other systems in terms of the calorie measurement and its method, the accuracy, and the flexibility.**

As you know many people are working on a useable heat balance calorimeter but SYSTAG is the first to realize it in a professional way. Also some are studying the problem of the changing U from HFC during crystallization or polymerization. One idea is from Prof. Reichert, Berlin, which will be adapted to Mettler's RC1. The problem, which is not solved, is the addition with changing A. It's only valid for a batch calorimeter. We see that the HBC is very complementary to HFC, therefore from the same experiment you can get the results of two measurement methods with the SYSTAG calorimeter. The remaining problem is to decide which measurement is valid! You don't have this problem with RC1 or SIMULAR because you have only one result. You have to take it or to leave it. But with two different measurement methods at once you can decide depending on the results and the experiment. If a viscosity change is expected, you can see when it happens and then choose the HB results in preference to HF. The same occurs with crystallization. We have seen that for a ramp down HB is better, for a ramp up HF and HB are both ok.

HF gives more signal and is less complex in mass, delay and time lags, therefore the curves are "cleaner". HB has more oscillation effects because the system is more complex and the model is a simple one.

With HF and HB you mostly see - because they are complementary - the limits of the results (not always but mostly). Therefore you can determine a "confidence range". If the deviations are about 5..10% then the experiment was running ok, if you get more, you must be careful and investigate it further.

To get an accuracy of less than 5% in any case you must very carefully adjust the experiment with two calibrations. With such adjustment you'll get about 1..3%.

If you are interested only in an approximate value you can use the HB information without any calibration which is also given on-line. For approximate information

(some Watts error) this is ok. This saves a lot of time for all these calibrations, cp determinations and so on....

### How to speed up experiments?

**We are now using a well known calorimeter, but we are not satisfied with the system because it takes a long time to get the result. Through calibration, Cp measurement, calibration, measurement, calibration, Cp measurement, calibration. We are searching for the quick procedure to get the real result.**

This procedure is the best in some cases but not all. What we have found until today is: If a very accurate result is necessary, a calibration must be done before and after the experiment in the isothermal mode (but at different temperatures) and be reaction-free. Between these two calibrations (or after) we require a ramp, also reaction-free. The basic equation in a ramp (and in general!) is:  $P_{Cp} + P_{WE} + P_{stirrer} + P_{reaction} + P_{loss} = P_{total}$ . If we have a reaction-free zone and have knowledge of the remaining four parts, all is easy.

But normally you don't know everything exactly!

- \*  $P_{stirrer}$  is measured and is normally approx. known +/-1 Watt, except that for low energy experiments it's necessary to tune it.
- \*  $P_{Cp}$  is known mostly by the components or can be estimated, but not exactly
- \* WE is the same, from calibration we know it approx., also the temperature behaviour is known, but not exactly.
- \*  $P_{loss}$  is calibrated and compensated

What we are doing: we estimate the cp and calculate the Cp-mix continuously and use this value, which is very accurate because the majority is solvent which is not fully used during the reaction and therefore remains stable.

Also the same occurs with WE. But at the end, the sum does not correspond with the measured value! Now we adjust the equation parameters in such a way as to fit the reaction-free measurement exactly. If we have a ramp part of about 20..30°C difference it can be fitted very exactly. With this fitting we have compensated all the remaining errors from Cp, WE, stirrer and  $P_{loss}$ . We are in the end not interested in the parts separately, we are looking only for  $P_{reaction}$ . That's the reason, we can do that. A similar but less accurate approach is the cp determination from Mettler's RC1 with the very inaccurate WE (only at 50°C).

### I do not like a Black Box, how does Calo 2000 work?

**From the point of view of the design or design concept, we want to understand why the basic system design gets the real value or calibrates the raw signal. Almost all instruments are like a Black Box at this point, not an open system. Our user should understand it.**

First I recommend a training at SYSTAG (or at the customer site, but then they are more disturbed by daily business!). They will get a basic knowledge and understanding about calorimetry, the different types of calorimeter and all about influencing parameters.

The basic design was described previously. Before we change from the "Kelvin" range we calibrate the system. The influences of heat transfer fluid, the ambient temperature and the cabinet temperature will all be calibrated. Therefore the "raw" signal is no longer "raw", it's already calibrated concerning the above mentioned influences. Thereafter we change to the "Watt" range. From this moment we can give results which are already good (not yet very accurate but good enough for a first judgement), also additional correction will be included for change of area A (only for HF). The resulting information can be given on-line. Later it can be fine tuned to an accurate zero and span as well as for an accurate WE (and cp, stirrer, and P\_loss) correction.

### Calo 2000 is very sophisticated but what will other competitors do in the future?

We understand that the CALO 2000 system is a very sophisticated system but we want to know if this is a trend or not, which means that all other competitors will follow the same new technology of CALO2000 in the near future.

If I'm God I can give you the answer but as I'm a human I cannot say yes or no.

If a supplier is to survive in the long-term he has to develop a system which fits customer needs. If more accuracy is necessary any competitor has to develop new principles and systems.

The main problem is the very expensive and time consuming development. Also very wide and deep knowledge is essential. We do not believe that many competitors are able to develop such a system in their own house. Maybe some suppliers will stop or are searching for cheaper ways (for them, not for customers). But something must happen because too many people are afraid about the situation today.

### Questions from a pharmaceutical developer

Because we are active in a very specific field of pharmaceutical development, we would like to find out how the Calo 2000 solves the following problems.

1. How is the baseline measured before and after the reaction?
2. How does one obtain the exact baseline?
3. How is the cp of the reactor content calculated?
4. How is the permanent WE calculated?

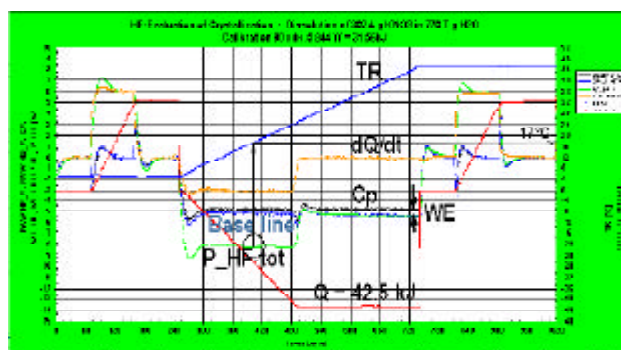
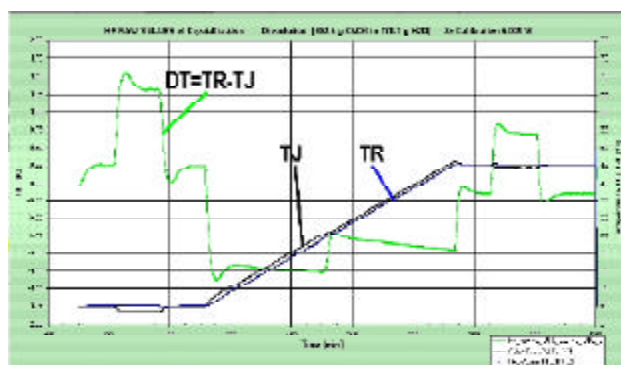
### Could you please clarify the technical background for us?

Some of these questions have already been clarified in some detail above. We don't want to go into any more detail, because that is not in the interest of SYSTAG (know-how divulgence).

### Problem baseline determination

#### How can the Calo 2000 find the correct baseline in the "non-isothermal" mode?

In the top diagram we see the green line. This portrays the measured temperature curve (TR\_TJout). As you can see, dissolving KNO<sub>3</sub> lasts from 250 minutes to 500 minutes, and from 5 to 25°C. After that, i.e. above 25°C no further reaction takes place (dissolving of crystals). We also call this a reaction free phase in the ramp.



We can therefore enlist the behaviour of the temperature difference between TR\_TJ\_out as calibration for the water equivalent (WE).

On the other hand we use the calibration power in the isothermal mode at 5°C and 45°C in order to calibrate the different behaviours of oil, glass etc. With this we achieve the same sensitivity for the 6 Watts power at 5°C as at 45°C. That is the basic principle of the Calo 2000 (and a bit more which we can't reveal however, since it is our know-how).

With this segment we are now in a position to calculate the baseline from 5°C to 25°C (see bottom diagram). After we know the correct baseline we can calculate the real power of the reaction (solution of crystals) dQ/dt very accurately.

The accuracy is 50 to 100 mW across the entire process range (Calo 2100).

### Does Calo 2000 also needs entries for water euqivalents of sensors, stirrers etc.?

A factor for the water equivalent correction can be entered with RC1 reaction calorimeter. Consequently sensors such as Pt-100 sensor for TR, calibration heating and obviously also the stir shaft can be compensated. This factor is obviously dependent on each reactor type. This factor is however only applicable to a process range of 50°C. In the meantime I know very well, that the cp of glass can change by more than 30% in a range of -30°C to +130°C! My final question: does Calo 2000 also need such a factor for the water equivalent or not?

As we can see, you have understood the problems! An example: the water equivalent of a glass stirrer in a 1 litre reactor at 50°C is approx. 75 J/K. This is almost entirely negligible with a reactor with approx. 1000 g glass and a varying temperature.

#### About temperature coefficient:

Most materials in the reactor are first compensated away with mathematics (not just varying cp but also the heat conductivity and the time delay of the measurement signals in the system)!

The residual error, which remains after that, such as unknown behaviour of the heat transfer fluid (HTF), cp and thickness as well as mix from steel, glass and PTFE in the system are calibrated in advance by SYSTAG across the entire process range with a calibration programme!

Alternatively the client can do it himself with supplied recipes and transmit the data obtained to SYSTAG. We then calculate the correction value across the entire process range. This results in the highest flexibility for the customers, in order to use their own reactors later.

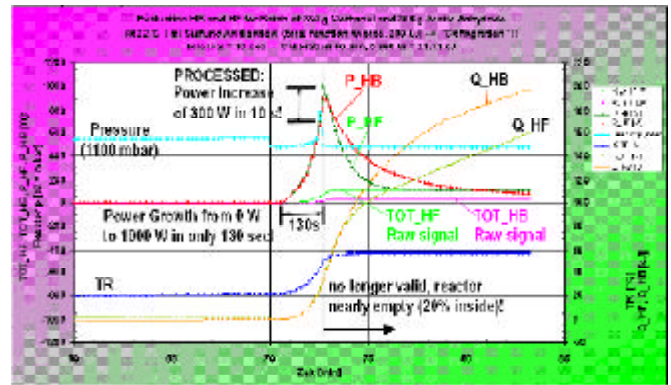
### Some remarks about the following questions

On our folio (see next diagram) an experiment with 3 mol acetic anhydride as batch in 12 mol methanol is illustrated. This experiment was started as batch at 20°C. Later the reaction pops, whereby an immense overpressure occurs in the reactor, the reactor lid temporarily lifts and 80% of the contents are blown into the cabinet! Obviously therefore the results can no longer be evaluated representatively!

We therefore base the following questions partly on a lack of information from the client. After this incident the system is switched off with the Emergency Off key, because there is a risk of explosion. The measurement however continues.

### Is the experiment actively controlled?

Can the data from the experiment from part 1, page 18 (see above diagram) be explained to gain a better understanding?



Was this experiment carried out in an active or a passive mode?

On the basis of the data it appears the active control was selected, but the reactor temperature however does not return to the original value after the puffing. Why is that?

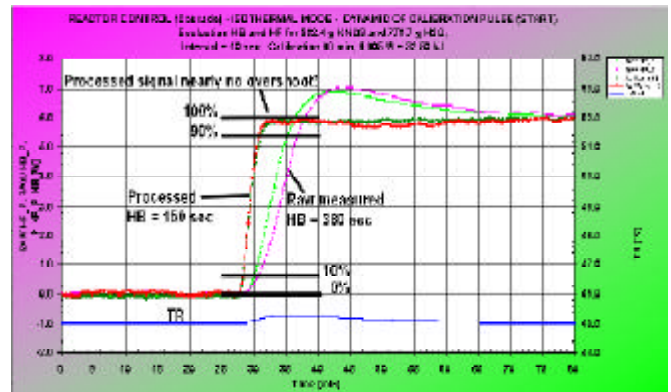
Depending on your version (active = reactor control, passive = jacket control) the experiment is carried out in the active mode. The system was immediately switched to the emergency off position after the popping and all consumers are switched off (danger of explosion!). The data recording however continues but each control will by now be out of operation.

### Can I calculate the water equivalent easily on the basis of the experiment and the material data?

In this experiment a methanol cp is assumed with 2.52 J/g at room temperature. When we assume a cp of 2 J/g.K for the acetic anhydride and with the difference of the reactor temperature calculate the water equivalent WE, we obtain another result as is given in part 1 on page 18. Why is that?

$$„WE\_total“ = (384.0 \text{ g} * 2.52 \text{ J/g.K} + 306 \text{ g} * 2 \text{ J/g.K}) * (58 - 20 \text{ K}) = 60 \text{ kJ}$$

The calculation is not as simple as it may seem! This calculation gives the cp and not the WE. The WE is the heat which is needed to temper the used part of the reactor with probes and stir shafts etc.



Firstly: the delay time, which occurs with the measurement, is at least 60 s. In the above diagram you can see approx. 100 – 150 seconds (from part 2, page 15). With this 150 seconds however the delay time of the calibration itself is also obtained! If this time is taken into account, then the measured signal after popping is 120 kJ at approx. 60°C. The thermal behaviour however has changed considerably after the ventilation (popping). Oil circulation is no longer available and as a result it takes longer to measure a temperature difference. Furthermore, this differential measurement is no longer meaningful because of the missing circulation.

As can be seen from the diagram, the total heat  $Q$  from the HB signal reaches approx. 200 kJ, approx. 10 minutes after Power Off. This result is of course no longer meaningful! The theoretical heat of the reaction lies at approx. 67.9 kJ/mol. The signal of approx. 200 kJ (read from the curve) is not so far removed from the theoretical 204 kJ for a 3 mol usage, but is nevertheless not reliable.

The WE is calculated via the evaluation software and subtracted from the measured total power of the HB and HF signals. The same happens with the sensor  $c_p$ , etc.

The reactor WE can be compared with the result of the above evaluation. With this experiment some 4 kg glass take effect in the HB signal. Here applies: 4000 g glass with a  $c_p$  of approx. 1 J/K.g and a  $dT$  of 38 K results in a WE of approx. 152 kJ.

From this can be concluded that the reaction power is calculated from the  $C_p$  of the sensors etc., and the WE of the reactor and the measured Delta-T ( $T_R - T_{J\_out}$  for HF and  $T_{J\_out} - T_{J\_in}$  for HB).

The sum of these components is used for the calculation of Q-HB and Q-HF.

#### **Additional remarks**

In order to be able to interpret the results correctly, sufficient basic knowledge of calorimetry must be available, especially about how the Calo 2000 basically operates.

The above way of looking at the problem of interpretation shows that across the world there is a requirement for instruction in the field of calorimetry. SYSTAG therefore offers specific courses. Investigate these by looking at "Coaching to Success" at your nearest representative.