



Calo 2000

- A little theory**
- Principle of heat flow & heat balance calorimeters**
- Sensitivity & Dynamics**
- 4 operation types:**
 - 1) Reactor- or 2) Jacket Control,
 - 3) isothermal and 4) non-isothermal

Chapters

A little theory and practice about calorimetry

Principle of heat flow and heat balance calorimeters

A characteristic of Calo 2000: high sensitivity with extreme dynamics at the same time!

Something special of Calo 2000: All 4 basic operation types of experiment are possible

Absolutely unique of Calo 2000: Reproducibility and accuracy

Last, but not least another feature of Calo 2000: Excellent reaction dynamics

A little theory and practice about calorimetry

The first genuine non-isothermal reaction calorimeter

The Calo 2000 system: a revolutionary new development. For the first time a real non-isothermal reaction calorimeter is available with sensitivity as never before. Its area of use are processes which until now were difficult to access by reaction calorimetry, such as crystallization, polymerization and fermentation and where reliable data are required about the processes' heat power.

All reaction calorimeters currently on the market are based on developments back in the early 70s and 80s. These technologies were never substantially developed any further, even though they fail to match the requirements of many processes in a variety of respects. It has not been possible, for example, to obtain reliable results for crystallization, fermentation or polymerization processes. This is due amongst other things to the fact that the reaction calorimeters in these processes have to be highly sensitive at variable reactor temperatures. Through a revolutionary new development – the "CALO 2000" system – we now have at our disposal for the first time a genuine non-isothermal reaction calorimeter with hitherto unequalled sensitivity.

In principle, two basic methods of reaction calorimetry are known: heat flow calorimetry (HFC) and heat balance calorimetry (HBC). Various derivations and combinations of these two techniques are available on the market, but they can always be traced back to these two basic principles. The most widely used method today is still HFC, a technique that goes back to a collaboration in 1966 between the father and inventor of the method, Dr. Willy Regenass, Ciba, and SYSTAG AG, Switzerland.

The poor technological state of affairs with the reaction calorimeters currently on the market is partly due to insufficient attention being paid during development in the past to physical factors, despite the fact that the main factors influencing the results of measurement both by HFC and by HBC are of a physical nature. These factors include pressure and temperature, viscosity, vapour pressure, agitator speed and torque, thickness of liquid films, c_p , the water equivalent, etc. These factors are to some extent mutually dependent and all their effects must be taken into account in the interpretation of reaction calorimetry data.

The combination of HFC and HBC in a single system with parallel analysis of signals from both methods, as presented here, is entirely new. Thanks to its technological lead, SYSTAG has succeeded in combining the two methodological approaches to reaction calorimetry in one system in such a way that their respective disadvantages are

largely eliminated. For the first time, the chemist is now in a position also to subject reaction calorimetry results to critical analysis and to establish confidence intervals. Interlaboratory studies (co-operative tests) will thus become a thing of the past. Furthermore, the maximum sensitivity achieved with the new system is below 50 mW/kg.

Heat flow calorimetry (HFC)

With HFC, the difference between reactor temperature and jacket temperature is used here to determine the heating power of a reaction. When an exotherm is generated, the temperature of the heat transfer medium in the reactor jacket falls – when an endotherm occurs, it rises. The difference from the inner temperature of the reactor is a measure of the heating power of the reaction.

The equation:

$$HF [W] = (TR - TJ_Out) [K] * A [m^2] * U [W/m^2.K]$$

HF:	Heating power
TR:	Reactor temperature
TJ_Out:	Jacket temperature at outlet
A:	Heat transfer surface area between test material and reactor jacket
U:	Heat transfer coefficient

The system is calibrated using an extremely stable electrical calibration heating mechanism immersed in the solution. The disadvantage of HFC is that the results are dependent on a multiplicity of factors. These briefly are as follows:

- * **Since the measurement is dependent on "A", the metered addition of substances leads to a reduction of the result, while the reaction energy remains the same**
- * **Temperature gradients between reaction material and added substances must be compensated arithmetically**
- * **A change in agitator speed or viscosity brings about changes in the wetted surface area ("A") and in the thickness of the liquid film and thus the heat transfer ("U").**

They do not by any means show linear behaviour characteristics, the results of HFC always show a deviation from the real heating power of the reaction.

With non-isothermal HFC, i.e. if the heating power is to be measured during a temperature rise, the following factors must additionally be taken into account:

Principle of heat flow and heat balance calorimeters

- * **The c_p (specific heat of the reaction material) and water equivalent (c_{pWE} ; specific heat of the reactor) change with the temperature**
- * **The viscosity of the heat transfer medium in the jacket changes with variations in temperature. This causes a change in the liquid film and thus an additional change in heat transfer.**
- * **The equilibrium between liquid and gaseous phase does not remain constant, and the heat transfer through the gaseous phase to the unwetted surface area changes.**
- * **The heat transfer between the reactor and ambient surroundings varies while room temperature remains unchanged.**

With non-isothermal HFC, therefore, a calibration procedure – as is customary with isothermal HFC – does not produce results anywhere near significance. The problem consists above all in the fact that both c_p and the water equivalent change during the test, so that no base line can be obtained by simple calibration before and after the reaction. A completely new approach has therefore been developed in which the water equivalent is calibrated "live" during the experiment.

Heat balance calorimetry (HBC)

With HBC, the difference between jacket inlet and jacket outlet temperature is measured in order to calculate the heating power. The heat of the reaction is dissipated via the heat transfer medium in the jacket. The heating power released in this way is measured however through the increase in the temperature of the heat transfer medium.

The equation:

$$HB [W] = (T_{J_Out} - T_{J_In}) [K] * c_p [J/g.K] * r [g/ml] * F [ml/s]$$

HB:	Heating power
T _{J_In} :	Jacket temperature at inlet
T _{J_Out} :	Jacket temperature at outlet
c _p :	Specific heat of the heat transfer medium
r:	Density of the heat transfer medium
F:	Flow rate

The results obtained from this measurement, in contrast to those obtained by HFC, are to a large extent independent of the wetted surface or the stability of the heat transfer, so that viscosity changes, changes in agitator speed, or evaporation effects do not have to be taken into account

here. Specific heat and the density of the heat transfer medium can also be calibrated at a constant flow rate with isothermal HFC. With non-isothermal HBC, however, the fact that the latter variables are independent of temperature can influence the result of the measurement. Furthermore, of course, effects resulting from the metered addition of substances also have to be taken into account just as they do with HFC.

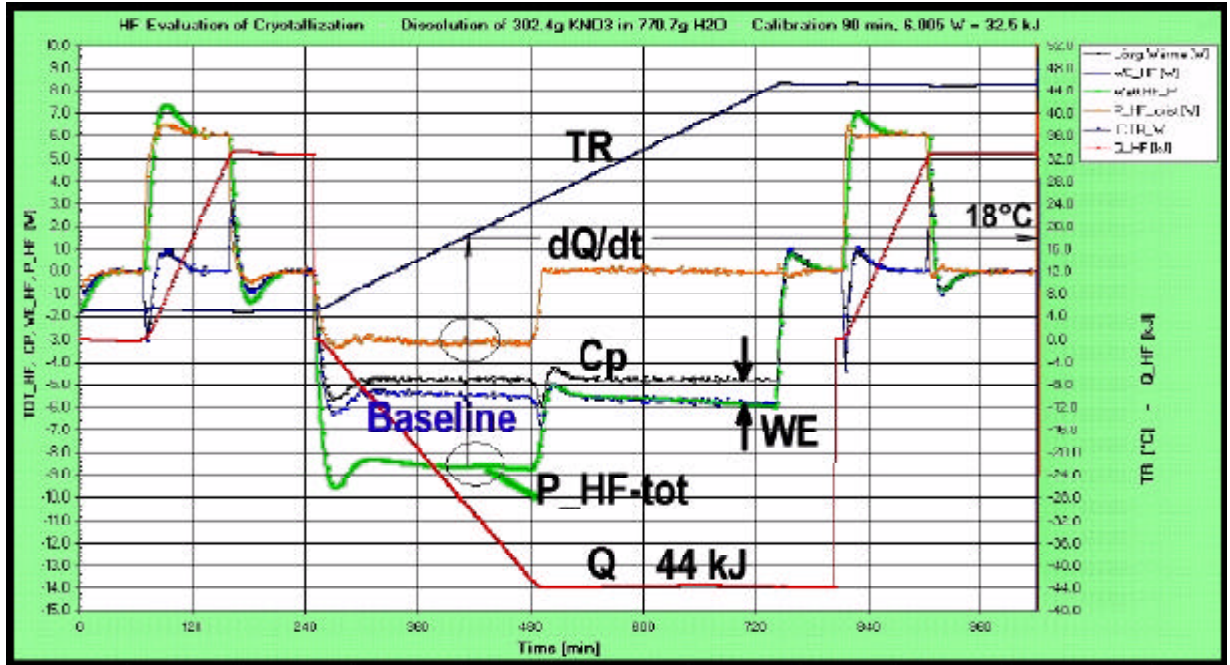
The hurdles to obtaining any conclusive results by means of HBC lie above all, however, in the considerable complexity of the instruments needed. The reasons for this are essentially as follows:

- * **For technical reasons, the flow rate of the heat transfer medium cannot be reduced ad libitum, so that signal strength remains minimal. This means that a low-noise measurement is required.**
- * **The slightest variations in room temperature affect the results of measurement with isothermal HBC, and fluctuating differences between reactor temperature and ambient temperature with non-isothermal HBC have a considerable influence on the measurement. This necessitates encapsulating the reactor in an insulating cabinet and resetting the jacket temperature of the reactor in this cabinet when using non-isothermal HBC.**
- * **The flow rate and thermal stability of the heat transfer medium must be very constant, which necessitates using a high-quality and optimized thermostat.**

The solution to these problems through rigorous "refinement" both of instrumentation and control technology and of process engineering represents the primary major component of the technological innovations embodied in "CALO 2000". This permits the application of HBC for the first time in a commercial system. The second important component is the mathematical processing of the signals. Furthermore, a recalculation of the baseline by reference to a water equivalent calibrated after the test is a prerequisite both with HFC and with HBC. Only in this way can factors such as evaporation influences, varying agitator speeds or viscosities, changing ambient temperatures, etc. be offset.

For processes in which reaction calorimetry has to date been difficult to apply, such as crystallizations, polymerizations and fermentations – but also in any circumstances where reliable data on the heat flow of processes are required – CALO 2000 is the first system to offer an adequate solution.

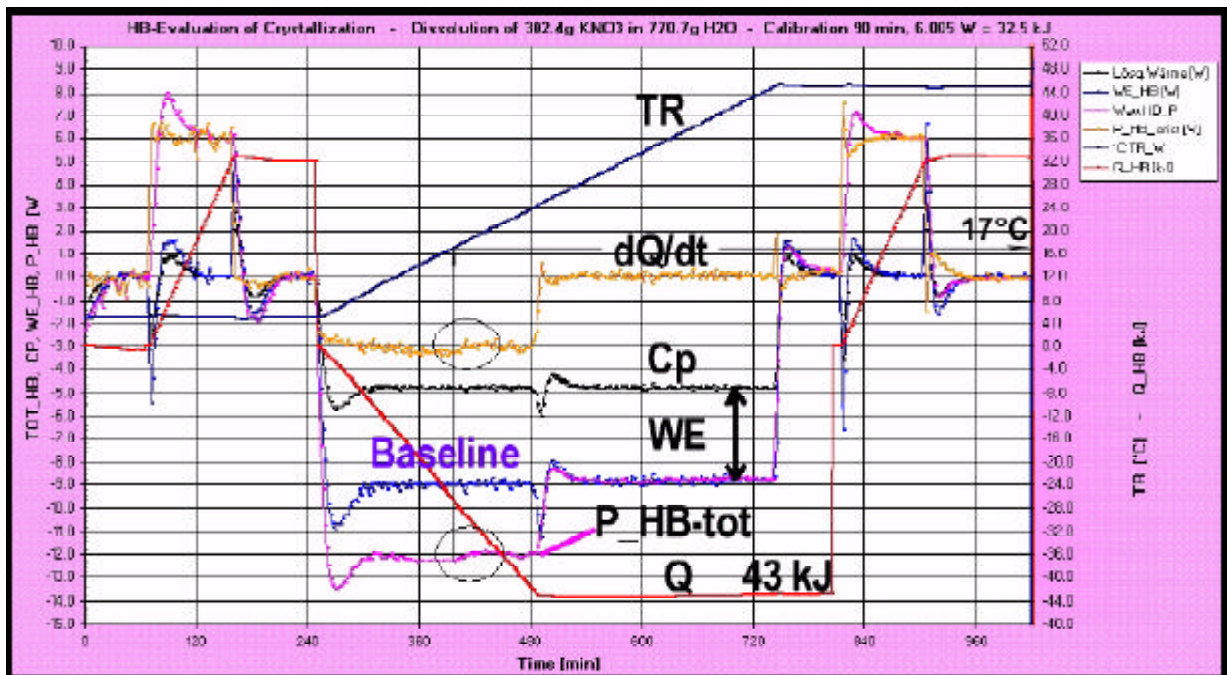
Two simultaneous measurement principles in one experiment



Dissolution heat of a supersaturated KNO₃-H₂O solution when heating from 5°C to 45°C.

The green figure shows the HFC results and the red figure shows the HBC results in one and the same study.

TR = reactor temperature, P_HF-tot or P_HB-tot = total energy in Watts, Cp = energy required in Watts for heating the total mixture in the reactor, WE = water equivalent in Watts, which is precisely adjusted following the experiment, dQ/dt = reaction energy in Watts (P_HX-tot - (Cp+WE)).



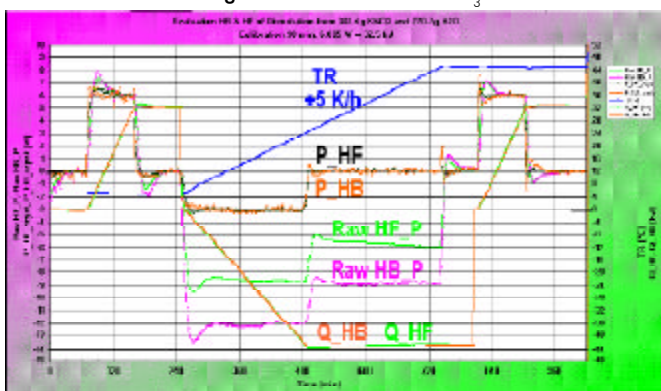
Basic R & D report

A characteristic of Calo 2000: high sensitivity with extreme dynamics at the same time!

Weak solution heat with slow ramp

In a 1-litre cylindrical glass reactor 3 mol KNO_3 in 770 g H_2O with a ramp gradient of +5 K/h in a range of +5°C to +45°C is dissolved. The measured power was approx. 3 Watts, as the following diagram 3 shows. Raw HB_P is the total power of the heat balance (HB), already normalized through the entire temperature range, and Raw HF_P, the total power of the heat flow (HF). The mathematical evaluation gives P_HF and P_HB as real reaction powers, i.e. after deduction of Cp of the entire reactor contents and the total water equivalent, which varies strongly across the total temperature range. The measurement results of HF and HB lie within 2%.

Diagram 3 Dissolution of KNO_3



Strong endothermic

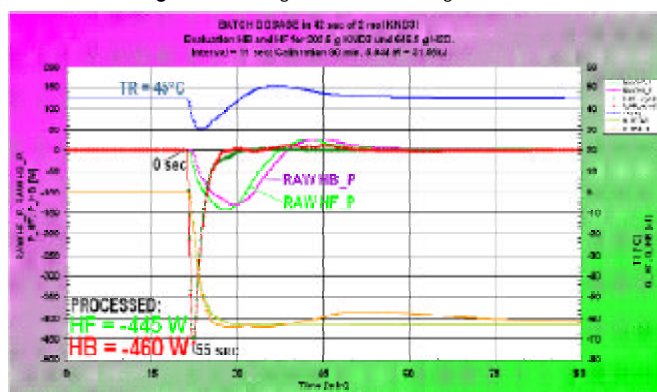
2 mol KNO_2 is added to the dosage in isothermal condition within 42 s in order to determine the solution heat at 45°C in 646 g H_2O . You take into account the two almost identical power peaks after the mathematical evaluation with only 13 s delay between end of dosage and the maximum power peak. This was -445 Watts for the heat flow (HF) and -460 Watts for the heat balance (HB). The confidence limit lies therefore at approx. +/- 2%.

In addition you need to take into account that the pre-normalized raw signal RAW HF_P or RAW HB_P (which each conventional calorimeter normally delivers) has a completely different chronological behaviour than the mathematical processing!

The subsequent process shows clearly the congruence between HF and HB signal, which are both equal

and which also no longer indicate any significant time differences.

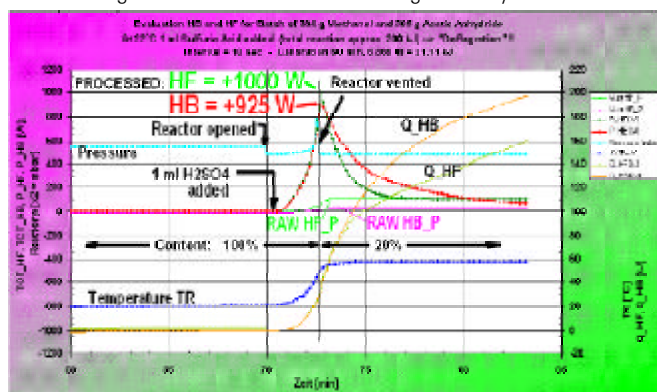
Diagram 4 Strong exothermic during dissolution



Run away reaction as extreme power detection test

3 mol acetic anhydride was present in 12 mol methanol as a batch at 20°C and the reaction is started with 1 ml catalyst (H_2SO_4). A sharp increase in the reactor temperature TR in accordance with Arrhenius is determined! The closed 1 litre glass reactor has lifted the lid after 130 sec with a 0.6 bar overpressure, moved the lid from the hinge and blown 80% of the content out into the cabinet. In accordance with the mathematical processing we again obtain nearly congruent results of approx. 1000 Watts with a confidence limit of approx. +/- 4.5 %.

Diagram 5 Extreme exothermic during run-away reaction



R&D report no.1:

Something special of Calo 2000: All 4 basic operation types of experiment are possible

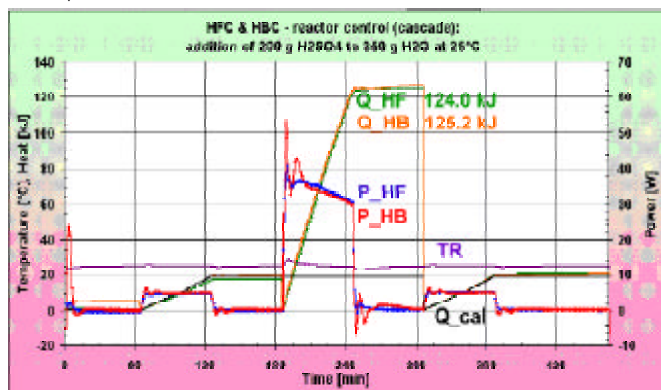
Basis of experiment

The following experiments are carried out as a system test at the request of a client. A readily available bottle of H_2SO_4 was used. Its concentration was unknown because it was previously used several times for water equivalent calibrations. We estimate the concentration at approx. 87%. An extremely long calibration impulse of 60 min was selected deliberately (which is normally only needed for basic calibration), so that accurate analyses in a static and a dynamic condition are possible. The dosage of 200 g is also carried out over 60 min. As supply 350 g water in 1 litre cylindrical glass reactor was available (approx. 1/3 as start volume).

All diagrams show the TR reactor temperature, the resulting reaction power P_{HF} (Heat Flow) and P_{HB} (Heat Balance) as well as their integration with Q_{HF} Q_{HB} .

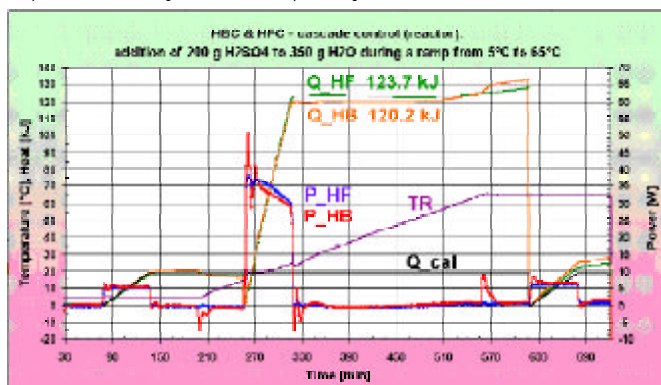
Isotherm Fix-temperature

The reactor is controlled at a stable temperature, and therefore the jacket temperature must change for the heat transport.



"Isotherm" Ramp

The reactor is equipped and controlled with a ramp setpoint value, and therefore in addition the jacket temperature must be changed for the heat transport during the reaction.



In addition the integration of the Q_{cal} calibration heating is also shown. Consequently the four operation types can be compared really well and the advantages and disadvantages are highlighted.

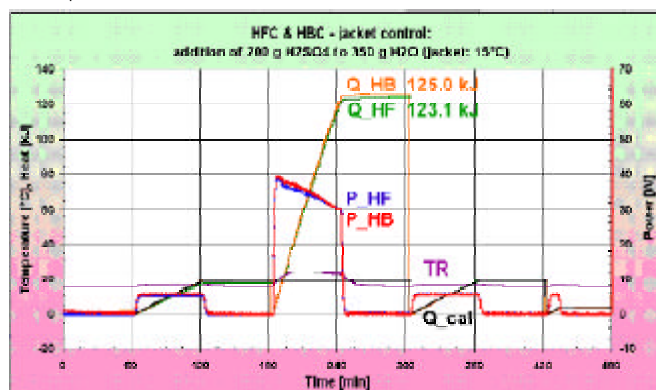
Conclusion

As basis only the basic system calibration with 1 litre water in a range of 5°C to 85°C is used. All measurements were only carried out with this basic calibration, without any subsequent further corrections later on. In plain English this means: what you see here is the actual result, which is also possible on-line. Calibration headings or cp determinations are not necessary for this quality result before or after the experiment.

At last a calorimeter which also drastically shortens the experiment time, apart from a non-isothermal method of operation!

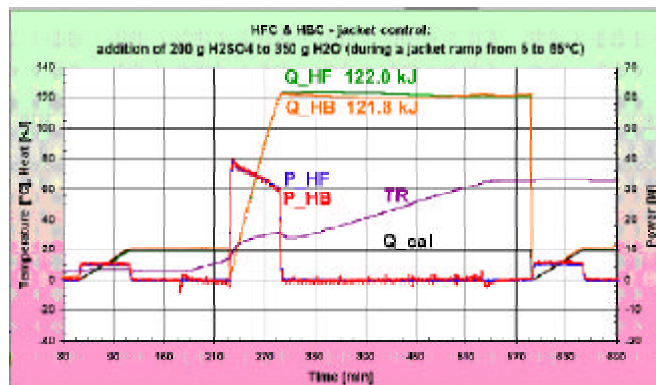
Isoperibol Fix-temperature

The jacket is controlled at a stable temperature, and therefore the reactor temperature must change for the heat transport.



"Isoperibol" Ramp

The jacket is equipped and controlled with a ramp setpoint value, and therefore in addition the reactor temperature must be changed for the heat transport during the reaction.



R&D report no.1 (continuation): Absolutely unique of Calo 2000: Reproducibility and accuracy

Basis of experiment

Diluting H_2SO_4 in H_2O as before is used as an **inorganic experiment**, and an alcoholysis of acetic anhydride is used as an **organic experiment**. It shows that the organic experiment indicates a somewhat higher error rate, so that the second four experiments are initially not corrected (only basic calibration) and subsequently (off-line) are corrected more precisely (with calibration). From these three groups a statistic with the respective standard deviation is generated.

Standard deviation

For the four experiments (isothermal fix, isothermal ramp, isoperibol fix and isoperibol ramp) we obtain 8 results, 4 for HF and 4 for HB. From this we can already form a good opinion.

Dilution of H_2SO_4 in water

The average value was 123.13 kJ, and the standard deviation 1.30%, whereby the maximum peak deviations were -2.38% and 1.69%.

Alcoholysis of acetic anhydride, uncorrected

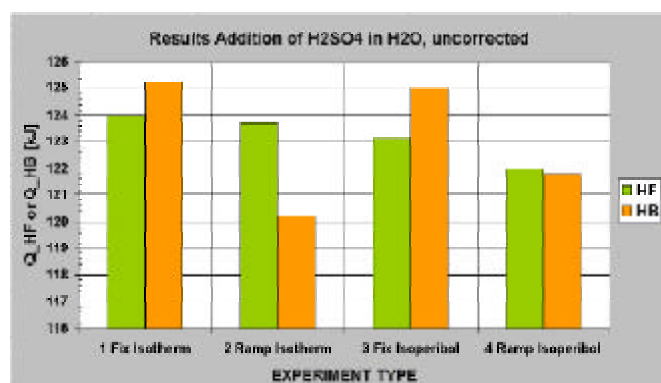
The average value was 65.88 kJ, and the standard deviation 2.49%, whereby the maximum peak deviation was -3.92% and +3.97%. For the theoretical reaction value of 67.9 kJ the average deviation was in addition -2.98%.

Alcoholysis of acetic anhydride, off-line corrected

The average value was 68.18 kJ, and the standard deviation 1.92%, whereby the maximum peak

Inorganic, water base: solution of H_2SO_4 in H_2O , uncorrected, only with basic calibration

The four experimental types each with two results are displayed here. Average value = 123.13 kJ and standard deviation = 1.30%.



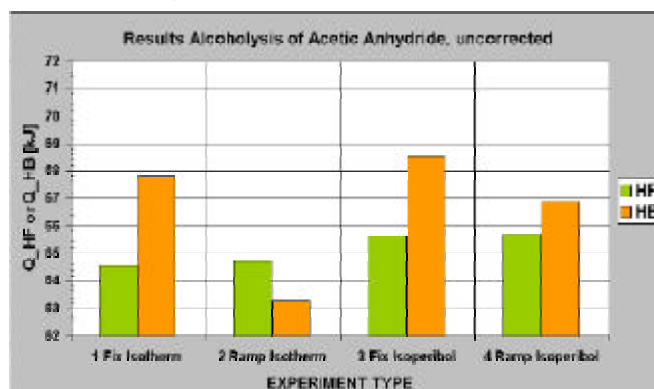
deviations were -2.23% and +4.43%. For the theoretical reaction value of 67.9 kJ the average deviation was in addition +0.41%. When the somewhat high dosage (102.5 g. instead of 102.1 g.) is taken into account, this result decreases by -0.39% to +0.02%.

Final conclusions

For liquid solutions (higher cp) the uncorrected values are already very accurate (standard deviation 1.3%), and organic solutions with only about half the cp are correspondingly more inaccurate (standard deviation 2.49%). When we take into account the peak values of the deviations during an organic experiment, these lie opposite the theory in a range of +0.4 to -7.3%. We can take for granted that **without calibration** and precise correction a typical accuracy of 5...10% is reached. On the other hand, **with calibration** and precise correction an accuracy of 1...3% is reached.

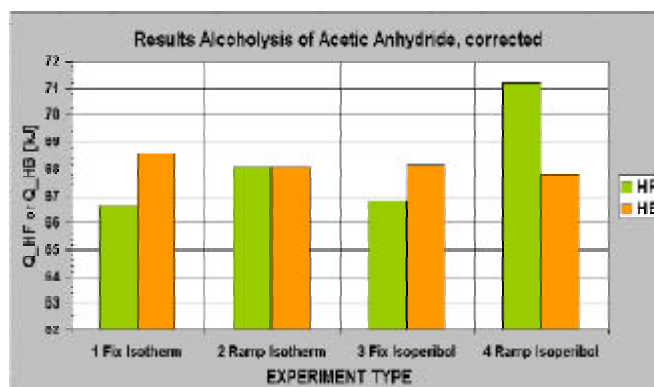
Organic, methanol base: alcoholysis of acetic anhydride, uncorrected, only with basic calibration.

The four experimental types each with two results are displayed here. Average value = 65.88 kJ, standard deviation = 2.49% (theory 67.9 kJ).



Organic, methanol base: alcoholysis of acetic anhydride, uncorrected, subsequently additional off-line corrections

The four experimental types each with two results are displayed here. Average value = 68.18 kJ, standard deviation = 1.92% (theory 67.9 kJ).



R&D report no. 2:

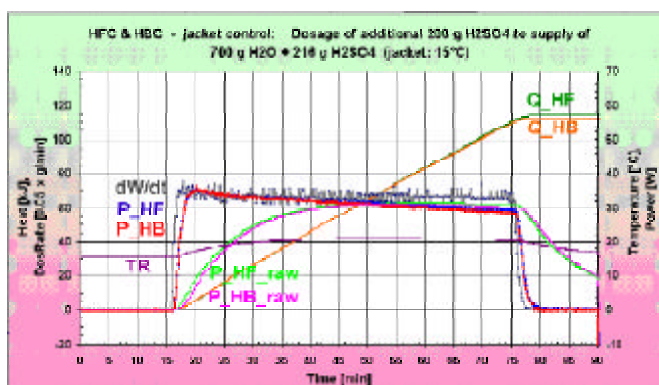
Last, but not least another feature of Calo 2000: Excellent reaction dynamics

Excellent dynamics

The **Calo 2000** principle allows a very good account of reaction dynamics. This is absolutely independent, regardless of whether a lot or a little material is supplied to the reactor or regardless of whether the cp is high or low. Until now everything must be carried out with an as good or an as fast a control as possible, so that the dynamics are as good as possible. With **Calo 2000** the times in which temperature needs to be taken into account are finally over.

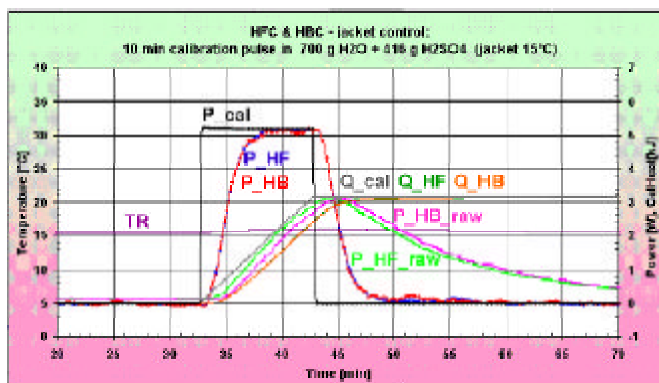
Here the H_2SO_4 dosage is shown over 60 min.

The dW/dt dosage rate and the displayed P_{HF} and P_{HB} are separated from each other by approx. 60 s, but are nevertheless very accurately drawn. The dosage has a very weak overshoot, which can also be recognized by the reaction power! The reaction power however drops with increasing concentration, which can be measured very accurately in Calo 2000. This can be compared with the P_{HF_raw} value and P_{HB_raw} value, which show a lag of approx. 20 min.



Calibration impulse of 10 min. with a jacket control and a full reactor with a high cp!

You recognize very quickly the raw values (P_{HF_raw} and P_{HB_raw}), which are derived from the temperature measurement and which "creep" very slowly. From this the signal processing in the Calo 2000 gives the P_{HF} and P_{HB} , which are only delayed a little: a) deadtime + time constant of calibration heating itself and b) approx. 60 s time constant through filtering. More is not needed!



Also, **Calo 2000** displays the entire range of, for example, 50 mW up to >1000W in a 1 litre glass reactor, all with the same dynamics!

Limits of dynamics

In **Calo 2000** a compromise must be sought between higher sensitivity and good dynamics. The compromise must be such that for the benefit of a high sensitivity of <50 mW a delay time constant of about 60 s is accepted. This becomes necessary because of complex filter algorithms. That however is all.

Isothermal creates the best dynamics!

It is in the nature of things that with a "simple" control, the jacket control (this is in reality in the **Calo 2000** not as simple as everything else is), a really stable control becomes possible. This is immediately shown in the dynamics graphic.

Where isothermal and where isoperibol?

In production many installations are operated isoperibol. A reaction calorimeter, which mirrors this operation, is the best. On the other hand during calculations with the Arrhenius evaluation constant temperatures are demanded frequently. An isothermal operation is demanded for such tests. For the first time **Calo 2000** offers you freedom of choice!

Isothermal experiment: alcoholysis of acetic anhydride

For verification purposes a 10 min calibration impulse of 5.2 W can be seen at the start. This is followed by a 10 min rest time, after which the dosage of 1 mol acetic anhydride starts for a further 10 min. The second calibration impulse, again of 10 min., must only be used for the final monitoring. Such an accumulation was not planned. Consequently this impulse does disrupt more than it needs to. Again take into account the good dynamics in comparison to the raw values.

