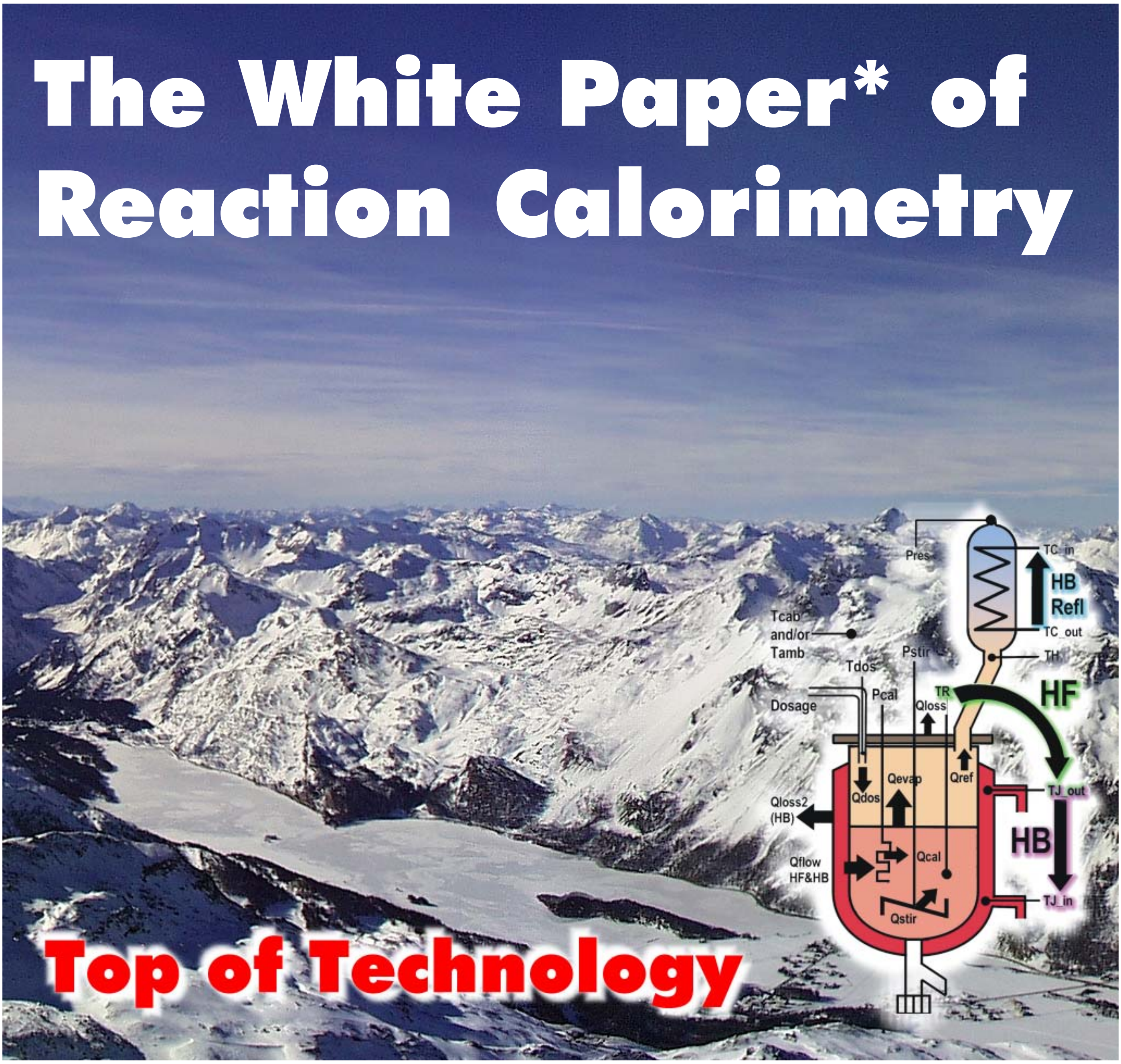
# The White Paper* of Reaction Calorimetry



* The innovative insight emerged during a stay in a wintery white Engadine, hence the name "White Paper"

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# Contents

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# EDITORIAL
# Reaction calorimetry's white paper

Peter E. Meier, dipl. Eng., ETH, is SYSTAG's director and simultaneously also significantly involved in the development of the Calo 2000.

In this white paper we show the many possibilities which today's state of the art technology in reaction calorimetry offers you. And this not just at high prices! Equipment, which definitely meets your demands, is also available for the not so full purse.

In the last two decades practically nothing of importance has happened with regard to new developments in reaction calorimetry, because we are dealing with a niche product. Only because of technology leader SYSTAG's immense experience (since 1966 always present with the development of reaction calorimeters!) and the courage to try something new has this breakthrough in reaction calorimetry been achieved!

The development of an accurate non-isothermal calorimeter has finally been achieved with the new Calo 2000 equipment family. Until now all reaction calorimeters were pure *isothermal heatflow* calorimeters, although that was disputed at the time! In order to obtain a somewhat useable result in a non-isothermal application, any amount of mental acrobatics was needed! These mental acrobatics fail however every time when we are trying to make sensible statements about the base lines, i.e. simply to measure the reaction power (and only the reaction power).

A selection for every need and purse is now available with the existing equipment family. More important however is: many simple, isotherm calorimeters can be fitted later to non-isothermal calorimeters.

Even when you start small, you have many options to upgrade both *"Silver Line"* and *"Gold Line"* at a later date. On the other hand changing from one to the other line is not recommended – for economy reasons.

The first breakthrough lies in the first realisation of *sensitive heat balance calorimetry*, which can make *simultaneous* measurements with the heatflow calorimetry. Consequently unpleasant effects of heatflow calorimetry can be counterbalanced with the *heat balance calorimetry*, such as change of A (surface covered) and U (heat flow number).

The second breakthrough can be found in the clever solution of the total balancing of the entire system. Many differential equations need to be solved. The advantage is that the solution method makes the Calo 2000 into a simple system, which can be calibrated.

It is logical that with an exact balancing also exact results – without mental acrobatics – can be achieved. The following is evidence of that: the Calo 2100 and 2200 calorimeters already give results within the range of 5 - 10% *without any further calibrations during the experiment!* Also, all four operation types are possible with the same accuracy (!): isotherm (reactor control) and isoperibol (jacket control) as well as "isotherm" ramp (reactor control, isotherm with regard to setpoint value of the ramp) and "isoperibol" ramp (jacket control, isoperibol with regard to setpoint value of the ramp).

The advantages are obvious: experiments can be carried out faster and unstable reactions are a thing of the past!

Summarizing, we can say:

* decreased experiment times
* unstable reactions are a thing of the past
* polymerization can finally be measured accurately
* because of the high sensitivity crystallization and fermentation can finally be measured calorimetrically.

We now wish you an interesting time when studying the following documentation! Please feel free to contact us, we will be happy to be of further assistance.

Yours, Peter Meier.

# The largest selection of reaction calorimeters in the world: SysCalo SC1...SC4; can be extended to

## Introduction

Reaction calorimetry is becoming more and more important, because the time from development to a marketable commodity needs to be shorter and shorter. Even at the beginning of the development process the procedure and safety has to be optimized. For this calorimetric data is needed. Depending on the system (with or without cooler-balance calorimetry) we deliver:

- **Reactor and cooler: power and heat curves**
- **Accumulated heat after partial dosage**
- **Adiabatic temperature increase through total heat or through**
- **Accumulated heat at any time for reactor & cooler terms**
- **Diagram of the kinetics for your reaction**
- **At last also polymerization, crystallization and fermentation with higher accuracy**

You can carry out your experiments, depending on calorimeter type, using isotherm, non-isotherm, and isoperibol (i.e. only pure jacket control). In all these cases you will obtain a good accuracy, providing we are dealing with a member of the Calo 2000 series!

SYSTAG, as the pioneer and technology leader in calorimetry, now offers a completely new solution!

From a basic selection of 2x4 basic systems (the **SILVER LINE** with SysCalo SC1 to SC4, or with non-isothermal calorimeter Calo 2902 to Calo 2904 and the **GOLD LINE** Calo 2001 to 2004) you select the one most suitable for you and supplement this modularly to suit your individual needs.

## Examples

If you want to obtain initial calorimetric data from your reactor during the routine process optimization of more simple applications – without increased experimental effort – your solution is SysCalo SC1.

If you expect multiple step reaction procedures with various monitoring functions and calorimetric evaluations even with reflux, your solution is SysCalo SC2.

When the functional structure of your test equipment is different each time, i.e. a recipe control, but one which is just as accurate as a detailed protocol, your solution can only be SysCalo SC3.

When your application exceeds the 'normal' technical effort, or if more complex functions with a multitude of measurement signals are available and a high degree of accuracy and reproducibility is required, then the most

**SysCalo SC1** with gas dosage, 60 bar

**SysCalo SC4** with 5 valve dosages

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# Calo 2902...2904 and the top models Calo 2100 ... Calo 2400

suitable solution is the scientific SysCalo SC4.

However, as soon as you need to work with combined calorimetry, i.e. **heatflow with simultaneous heat balance** in the reactor, only the Calo 2100 to 2400 models come into question. What are these models used for?

## Calo 2100

This is the **universal piece of equipment**. Apart from both calorimetry methods it also has the **highest sensitivity**, together with the Calo 2200. This is achieved with a temperature-stabilized cabinet and the build-in refined heating. The Calo 2100 is suitable for all types of experiments and represents the newest scientific piece of equipment. **Syntheses, polymerization, crystallization and fermentation** can be measured with these, depending on your individual installation. Accuracy (with calibration per experiment) of up to 1% is achievable!

## Calo 2200

This piece of equipment is build as the Calo 2100 but is specially equipped for **crystallization**. With this you can seed crystals and measure turbidity.

## Calo 2300

Here the cabinet for the stabilization of the surroundings has been left out. Consequently the sensitivity is slightly reduced and with a heat balance measurement only suited for an isothermal condition. It is <u>the pre-defined</u> apparatus for **polymerization**, which heat balance measurements definitely need (strong viscosity changes!) but which delivers more reaction power in comparison to crystallization or fermentation.

## Calo 2400

Here the cabinet for the stabilization of the environment is also left out. In addition this apparatus is *<u>not equipped with heat balance measurement</u>*, because its components can no longer be obtained for this temperature range. With this system therefore accurate non-isothermal heatflow measurements in an extended temperature range of approx. -80°C (or even lower, depending on the thermostat) up to a maximum of +300°C are possible. It is therefore the equipment **for all temperature extremes**.

**Calo 2100** with Tango for limited temperature range 0 - 100°C

**Calo 2100** with open door

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# Further services from SYSTAG: Coaching to success!

## Final conclusions

The previous examples show that no individual system can fulfil all demands. SYSTAG therefore offers a selection from which you can put together the optimum menu, just as with a Chinese dinner. Apart from the different degrees of automation the vessels and the thermostats can also be optimized. With the Calo 2000 family however you must take into account that each system change leads to a new (and permanent) basic calibration. You can carry out the calibration runs yourself in a recipe-controlled manner. SYSTAG will calculate the appropriate parameter files on the basis of your experimental data and send them to you by e-mail.

In addition SYSTAG offers you special solutions, which meet your individual needs.

## Exchange of knowledge

Reaction calorimetry is an area of expertise, which concerns itself more with physics than with chemistry. For these reasons it is not necessarily the chemist's favourite area of work. Should this appear like a closed book, then SYSTAG offers you appropriate training. This is always tailored to your individual needs.

Even for the use of a Calo 2000 version it is worthwhile attending a special Calo 2000 training, apart from the normal training, which demands a lot more understanding. Only he who knows what, how and why he does something, does it correctly! Please ask for our advice!

## On-site measurements in your laboratory by SYSTAG

In many cases you need calorimetric measurements, but the purchase of equipment is not possible for financial reasons or is not sensible. In such situations SYSTAG offers measurements in your own laboratory. For this purpose SYSTAG makes available an expert, together with the hire of apparatus in the "SILVER LINE". Consequently you are involved in the process and you learn at the same time what reaction calorimetry means. In this way you also obtain calorimetric information about your processes!

**SysCalo SC2** with FTIR and pH option, as low temperature (-85°C) version

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# Advice for components selection

## Reactors

The application primarily determines the type of reactor. With glass reactors you have a choice between double or triple jacket and between cylindrical or conical shape. Next come the pressure resistant up to approx. 6 bar, followed by autoclaves up to 60 bar or more. In addition, with each type you have the choice of different sizes. This already shows the necessity for the enormous variety of equipment needed for reaction calorimetry.

Cylindrical double jacket reactors are standard and the best value for money. *For crystallization*, cylindrical reactors must always be used, because these achieve the best stirrer operation!

Conical reactors allow a high filling proportion of around 1:6 against a cylindrical one with1:2 to 1:3, but these are harder to stir.

Triple jacket reactors are necessary for very high and above all for low temperatures. Apart from giving good isolation they prevent the forming of ice on the surface and as a result the view of the inside remains clear. In the Calo 2000 series this is essential.

Value for money standard glass reactors can only be used from vacuum up to atmospheric pressure. These are therefore optimally suited for reflux and distillation. For closed systems, as absolutely essential in the Calo 2000, SYSTAG has designed a special set-up to guard against overpressure.

For higher pressures special glass or steel reactors are needed.

## Thermostats

You can basically differentiate between water cooled thermostats (approx. 50°C to 300°C) and thermostats with built-in cryostats (-120°C to +300°C). The latter are more expensive, but ideal for calorimetry.

Depending on the installation larger thermostats with more power are needed in the Calo 2000.

## Calibration heaters

Initially the size of the vessel or the volume used decides the calibration power, typical 5...40 Watts. This must result in a sufficiently accurate measurable response signal (Delta T = TR – TJ for HFC or TJ_out - TJ_in for HBC). In all cases a true watt meter is available, which allows a precise calibration. In the Calo 2000 you usually only work with 5 Watts, so that a highly accurate zero line can be determined.

**Calo 2100** - Development system at SYSTAG

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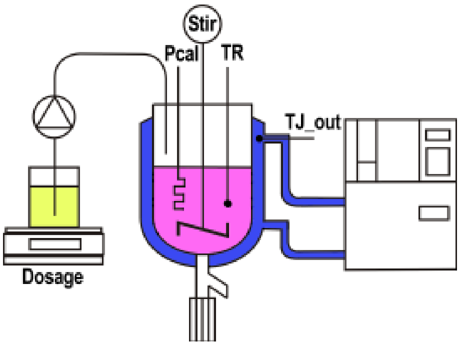
# IMPORTANT for further understanding: pictograms and their clarification.

**HBC = Heat Balance Calorimetry** **HFC = Heat Flow Calorimetry**

## Calorimetry method (always referring to reactor!): simultaneous HBC & HFC

For the first time it is possible, not only to use heatflow calorimetry (HFC) but also to use heat balance calorimetry (HBC) in the same experiments. This opens up completely new possibilities in chemical heat measurements. The big advantage is that both methods are very complementary (see section "comparison HFC – HBC", page 13). Furthermore, there is the invaluable advantage of making a comparison between the possibility of the measurement accuracy yourself: when both results lie very close together, the measurement accuracy is correspondingly high. When deviations are present, it is possible to decide on the basis of the knowledge of the process, which applies more!

## Method: only heatflow



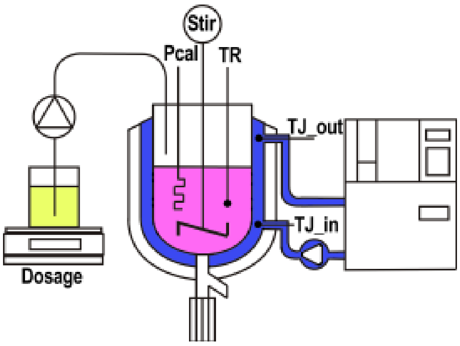
**The equation:**

$$HF\,[W] = (TR - TJ\_Out)\,[K] * A\,[m^2] * U\,[W/m^2.K]$$

| | |
|---|---|
| *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 heatflow calorimetry most commonly used to date is an extremely robust measuring method with a very good measurement signal. The jacket protects the measurement system extensively against outside influences. In comparison the measurement is extremely dependent on the fullness, the viscosity and the stirrer vortex (whirl). Furthermore, each build-up of solids near the wall poisons the measurement because the transfer co-efficient changes massively and never linearly.

## Method: only heat balance



**The equation:**

$$HB\,[W] = (TJ\_Out - TJ\_In)\,[K] * cp\,[J/g.K] * r\,[g/ml] * F\,[ml/s]$$

| | |
|---|---|
| *HB:* | *Heating power* |
| *TJ_In:* | *Jacket temperature at inlet* |
| *TJ_Out:* | *Jacket temperature at outlet* |
| *cp:* | *Specific heat of heat exchange medium* |
| *r:* | *Density of heat exchange medium* |
| *F:* | *Flow rate* |

The heat balance calorimetry (HBC) has the big advantage that all influences, which can influence the transfer between the reactor material and the jacket, have no consequence. Looking at it from this point it is the ideal method. However there are also important disadvantages to report: the measurement signal is significantly smaller and the surrounding temperature has an influence on the measurement result, which should not be underestimated. In addition, the water equivalent for non-isothermal measurements is a much greater influence than with the heatflow (HFC) method. Both methods together on the other hand are an invincible team!

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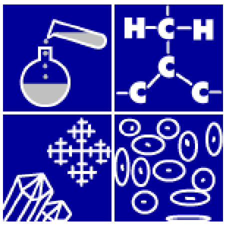
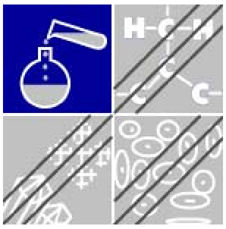
# Pictograms and their clarification: Applications and types of operation

## Applications: all



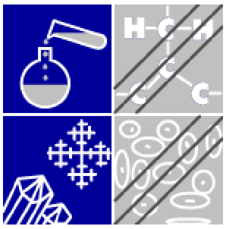
The four symbols stand for a) synthesis, b) polymerization, c) crystallization and d) fermentation. These are only very generally used terms and are correspondingly interpreted a little further.

## Application: predominantly syntheses



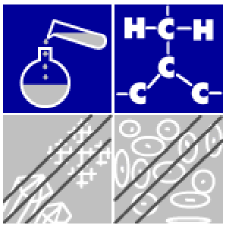
The synthesis is the most common application, just as other less critical reactions. "Critical" must be understood in measurement technique sense and not with regard to chemistry!

## Application: synthesis, crystallization



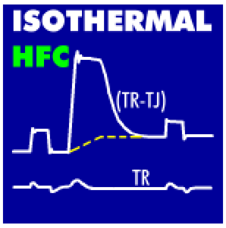
The crystallization deserves special attention. The equipment is specially designed for this, particularly with regard to accessories. Measuring the smallest reaction powers (for example 0.5 W) with the highest temperature range is particularly important here.

## Application: synthesis, polymerization



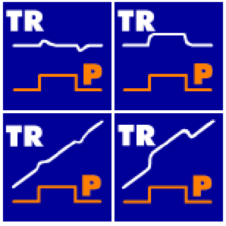
Apart from synthesis, polymerization can be measured optimally as long as a specific power has accrued, such as for example 50 Watts. Consequently less effort with regard to surrounding influences needs to be made.

## Isotherm HFC conventional



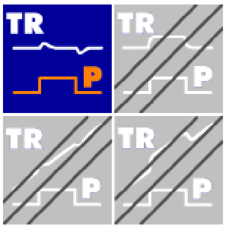
As before the method with calibration and baseline adjustment is used for correction of changed heat transfers for the entire range of isothermal calorimeters. Isothermal calorimetry requires no knowledge of cp or water equivalent.

## Operation type: all modes



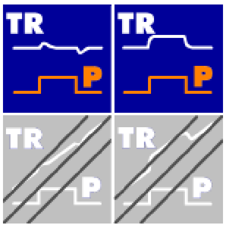
The four symbols stand for all conceivable types of operation: isothermal (left bar) and isoperibol (right bar), both with regard to regular (top line) or ramp setpoint value (bottom line). Isotherm can be achieved with a reactor control (cascade control) and isoperibol with a jacket control.

## Operation type: only isothermal



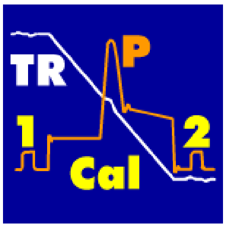
All calorimeters used to date are the isothermal type, with greater or lesser "mental acrobatics" to achieve quasi non-isothermal types of operation which however never give solid results and therefore always result in "Circle experiments".

## Operation type: isothermal & isoperibol



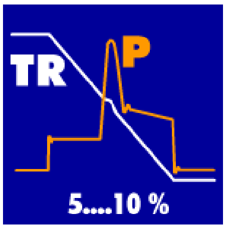
Isothermal and isoperibol at a constant setpoint value are used above all with polymerization, because this makes the measuring apparatus cheaper, and delivers nonetheless excellent results with viscosity changes, as well as a really accurate kinetics.

## Non-isothermal with calibration



The non-isothermal operation type with calibration at a high or a low temperature level gives the most accurate results, because the measurement can still be precisely evaluated off-line. Also, this method is necessary with economical non-isothermal variants ("Silver Line").

## Non-isothermal without calibration



With the new top models the non-isothermal type of operation without any calibration already gives excellent accuracy. Consequently the throughput increases markedly and with chemically unstable reactions can at last be measured without worries.

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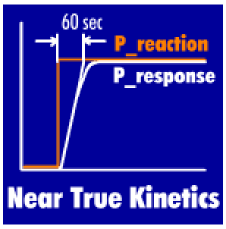
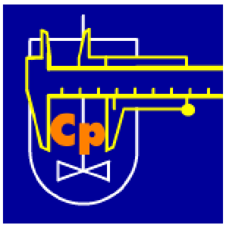
# Pictograms and their clarifications: kinetics, sensitivity, A, U, cp, etc.

## Excellent kinetics



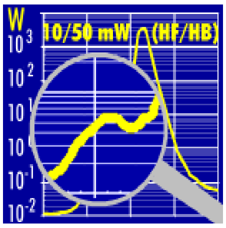
With the Calo 2000 series the desire for a very good picture of the kinetics is fulfilled, during which isoperibol operation outside a 60 second delay practically gives no further errors, regardless of a lot or a little substance and regardless of a small or a large cp!

## Automatic cp determination



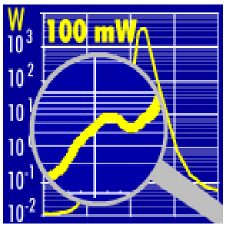
The determination of the cp is automated with an internal recipe, which however is only needed for an adiabatic heating. In all other cases an extensive accurate pre-calculation or estimation is sufficient.

## Highest sensitivity



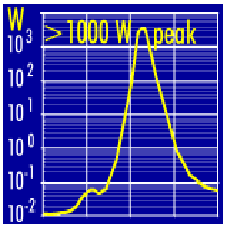
For crystallization and fermentation the highest sensitivity is demanded, which is possible with HFC down to 10 mW and with HBC down to 50 mW. We are dealing with detection limits, which can however only be achieved with calibration for each experiment.

## Very good sensitivity



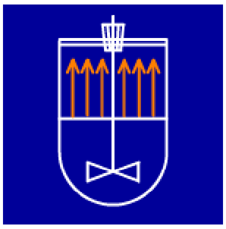
Without additional stabilising of the surrounding temperature via the cabinet a very good sensitivity can be achieved with the Calo 2000 principle with the HFC during isothermal operation.

## Extreme dynamics



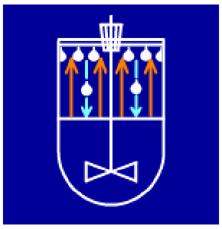
Thanks to extensive evaluation mathematics, which the system reproduces very accurately, we now also receive a power dynamics never previously seen, which corresponds almost exactly to real process kinetics. The isoperibol type of operation is ideal.

## Closed system



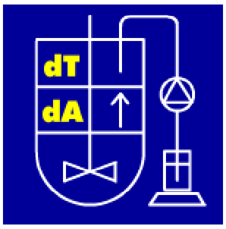
For accurate measurements of small powers we are dependent on a closed measurement system, because evaporation errors make a significant difference! With a simple method this can definitely be carried out in a glass reactor.

## No condensation, therefore no "reflux"



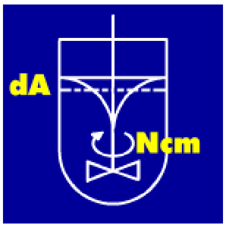
Condensation on the lid of the system presents a special problem, which can lead to an actual "reflux", which obviously produces large measurement errors. This can be kept under control with appropriate surrounding conditions.

## Complete corrections



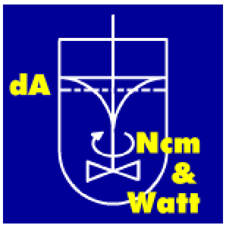
There are further problems for dosages. These are a change of the covered wall surface, and consequently the transfer coefficient U (only with HFC), as well as a power inlet as a result of unequal temperatures of the reactor contents and the dosed educt. Both are corrected.

## Vortex correction, torque stirrer



With HFC the stirrer whirl also produces an additional error, which can be calculated out manually and which can be taken into account in the evaluation. The torque is also measured with the HFC and HBC and shown in Ncm.

## Vortex correction, torque and power



As mentioned above, the vortex correction is carried out via a manual entry. The torque is also measured in Ncm with HFC and HBC in Calo 2000 and also indicated directly in Watts.

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# Pictograms and their clarifications: on-line info, resolution, temp. range, turbidity

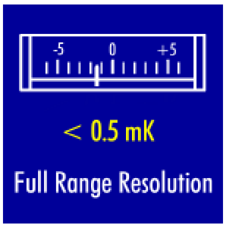
## On-line guidelines with HFC: P & Q

With the Calo 2000 series on-line information can also be obtained immediately. The accuracy however does not reach an off-line evaluation, but is sufficiently accurate for first considerations. This is ideal for a higher power range (around 30 .. 50 Watts).

## On-line guidelines HFC/HBC: P & Q

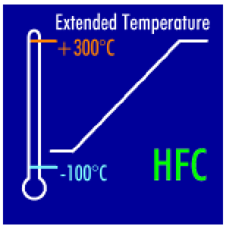
On-line information – as already described above – but for HFC as well as HBC. The same restrictions apply.

## Extreme measurement resolution



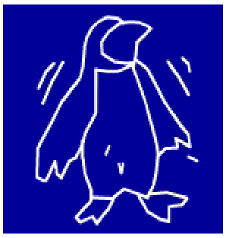
In order to obtain a good model picture as well as a high sensitivity the measurement value recording must be put on a totally new footing. Calo 2100 to 2400 resolves the entire range under 0.5 mK.

## More extreme temperature range



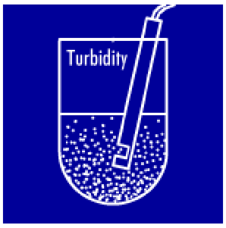
Because the HBC is subject to more limitations a model has been developed (The Calo 2400) which however only allows HFC operation, but which can cover the entire temperature range and which also allows a real non-isothermal calorimetry.

## High accuracy at low temperature



Low temperature measurements are tricky because of freezing of air moisture (or melting). Large measurement errors result. This is also the case with HFC, although this method is fundamentally better protected against the environment. For this, systems 2100 and 2200 in a cabinet are used.

## Turbidity measurement integrated



For the crystallization not only the power change but also the turbidity is used for further detection. For these reasons a turbidity measurement apparatus is already integrated in Calo 2200.

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# Brief summary:
# Reaction calorimetry in new dimensions

## Highlights

**Calo 2000**, the first non-isothermal Reacton Calorimeter

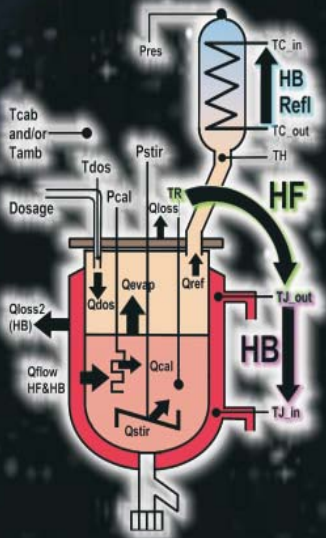
Two complimentary measurements are possible simultaneously in one experiment: HF (Heat Flow) and HB (Heat Balance)

Without any calibration or cp determination during the experiment: approx 5 … 10% accuracy is possible.

With calibration, an accuracy of up to 1%

All 4 basic types of experiment are possible:
- Isotherm fix-temperature (reactor controlled)
- Isoperibol fix-temperature (jacket controlled)
- "Isotherm" ramp (reactor controlled)
- "Isoperibol" ramp (jacket controlled)

Clear dynamic reproduction of the reaction



The new Calo 2000 series offers many advantages of which you have only dreamed about up to now! In the following pages please study the different pieces of equipment and select the one most optimum for you. It doesn't always have to be a Calo 2100 or Calo 2200. Because of our immense experience of new research you obviously also benefit from all knowledge of the simpler models, such as SysCalo SC1 .. SC4. You also benefit from the lead, which SYSTAG has gained during the last few years thanks to massive development investments!

If you want to know more about the difference between a simple isothermal HFC and a non-isothermal HBC, even combined with HBC, you must study the remaining pages of this white paper forthwith. There you can see from live experiments what is possible and where the limits lie.

# Brief comparison between HFC and HBC:
# Ideal, because they are extremely complimentary!

| Situation | Heat Flow Calorimetry | | Heat Balance Calorimetry | |
|---|---|---|---|---|
| **On-line information of reaction power** | – | **Not easy, baseline much less stable with conventional method** | + | **Possible as first information (10..20%)** |
| **Water Equivalent (WE)** | + | **Small (only 1/4 of HB)** | – | **Large, the whole jacket (also outer wall) is included in WE** |
| **Measured raw signal** | + | **Large, approx. 200 mK/W** | – | **Very small and noisy, approx. 20 mK/W** |
| **Independent of additions, stirrer vortex and viscosity changes** | – | **Very sensitive to changes of U * A** | + | **Nearly independent, also possible without stirring measurements** |
| **Crystallization** | – | **Normally no useful results** | + | **Good results** |
| **Polymerization** | – | **Not very accurate - with changing viscosity U changes also!** | + | **Independent from viscosity** |
| **Fermentation** | + | **Good sensitivity - base line calculation necessary - useful during stable mass balance in reactor** | + | **In every case good results but signals more noisy** |
| **Independence of room temperature** | + | **Jacket is a good shield** | – | **Very sensitive, surrounding must be temperature stabilized for high sensitivity** |
| **Independence of thermostat model** | + | **Not critical, jacket temperature measured at jacket outlet (good filtering)** | – | **Only optimized thermostats, extreme low-noise jacket inlet necessary** |

Both measurement methods show a very complementary behaviour, so that the advantages of one offset the disadvantages of the other method!

The heatflow calorimetry is almost independent of the surrounding temperature, because the jacket is an excellent shield. This is unfortunately not the case with balance calorimetry. In addition the heatflow calorimetry gives a significantly greater useful signal, which allows higher sensitivities.

On the other hand, the heat balance calorimetry is almost completely independent of viscosity changes (polymerization), filling level (dosages), wall thickness (crystallization and heat exchange fluid flow speed/viscosity) and the stirrer vortex (change of torque).

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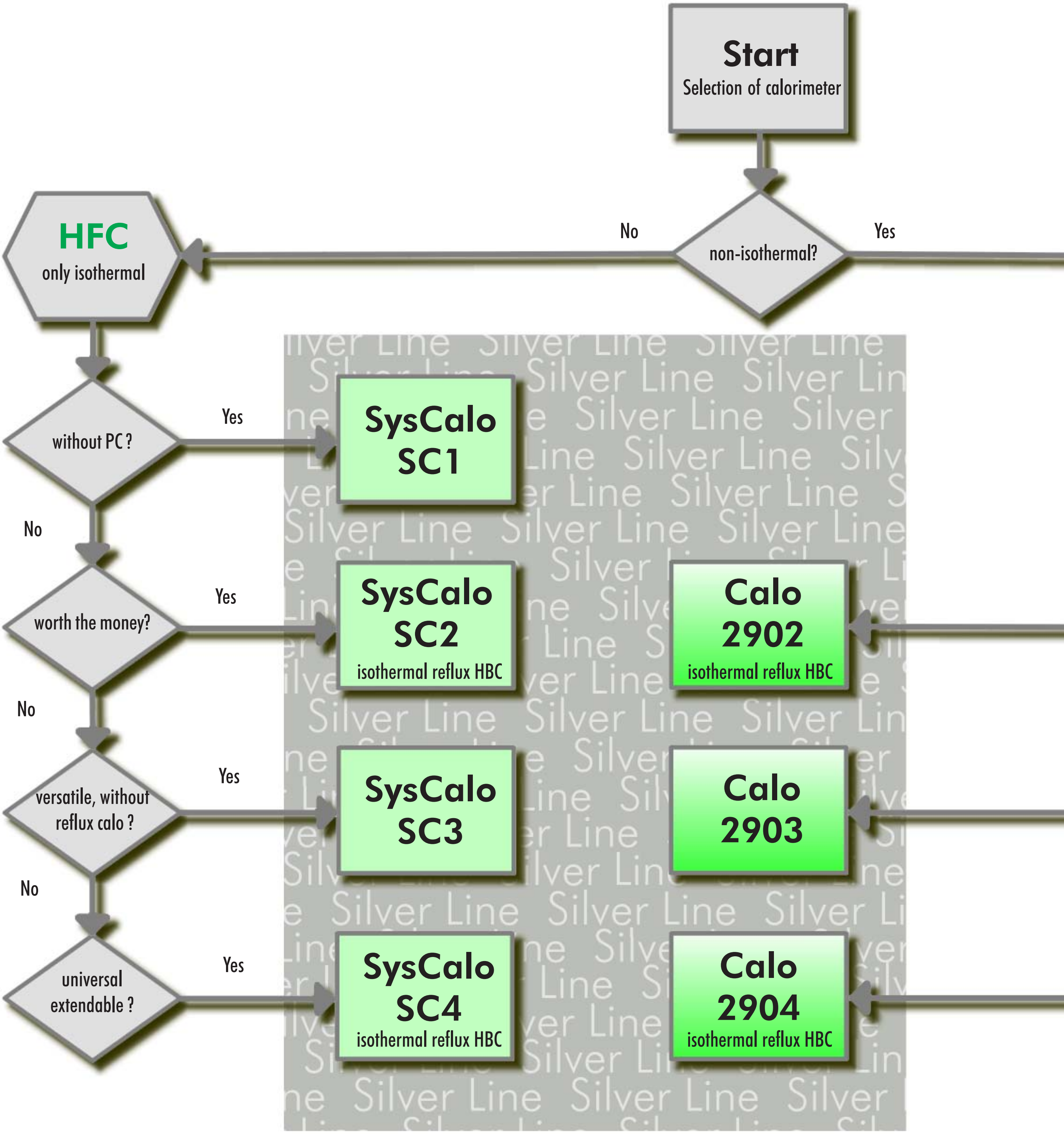
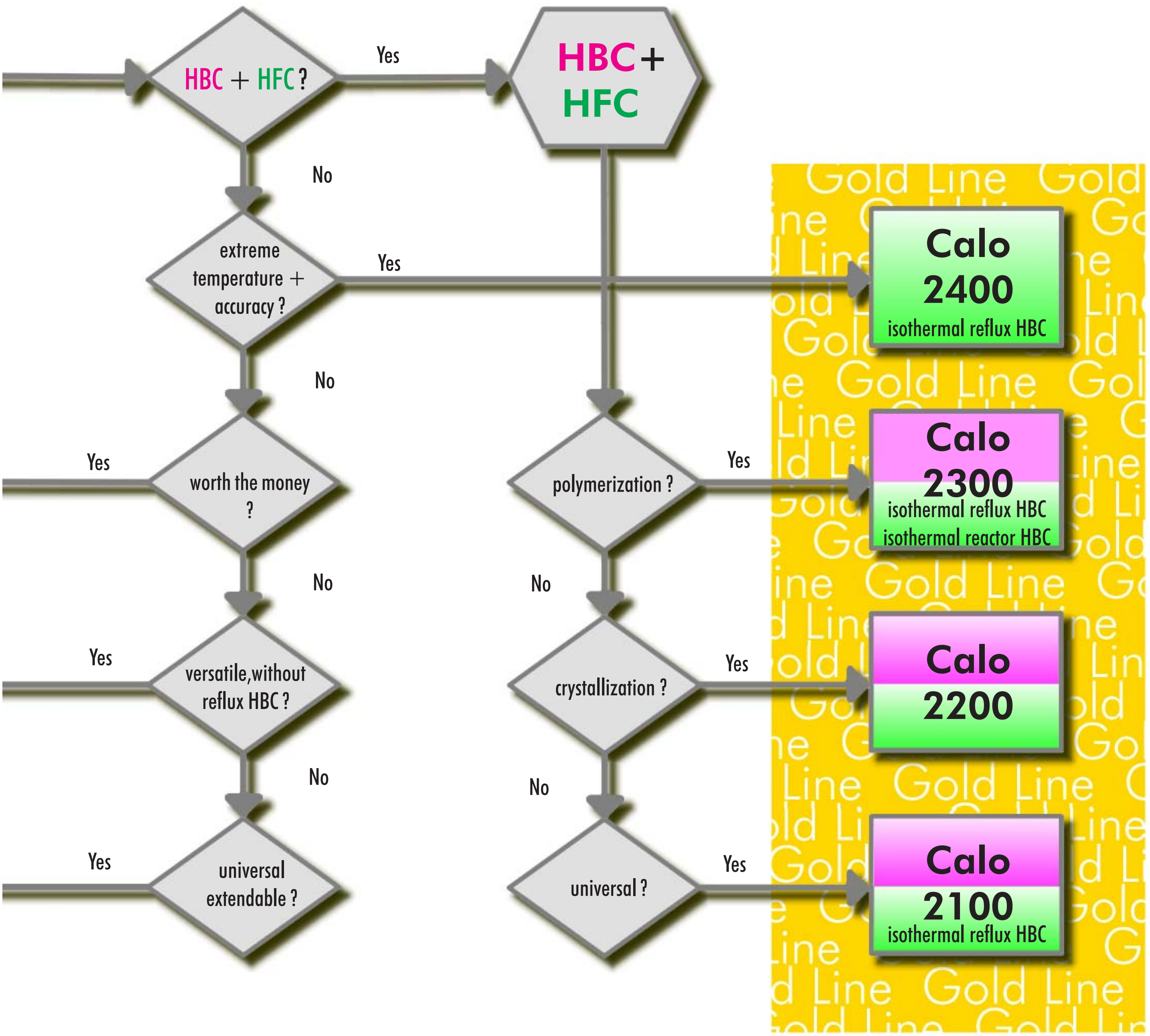
# Decision flow-chart for reaction calorimeter selection





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# SysCalo SC1 - the most economical calorimeter

## Characteristics

This heat flow calorimeter is the most economical solution in the entire SysCalo range. The basic version comprises of a 1 litre double jacket reactor with a Tango Thermostat. A gravimetric dosage is also available.

Two MIDILABs are used for operation and controls. This equipment assembly has time controlled programme steps. Consequently, simple runs, such as temperature control, dosing, reaction period, calibrating etc., can be operated automatically.

In addition, MIDILABs allow temperature monitored dosages (if exothermy is too strong, hold until cooled down again) and when necessary a recording of additional parameters such as a pressure or vacuum control. This makes it obvious that this system can be built to a particular specification.

The MIDIVIEW programme, which can be run on a simple PC, is used for data recording. The calorimetric evaluation is carried out off-line after the experiment. In SysCalo SC1 there is no balance calorimetry in the reflux cooler.

The system can subsequently be equipped to a SC2 or even a Calo 2902 non-isothermal heat flow calorimeter.

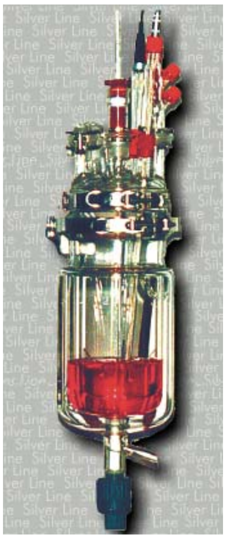
## System Configuration

| | |
|---|---|
| Reactor | 1 litre double jacket, cylindrical |
| Stirrer | IKA Eurostar (manual) with anchor stirrer |
| Dosage | 1x gravimetric from balance 2000 g |
| Thermostat | Unistat Tango -40 to +200°C |
| Temp.-meas. | TR, TJ and TH (head) |
| Calorimetry | Heat flow calorimetry in reactor |
| Calibration | 20 Watt with supply and measurement |
| Temp. control | MIDILAB TC for jacket and cascade control, 20 programme steps |
| Dosage control | MIDILAB DC with direct connection for balance and pump |
| Construction | without tripod, but with double reactor bracket for installation into fume cupboard |
| PC | Optimized Pentium PC, colour printer, colour screen |
| Programme | Windows 98, MIDIVIEW, SysGraph with module KaloGraph |
| Options | See later |

### Standard Configuration

1 gravimetric dosage

1 l double jacketed reactor



Unistat Tango

Midilab Temperature and Dosage Controller

15" colour monitor with Midiview

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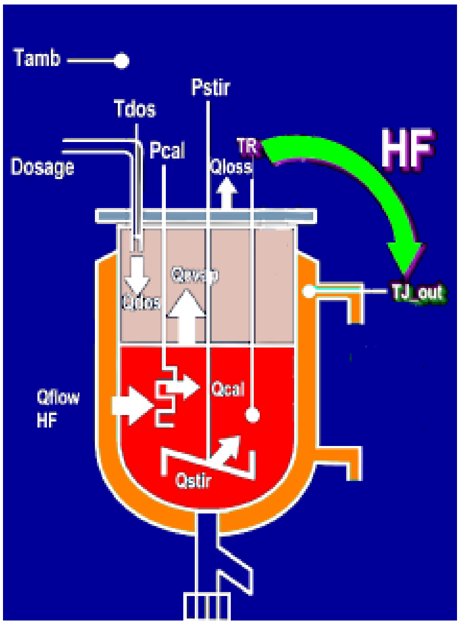
# Capabilities of SysCalo SC1

## Short informmation with typical values

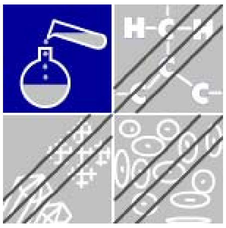
| | |
|---|---|
| Resolution of TR, TJ | 0.07 K |
| Resolution of (TR-TJ), reactor - jacket | 0.07 K |
| Sensitivity of HFC, reactor, isothermal | 1000 mW |
| Accuracy of HFC, reactor, isothermal | 5 % |
| Water equivalent determination | manually |
| cp determination | manually |

## Measuring concept

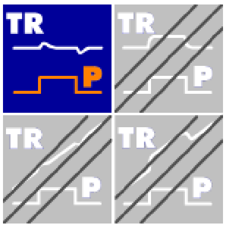


Method: only heatflow

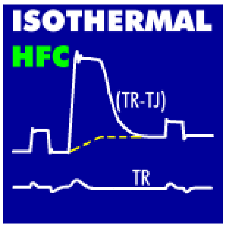
Application: predominantly syntheses



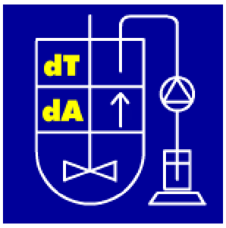
Operation type: only isotherm



Isotherm HFC conventional



Complete corrections



## Upgrade to SC2 as well as Calo 2902 (see next page)

# SysCalo SC2 - the highly competitive calorimeter

## Characteristics

The SysCalo SC2 heat flow calorimeter is a further development of the smaller SC1. Simple operation and a high functionality are very obvious from the start. With the integrated recipe control complex recipes can be carried out, which are run fully automatically. Process steps can be initiated or interrupted not only chronologically but also by events.

Apart from fully automatic processing with recipes the experiment can also be carried out manually step by step. Even when the experiments are carried out for the first time, operation from synoptic is considered more and more. In addition such manually executed experiments can obviously also be evaluated calorimetrically!

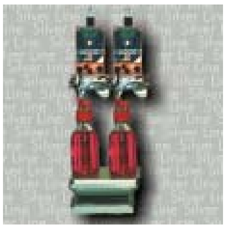
The system can subsequently be extended to a Calo 2902 non-isothermal heat flow calorimeter.

## SystemConfiguration

| | |
|---|---|
| Reactor | 2 litre double jacket, cylindrical |
| Stirrer | Heidolph with anchor stirrer, 40-2000 rpm, remote control and torque measurement |
| Dosage | 2 x gravimetric from 6200 g balance |
| Thermostat | Unistat Tango -40 to +200°C |
| Temp.-meas. | TR and TJ |
| Calorimetry | Heat flow calorimetry in reactor, heat balance calorimetry in cooler |
| Calibration | 40 Watt with supply and measurement |
| Temp. control | MIDILAB TC for jacket and cascade control |
| Dosage control | MIDILAB DC with direct connection for balance and pumps (a max. of 4 pumps) |
| Reflux | Cooler and magnetic separator available |
| Construction | without tripod, but with double reactor bracket for installation into fume cupboard |
| PC | Optimized Pentium PC, colour printer, colour screen |
| Programme | Windows NT 4.0, FIX/MMI, SYBAREX 3 and SysGraph with module KaloGraph |
| Options | See later |

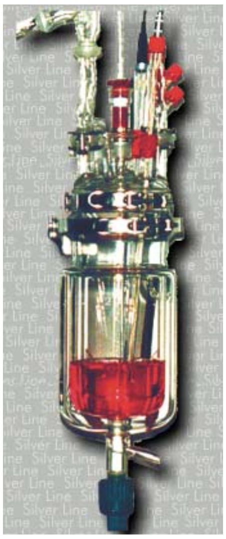
### Standard Configuration

2 gravimetric dosages



Reflow condenser and separator

2 l double jacketed reactor



Recipe control SYBAREX 3

17“ colour monitor with synoptics

Unistat Tango

Midilab Temperature and Dosage Controller

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# Capabilities of SysCalo SC2

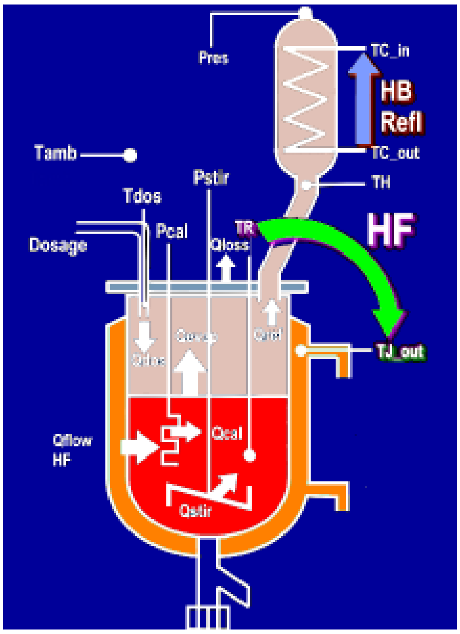
## SysCalo SC2 - Short inforrmation with typical values

| | |
|---|---|
| Resolution of TR, TJ | 0.07 K |
| Resolution of (TR-TJ), reactor - jacket | 0.07 K |
| Resolution of (TCout-TCin), reflux cooler | 0.01 K |
| Sensitivity of HFC, reactor, isothermal | 1000 mW |
| Accuracy of HFC, reactor, isothermal, with calibr. | 4 % |
| Accuracy of HBC, reflux, isothermal, with calibr. | 6 % |

## Upgrade to non-isothermal Calo 2902

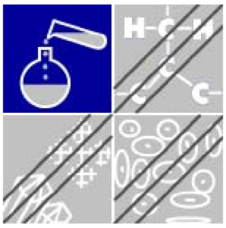
| | |
|---|---|
| Dynamics of HFC, reactor, isothermal | > 1000 W |
| Kinetics delay HFC, reactor | 60 s |
| Accuracy of HFC, reactor, isothermal, without calibr. | 20 % |
| Accuracy of HBC, reflux, isothermal, without calibr. | 20 % |
| Accuracy of HFC, reactor, isothermal, with calibr. | 2 % |
| Accuracy of HBC, reflux, isothermal, with calibr. | 4 % |
| Water equivalent determination | pre-calibrated, live exactly |

## Measuring concept

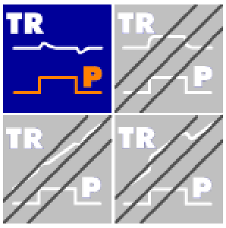


Method: only heatflow

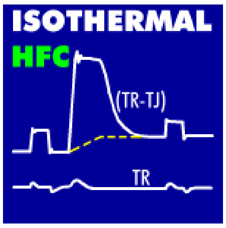
Application: predominantly syntheses



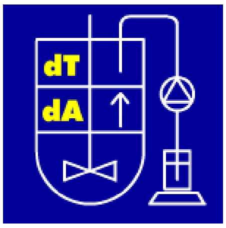
Operation type: only isotherm



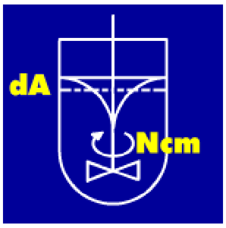
Isotherm HFC conventional



Complete corrections

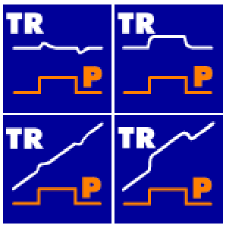


Vortex correction, torque stirrer

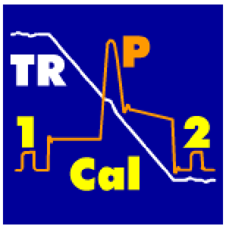


# Upgrade to non-isothermal Calo 2902 with the following additional features:

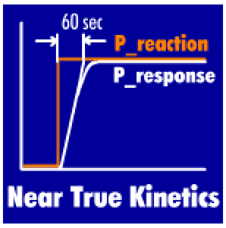
Operation type: all modes



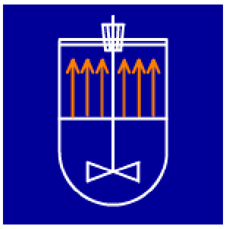
Non-isothermal with calibration



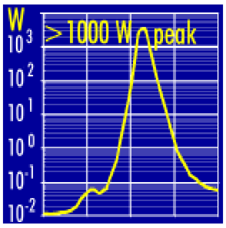
Excellent kinetics



Closed system



Extreme dynamics



On-line guidelines with HFC: P & Q

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# SysCalo SC3 - the versatile calorimeter

## Characteristics

The SysCalo SC3 consists of an automatic synthesis reactor with calorimetric option. The SysCalo SC3 fullfills practically all requirements in the development and syntheses laboratory. With the recipe editor fully automatic running recipes can be executed, which can be controlled not only chronologically but also by events.

Apart from the experienced, adaptive temperature control and the interfaces for 2 balances with up to a maximum of 4 dosages each, the SC3 has two additional universal control loops. These can be allocated as required by the user. For example a double sided pH control and a vacuum/pressure control can complete the system.

Apart from fully automatic processing with recipes the experiment can also be carried out manually step by step. Even when the experiments are carried out for the first time, operation from synoptic is considered more and more. In addition these manually executed experiments can obviously also be evaluated calorimetrically!

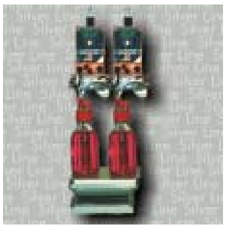
The system can subsequently be extended to a Calo 2903 non-isothermal heat flow calorimeter.

## System Configuration

| | |
|---|---|
| Reactor | 1 litre triple jacket, conical (allows processing from 150 ml up to 1000 ml) |
| Stirrer | Heidolph with propeller stirrer, 40-2000 rpm, remote control and equipped with torque measurement |
| Dosage 1 | 2 x gravimetric from balance 1, range 6200 g |
| Dosage 2 | 1 x gravimetric from balance 2, range 6200 g |
| Thermostat | Unistat Tango -40 to +200°C |
| Temp.-meas. | TR and TJ |
| Calorimetry | Heat flow calorimetry in reactor |
| Calibration | 20 Watt with supply and measurement |
| Temp. control | Jacket and cascade control |
| Dosage control | Connection for 2 balances and a max. of 4 pumps or valves each |
| Universal CTR1 | for example for pH |
| Universal CTR2 | for example for vaccum or pressure |
| Distillation | Measurement input head temperature TH and use of balance 2 as stop criteria |
| Add. meas. | pH and Taux always available |
| Construction | without tripod but with double reactor bracket for installation into fume cupboard |
| PC | Optimized Pentium PC, colour printer, 17" colour screen |
| Programmes | Windows NT 4.0, Office, FIX/MMI, SYBAREX 4, SysGraph with module KaloGraph |
| Options | See later |

### Standard Configuration

2 gravimetric dosages



1 gravimetric dosage

2 l triple jacketed reactor

Recipe control SYBAREX 4

17" colour monitor with synoptics

Unistat Tango

SYNTALAB Controller

SYSTAG

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# Capabilities of SysCalo SC3

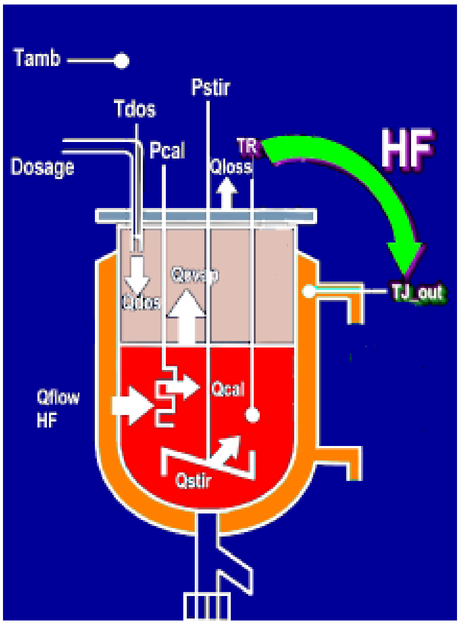
## SysCalo SC3 - Short inforrmation with typical values

| | |
|---|---|
| Resolution of TR, TJ | 0.006 K |
| Resolution of (TR-TJ), reactor - jacket | 0.006 K |
| Sensitivity of HFC, reactor, isothermal | 500 mW |
| Accuracy of HFC, reactor, isothermal, with calibr. | 2 % |

## Upgrade to non-isothermal Calo 2903

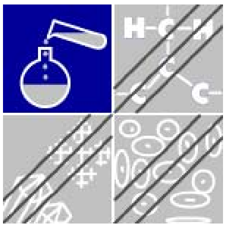
| | |
|---|---|
| Dynamics of HFC, reactor, isothermal | > 1000 W |
| Kinetics delay HFC, reactor | 60 s |
| Accuracy of HFC, reactor, isothermal, without calibr. | 20 % |
| Accuracy of HFC, reactor, isothermal, with calibr. | 2 % |
| Water equivalent determination | pre-calibrated, live exactly |

## Measuring concept

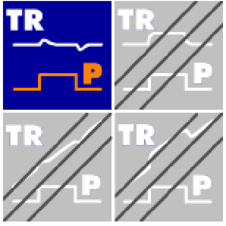


Method: only heatflow

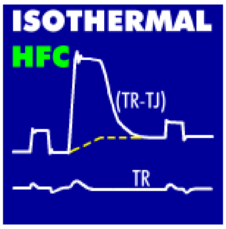
Application: predominantly syntheses



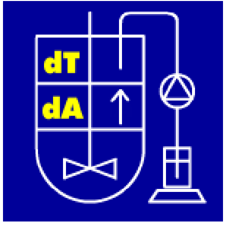
Operation type: only isotherm



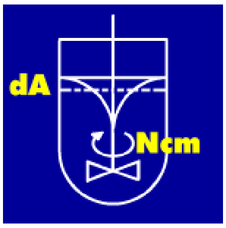
Isotherm HFC conventional



Complete corrections

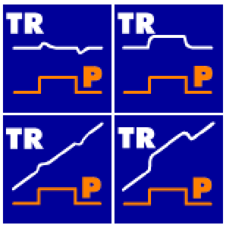


Vortex correction, torque stirrer

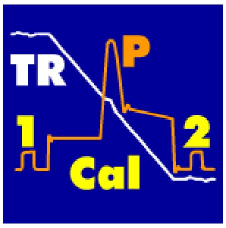


# Upgrade to non-isothermal Calo 2903 with the following additional features:

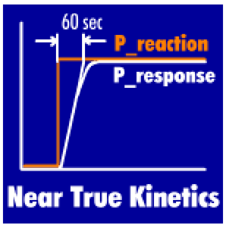
Operation type: all modes



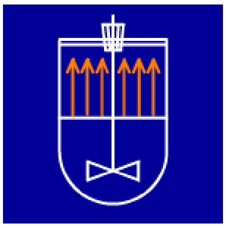
Non-isothermal with calibration



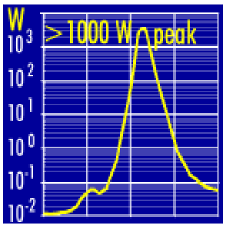
Excellent kinetics



Closed system



Extreme dynamics



On-line guidelines with HFC: P & Q

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# SysCalo SC4 - the expandable calorimeter

## Characteristics

The SysCalo SC4 is the ideal tool for scientific purposes. Special hardware modules ensure the highest signal resolution and the best possible reproducibility for calorimetric evaluation. Thanks to its modular structure this system offers an almost unlimited variety of uses. Extensive, fully automatically running recipes are the strengths of the SysCalo SC4.

Apart from fully automatic processing with recipes the experiments can also be carried out manually step by step. Even when the experiments are carried out for the first time, operation from synoptic is considered more and more. In addition these manually executed experiments can obviously also be evaluated calorimetrically!

The system can subsequently be extended to a Calo 2904 non-isothermal heat flow calorimeter.

## System Configuration

| | |
|---|---|
| Reactor | 1 litre triple jacket, conical (allows processing from 150 ml up to 1000 ml) |
| Stirrer | Heidolph with propeller stirrer, 40-2000 rpm, remote control, torque measurement |
| Dosage 1 | 2 x gravimetric from balance 1, range 6200 g |
| Dosage 2 | 1 x gravimetric from balance 2, range 6200 g |
| Gas dosage | Optional with mass flow controllers, also 2 or 3 parallel dosages with selectable %-ratio possible |
| Thermostat | Unistat Tango -40 to +200°C |
| Temp.meas. | TR, TJ, TH (head) and Taux (e.g. ambient) |
| Calorimetry | Heatflow calorimetry in reactor and heat balance calorimetry in the reflux cooler |
| Calibration | 20 Watt, glass, with supply and measurement |
| Temp.-control | Jacket and cascade control |
| Dosage control | Connection for 2 balances and 2 pumps each |
| Pressure control | for 0…60 bar (only with autoclaves) |
| Vacuum control | range approx. 20 … 1300 mbar |
| Purging | On/off valve for, for example, $N_2$ |
| Reflux | Cooler and magnetic separator available |
| Distillation | Is available as standard |
| pH control | one-sided control with Dosimat 715 |
| Construction | without tripod but with double reactor bracket for installation into fume cupboard |
| PC | Optimized Pentium PC, colour printer, colour screen |
| Programmes | Windows NT 4.0, Office, FIX/MMI, SYBAREX 1/V4, SysGraph with module KaloGraph |
| Options | See later |

### Standard Configuration

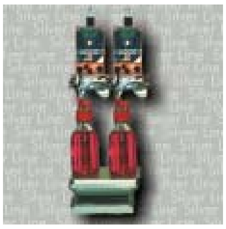

Gas dosage


Reflow condenser and separator


2 l triple jacketed reactor


Recipe control SYBAREX 1/V4


17" colour monitor with synoptics


2 gravimetric dosages


1 gravimetric dosage


pH control with Dosimat


Unistat Tango


Combilab control unit

SYSTAG
automatically better

# Capabilities of SysCalo SC4

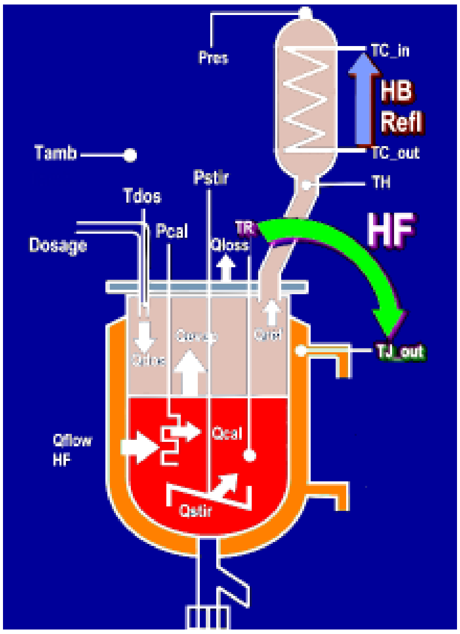
### SysCalo SC4 - Short inforrmation with typical values

| | |
|---|---|
| Resolution of TR, TJ | 0.006 K |
| Resolution of (TR-TJ), reactor - jacket | 0.001 K |
| Resolution of (TCout-TCin), reflux cooler | 0.001 K |
| Sensitivity of HFC, reactor, isothermal | 200 mW |
| Accuracy of HFC, reactor, isothermal, with calibr. | 2 % |
| Accuracy of HBC, reflux, isothermal, with calibr. | 4 % |

### Upgrade to non-isothermal Calo 2904

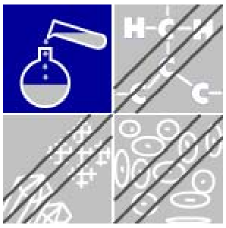
| | |
|---|---|
| Dynamics of HFC, reactor, isothermal | > 1000 W |
| Kinetics delay HFC, reactor | 60 s |
| Accuracy of HFC, reactor, isothermal, without calibr. | 20 % |
| Accuracy of HBC, reflux, isothermal, without calibr. | 20 % |
| Accuracy of HFC, reactor, isothermal, with calibr. | 2 % |
| Accuracy ofr HBC, reflux, isothermal, with calibr. | 4 % |
| Water equivalent determination | pre-calibrated, live exactly |

### Measuring concept

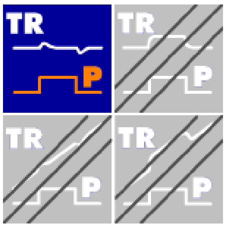


Method: only heatflow

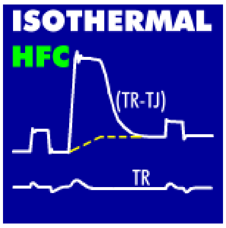
Application: predominantly syntheses



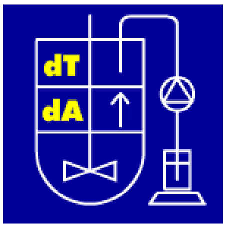
Operation type: only isotherm



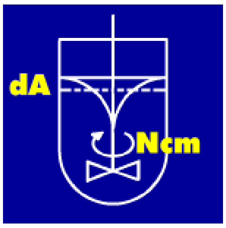
Isotherm HFC conventional



Complete corrections

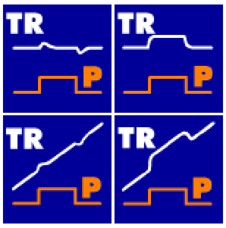


Vortex correction, torque stirrer

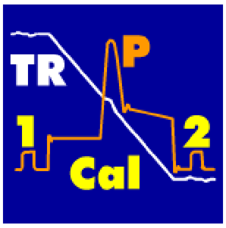


# Upgrade to non-isothermal Calo 2904 with the following additional features:

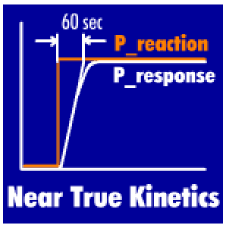
Operation type: all modes



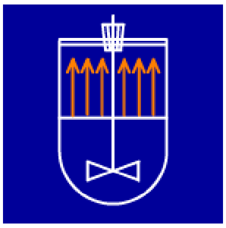
Non-isothermal with calibration



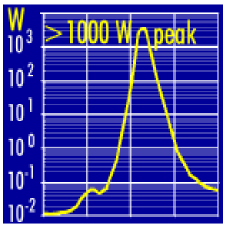
Excellent kinetics



Closed system



Extreme dynamics



On-line guidelines with HFC: P & Q

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# Calo 2100 - the universal high tech calorimeter

## Characteristics

Calo 2100 is the top model with simultaneous heat flow and heat balance calorimetry. Because of the highest signal resolution, sensitivities of up to 10 mW/kg (HFC, isothermal) are possible. In the temperature stabilized cabinet 50 mW/kg can be achieved, even during non-isothermal operation. The tiresome baseline problem is solved. The entire problem of varying surfaces, viscosity changes and vortex oscillations of stirrer is solved with heat balance calorimetry. This piece of equipment is therefore certainly the bee's knees for syntheses, polymerization, fermentation and crystallization.

Because of the new concept you immediately receive on-line information with 5 .. 10% accuracy and this without any calibration during the experiment itself. Consequently this is significantly faster and particularly unstable processes no longer present a problem! With a calibration the result can even be improved off-line to approx. 1 .. 2%.

Extensive fully automatic running recipes with manual intervention are the strong points of all equipment in the Calo 2000 series. Apart from fully automatic working with recipes the experiment can also be carried out step by step manually. Even with an experiment carried out for the first time operation is estimated from synopsis.

## System Configuration

| | |
|---|---|
| Reactor | 1 litre triple jacket, cylindrical (allows processing from 350 ml up to 1000 ml) |
| Stirrer | Heidolph with special propeller stirrer, 40-400 and 200-2000 rpm, remote control, torque measurement 200/40 Ncm |
| Dosage 1 | 1 (max.2) gravimetric from balance 1 (6200 g) |
| Thermostat | Unistat 160w -60°C to +200°C |
| Temp.meas. | Pt-100, type A |
| Calorimetry | Heatflow and heat balance calorimetry in reactor and heat balance calorimetry in reflux cooler |
| Calibration | 5 Watt, glass, with supply and measurement |
| Temp.-control | Jacket and reactor (cascade) control together with some other control loops |
| Pressure control | for 0…1300 mbar (0…60 bar with autoclave) |
| Vacuum control | range approx. 20 … 1000 mbar |
| Purging | On/off valve & continuous flow $N_2$ for cabinet |
| Reactor pressure | Automatic supervision and control for an absolute tight glass reactor |
| Reflux | Cooler and magnetic separator |
| Distillation | Is available as standard with balance |
| pH | Measuring standard, optional control |
| Construction | Built in cabinet. Hood and $N_2$ (max. 25 l/min) for cabinet, cooling water reflux and thermostat from customer |
| PC | Optimized Pentium PC, colour printer, colour screen |
| Programmes | Windows NT 4.0, Office, FIX/MMI, SYBAREX 1/V4, SysGraph + module Calo 2000 |
| Options | See later |

### Standard Configuration

1inert gas control for cabinet ($N_2$)

Reflow condenser, separator, dist.-cooler, balance

1 l triple jacketed reactor

Recipe control SYBAREX 1/V4

17" colour monitor with synoptics

1 cabinet, temp. controlled

1 gravimetric dosage

1 gravimetric dosage

Unistat 160w

Combilab control unit

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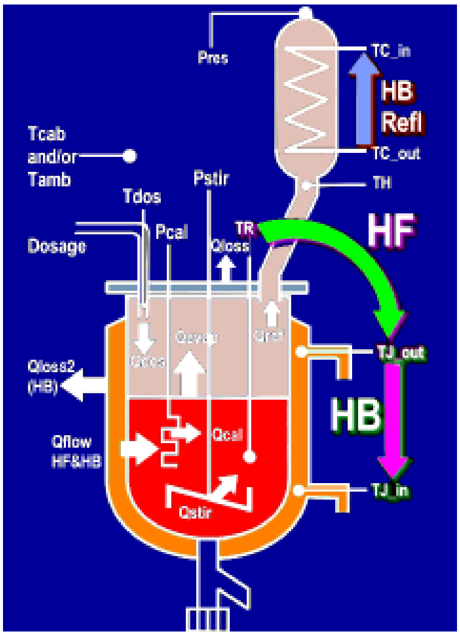
automatically better

# Capabilities of Calo 2100

## Calo 2100 - Short inforrmation with typical values

| | |
|---|---|
| Resolution of TR, TJ | 0.0004 K |
| Resolution of (TR-TJ), reactor - jacket | 0.0004 K |
| Resolution of (TCout-TCin), reflux cooler | 0.0004 K |
| Sensitivity of HFC, reactor, isothermal | 10 mW |
| Sensitivity of HBC, reactor, isothermal | 50 mW |
| Sensitivity of HBC, reflux, isothermal | 500 mW |
| Dynamics of HFC, reactor, isothermal | > 1000 W |
| Dynamics of HBC, reactor, isothermal | > 1000 W |
| Kinetics delay HFC, reactor | 60 s |
| Kinetics delay HBC, reactor | 60 s |
| Accuracy of HFC, reactor, isothermal, without calibr. | 5 % |
| Accuracy of HBC, reactor, isothermal, without calibr. | 5 % |
| Accuracy of HBC, reflux, isothermal, without calibr. | 8 % |
| Accuracy of HFC, reactor, isothermal, with calibr. | 1 % |
| Accuracy of HBC, reactor, isothermal, with calibr. | 1 % |
| Accuracy of der HBC, reflux, isothermal, with calibr. | 2 % |
| Water equivalent determination | pre-calibrated, live exactly |
| cp determination | automatic |

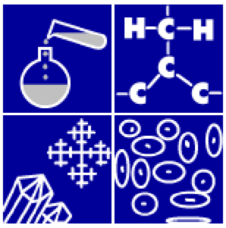
## Measuring concept



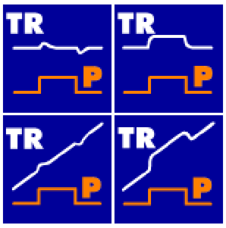
Method: simultaneous heatbalance and heatflow

**HBC**
**HFC**

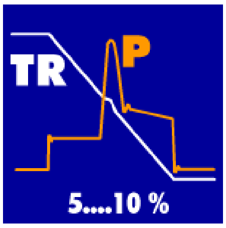
Applications: all



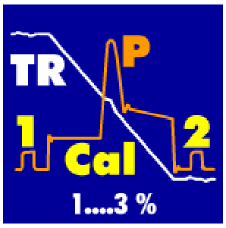
Operation type: all modes



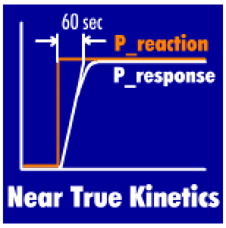
Non-isothermal without calibration



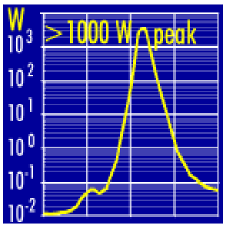
Non-isothermal with calibration



Excellent kinetics

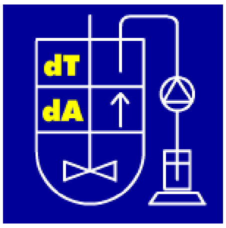


Extreme dynamics

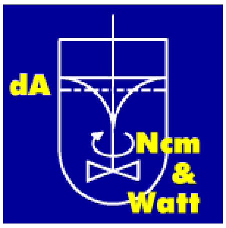


On-line guidelines HFC/HBC: P & Q

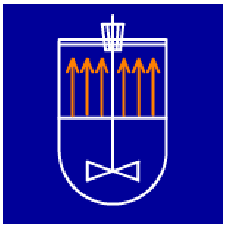
Complete corrections



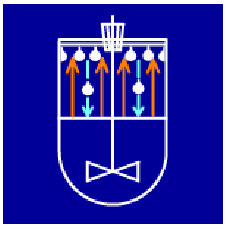
Vortex correction, torque and power



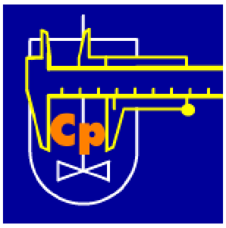
Closed system



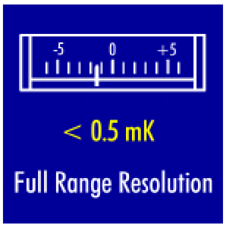
No condensation, therefore no "reflux"



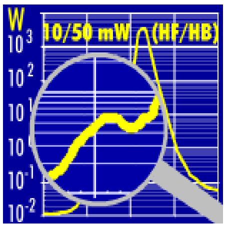
Automatic cp determination



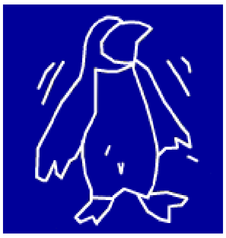
Extreme measurement resolution



Highest sensitivity



High accuracy at low temperature



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# Calo 2200 - the high tech calorimeter for crystallization

## Characteristics

Calo 2200 is another top model with simultaneous heat flow and heat balance calorimetry. Because of the highest signal resolution, sensitivities of up to 10 mW/kg (HFC, isothermal) are possible. In the temperature stabilized cabinet 50 mW/kg can be achieved, even during non-isothermal operation. The tiresome baseline problem is solved. The entire problem of varying surfaces, crystallization on the wall, viscosity changes and vortex oscillations of stirrer is solved with heat balance calorimetry. With the additionalset-up for seed crystal and the turbidity measurement this apparatus is particularly well equipped for the crystallization.

Because of the new concept you immediately receive on-line information with 5 - 10% accuracy and this without any calibration during the experiment itself. Consequently this is significantly faster for a first overview! With calibration the result is improved off-line to approx. 1 - 2%. A calibration and an off-line evaluation are always necessary for small crystallization powers.

Extensive fully automatic running recipes with manual intervention are the strong points of all equipment in the Calo 2000 series. Apart from fully automatic working with recipes the experiment can also be carried out step by step manually. Even with an experiment carried out for the first time operation is estimated from synopsis.

## System Configuration

| | |
|---|---|
| Reactor | 1 litre triple jacket, cylindrical (allows processing from 350 ml up to 1000 ml) |
| Stirrer | Heidolph with special propeller stirrer, 40-400 and 200-2000 rpm, remote control, torque measurement 200/40 Ncm |
| Dosage 1 | 1 (max.2) gravimetric from balance 1 (6200 g) |
| Thermostat | Unistat 160w -60°C to +200°C |
| Temp.meas. | Pt-100, type A |
| Calorimetry | Heatflow and heat balance calorimetry in reactor |
| Calibration | 5 Watt, glass, with supply and measurement |
| Temp.-control | Jacket and reactor (cascade) control together with some other control loops |
| Pressure control | for 0…1300 mbar (0…60 bar with autoclave) |
| Vacuum control | range approx. 20 … 1000 mbar |
| Purging | On/off valve & continuous flow $N_2$ for cabinet |
| Reactor pressure | Automatic supervision and control for an absolute tight glass reactor |
| Crystal seed | Injection of small amounts of powder or emulsion with $N_2$ |
| Turbidity | Measuring as standard |
| Construction | Built in cabinet. Hood and $N_2$ (max. 25 l/min) for cabinet, cooling water reflux and thermostat from customer |
| PC | Optimized Pentium PC, colour printer, colour screen |
| Programmes | Windows NT 4.0, Office, FIX/MMI, SYBAREX 1/V4, SysGraph + module Calo 2000 |
| Options | See later |

### Standard Configuration

1 inert gas control for cabinet ($N_2$)

1 turbidity meter

1 seed crystal unit

1 l triple jacketed reactor

Recipe control SYBAREX 1/V4

17" colour monitor with synoptics

1 cabinet, temp. controlled

1 gravimetric dosage

Unistat 160w

Combilab control unit

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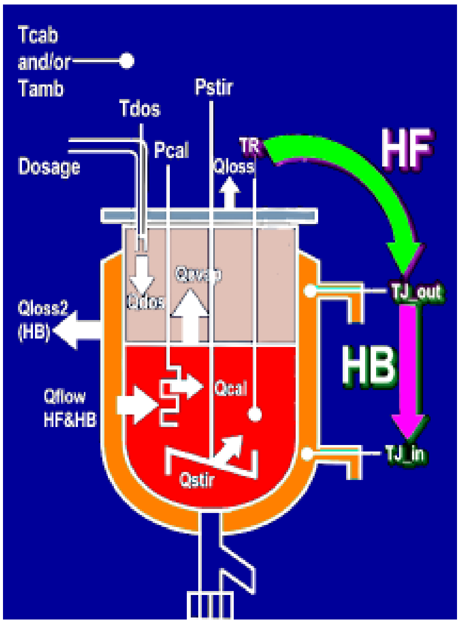
# Capabilities of Calo 2200

## Calo 2200 - Short informmation with typical values

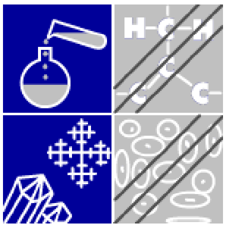
| | |
|---|---|
| Resolution of TR, TJ | 0.0004 K |
| Resolution of (TR-TJ), reactor - jacket | 0.0004 K |
| Sensitivity of HFC, reactor, isothermal | 10 mW |
| Sensitivity of HBC, reactor, isothermal | 50 mW |
| Dynamics of HFC, reactor, isothermal | > 1000 W |
| Dynamics of HBC, reactor, isothermal | > 1000 W |
| Kinetics delay HFC, reactor | 60 s |
| Kinetics delay HBC, reactor | 60 s |
| Accuracy of HFC, reactor, isothermal, without calibr. | 5 % |
| Accuracy of HBC, reactor, isothermal, without calibr. | 5 % |
| Accuracy of HFC, reactor, isothermal, with calibr. | 1 % |
| Accuracy of HBC, reactor, isothermal, with calibr. | 1 % |
| Water equivalent determination | pre-calibrated, live exactly |
| cp determination | automatic |
| Accuracy of turbidity measurement | 1 % |

Method: simultaneous heatbalance and heatflow

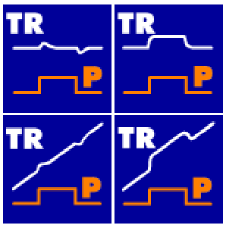
## Measuring concept



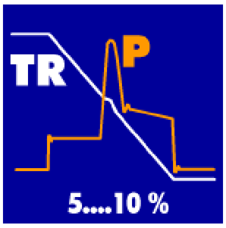
Application: synthesis, crystallization



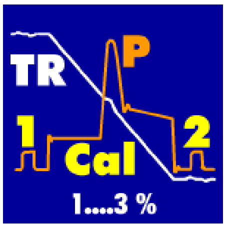
Operation type: all modes



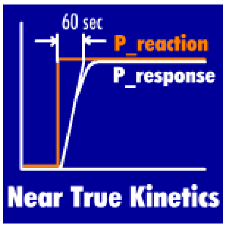
Non-isothermal without calibration



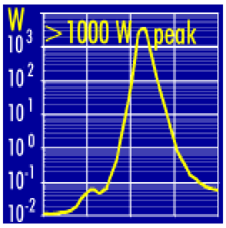
Non-isothermal with calibration



Excellent kinetics



Extreme dynamics

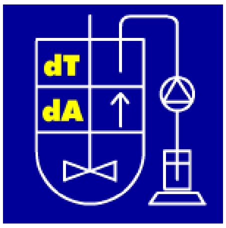


On-line guidelines HFC/HBC: P & Q

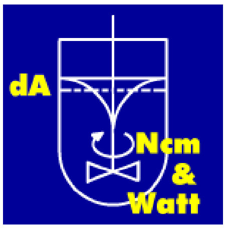
on-line

| | | P [W] | Q[kJ] |
|---|---|---|---|
| HF | Cal | 5.09 | 29.83 |
| | React | -432 | -54.95 |
| HB | Cal | 5.21 | 31.56 |
| | React | -445 | -56.35 |

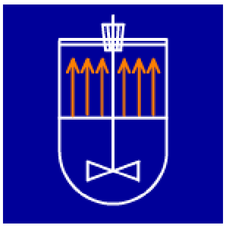
Complete corrections



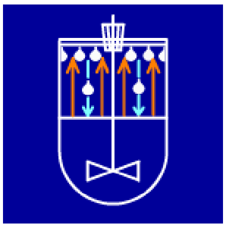
Vortex correction, torque and power



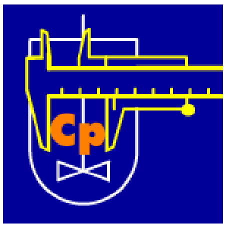
Closed system



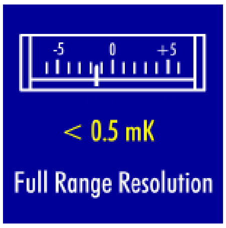
No condensation, therefore no "reflux"



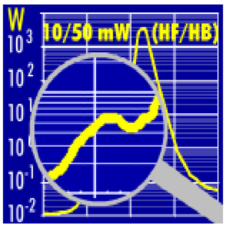
Automatic cp determination



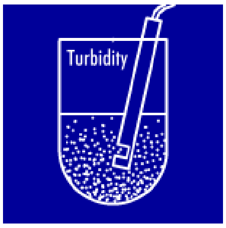
Extreme measurement resolution



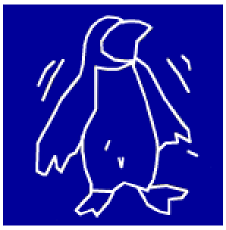
Highest sensitivity



Turbidity measurement integrated



High accuracy at low temperature



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# Calo 2300 - the high tech calorimeter for polymerization

## Characteristics

The Calo 2300 is a heatflow and simultaneous heat balance calorimeter. Because of the large signal resolution sensitivities of up to 100 mW/kg (HFC, isothermal) are possible. Because a temperature-stabilized cabinet is not available, the HBC is only isothermal. HFC on the other hand can also be used non-isothermally. The tiresome baseline problem is solved. The entire problem of varying surfaces, crystallization on the wall, viscosity changes and vortex oscillations of stirrer is solved with heat balance calorimetry. This equipment is therefore the ideal solutions for polymerization, because with this more power is generated than with crystallization.

Because of the new concept you immediately receive on-line information with approx. 10% accuracy. It is nevertheless always recommended to carry out the experiment with a short calibration (approx. 10 min.) so that in any case the off-line correction for high accuracy can be used. This is especially important when a stabilized cabinet is not available.

Extensive fully automatic running recipes with manual intervention are the strong points of all equipment in the Calo 2000 series. Apart from fully automatic working with recipes the experiment can also be carried out step by step manually. Even with an experiment carried out for the first time operation is estimated from synopsis.

## System Configuration

| | |
|---|---|
| Reactor | 1 litre triple jacket, cylindrical (allows processing from 350 ml up to 1000 ml) |
| Stirrer | Heidolph with special propeller stirrer, 40-400 and 200-2000 rpm, remote control, torque measurement 200/40 Ncm |
| Dosage 1 | 1 (max.2) gravimetric from balance 1 (6200 g) |
| Dosage 2 | 1 (max.2) gravimetric from balance 2 (6200 g) |
| Thermostat | Unistat 380HT -80°C to +200°C |
| Temp.meas. | Pt-100, type A |
| Calorimetry | Heatflow and heat balance calorimetry in reactor and heat balance calorimetry in reflux cooler |
| Calibration | 20 Watt, glass, with supply and measurement |
| Temp.-control | Jacket and reactor (cascade) control together with some other control loops |
| Pressure control | for 0…1300 mbar (0…60 bar with autoclave) |
| Vacuum control | range approx. 20 … 1000 mbar |
| Reactor pressure | Automatic supervision and control for an absolute tight glass reactor |
| Reflux | Cooler and magnetic separator |
| Distillation | Is available as standard with balance |
| pH | Measuring standard, optional control |
| Construction | Steel frames to be placed in a fume cupboard. From customer: cooling water for reflux |
| PC | Optimized Pentium PC, colour printer, colour screen |
| Programmes | Windows NT 4.0, Office, FIX/MMI, SYBAREX 1/V4, SysGraph + module Calo 2000 |
| Options | See later |

### Standard Configuration

Reflow condenser, separator, dist.-cooler, balance

1 l triple jacketed reactor

Recipe control SYBAREX 1/V4

17" colour monitor with synoptics

1 gravimetric dosage

1 gravimetric dosage

Unistat 380HT

Combilab control unit

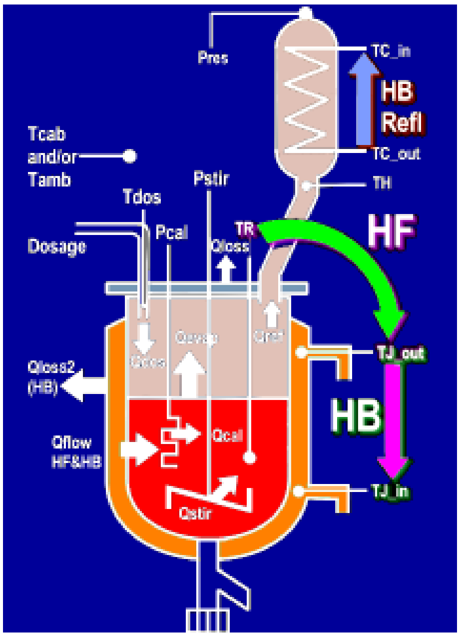
SYSTAG
automatically better

# Capabilities of Calo 2300

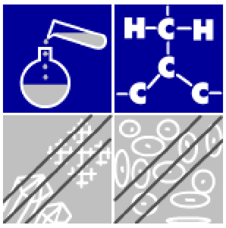
## Calo 2300 - Short informmation with typical values

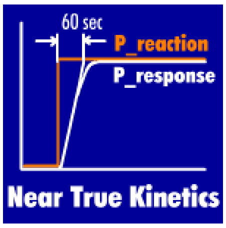
| | |
|---|---|
| Resolution of TR, TJ | 0.0004 K |
| Resolution of (TR-TJ), reactor - jacket | 0.0004 K |
| Resolution of (TCout-TCin), reflux cooler | 0.0004 K |
| Sensitivity of HFC, reactor, isothermal | 100 mW |
| Sensitivity of HBC, reactor, isothermal | 500 mW |
| Sensitivity of HBC, reflux, isothermal | 500 mW |
| Dynamics of HFC, reactor, isothermal | > 1000 W |
| Dynamics of HBC, reactor, isothermal | > 1000 W |
| Kinetics delay HFC, reactor | 60 s |
| Kinetics delay HBC, reactor | 60 s |
| Accuracy of HFC, reactor, isothermal, without calibr. | 10 % |
| Accuracy of HBC, reactor, isothermal, without calibr. | 10 % |
| Accuracy of HBC, reflux, isothermal, without calibr. | 20 % |
| Accuracy of HFC, reactor, isothermal, with calibr. | 1 % |
| Accuracy of HBC, reactor, isothermal, with calibr. | 3 % |
| Accuracy of HBC, reflux, isothermal, with calibr. | 4 % |
| Water equivalent determination | pre-calibrated, live exactly |
| cp determination | automatic |

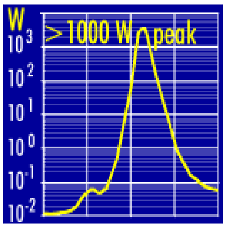
## Measuring concept

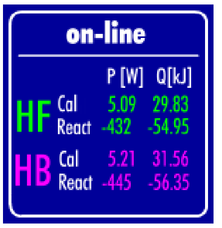


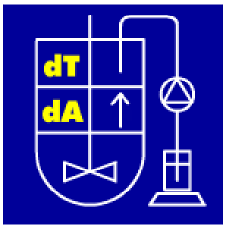

Method: simultaneous heatbalance and heatflow

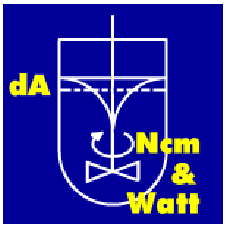

Application: synthesis, polymerization

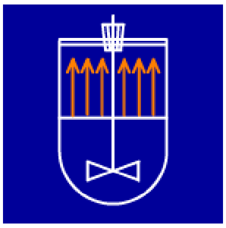

Excellent kinetics

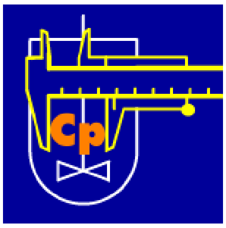

Extreme dynamics

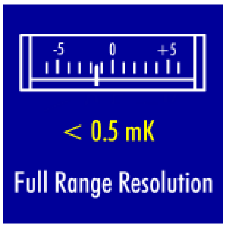

On-line guidelines HFC/HBC: P & Q


Complete corrections

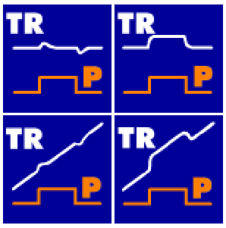

Vortex correction, torque and power

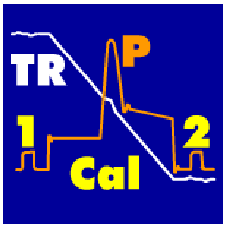

Closed system

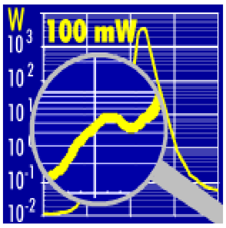

Automatic cp determination


Extreme measurement resolution

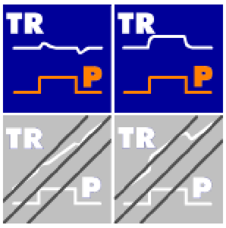

Method: only heatflow


Operation type: all modes


Non-isothermal with calibration


Very good sensitivity


Method: only heat balance


Operation type: isothermal and isoperibol

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# Calo 2400 - the high tech HF calorimeter for further temperature ranges (-80°C to +300°C)

## Characteristics

The Calo 2400 is a pure heatflow calorimeter, with an extreme temperature range, which is no longer allowed for balance calorimetry. Because of the larger signal resolution, sensitivities of up to 100 mW/kg (isothermal) are possible. Because a temperature-stabilized cabinet is not available, it is only possible to operate non-isothermally. The tiresome baseline problem is solved. This equipment is therefore the ideal solution for accurate extreme temperature calorimetry.

Because of the new concept you immediately receive on-line information with approx. 10% accuracy. It is nevertheless always recommended to carry out the experiment with a short calibration (approx. 10 min.) so that in any case the off-line correction for high accuracy can be used. This is especially important when a stabilized cabinet is not available.

Extensive fully automatic running recipes with manual intervention are the strong points of all equipment in the Calo 2000 series. Apart from fully automatic working with recipes the experiment can also be carried out step by step manually. Even with an experiment carried out for the first time operation is estimated from synopsis.

## System Configuration

| | |
|---|---|
| Reactor | 1 litre triple jacket, cylindrical (allows processing from 350 ml up to 1000 ml) |
| Stirrer | Heidolph with special propeller stirrer, 40-400 and 200-2000 rpm, remote control, torque measurement 200/40 Ncm |
| Dosage 1 | 1 (max.2) gravimetric from balance 1 (6200 g) |
| Dosage 2 | 1 (max.2) gravimetric from balance 2 (6200 g) |
| Thermostat | Unistat 360HT -60°C to +300°C<br>Working range for TR -40°C up to +280°C, with other thermostats down to -80°C or lower. |
| Temp.meas. | Pt-100, type A |
| Calorimetry | Heatflow calorimetry in reactor and heat balance calorimetry in reflux cooler |
| Calibration | 20 Watt, glass, with supply and measurement |
| Temp.-control | Jacket and reactor (cascade) control |
| Pressure control | for 0…1300 mbar (0…60 bar with autoclave) |
| Vacuum control | range approx. 20 … 1000 mbar |
| Reactor pressure | Automatic supervision and control for an absolute tight glass reactor |
| Reflux | Cooler and magnetic separator |
| Distillation | Is available as standard with balance |
| pH | Measuring standard, optional control |
| Construction | Steel frames to be placed in a fume cupboard.<br>From customer: cooling water for reflux |
| PC | Optimized Pentium PC, colour printer, colour screen |
| Programmes | Windows NT 4.0, Office, FIX/MMI, SYBAREX 1/V4, SysGraph + module Calo 2000 |
| Options | See later |

### Standard Configuration

Reflow condenser, separator, dist.-cooler, balance

1 l triple jacketed reactor

Recipe control SYBAREX 1/V4

17" colour monitor with synoptics

1 gravimetric dosage

1 gravimetric dosage

Unistat 360HT

Combilab control unit

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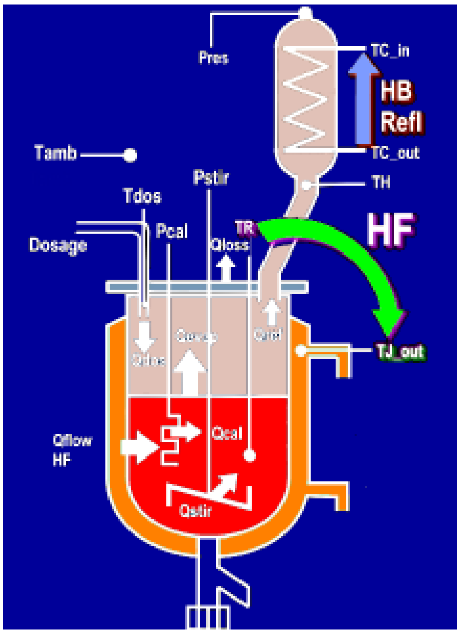
# Capabilities of Calo 2400

## Calo 2400 - Short informmation with typical values

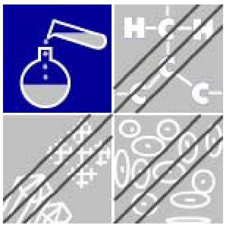
| | |
|---|---|
| Resolution of TR, TJ | 0.0004 K |
| Resolution of (TR-TJ), reactor - jacket | 0.0004 K |
| Resolution of (TCout-TCin), reflux cooler | 0.0004 K |
| Sensitivity of HFC, reactor, isothermal | 100 mW |
| Sensitivity of HBC, reflux, isothermal | 500 mW |
| Dynamics of HFC, reactor, isothermal | > 1000 W |
| Kinetics delay HFC, reactor | 60 s |
| Kinetics delay HBC, reactor | 60 s |
| Accuracy of HFC, reactor, isothermal, without calibr. | 10 % |
| Accuracy of HBC, reflux, isothermal, without calibr. | 20 % |
| Accuracy of HFC, reactor, isothermal, with calibr. | 1 % |
| Accuracy of HBC, reflux, isothermal, with calibr. | 4 % |
| Water equivalent determination | pre-calibrated, live exactly |
| cp determination | automatic |

## Measuring concept

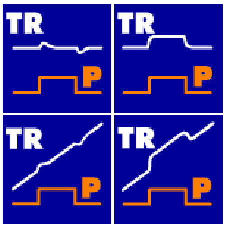


Method: only heatflow

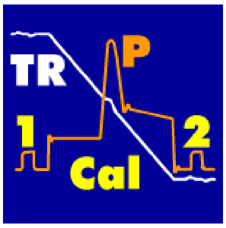
Application: predominantly syntheses



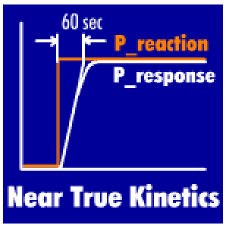
Operation type: all modes



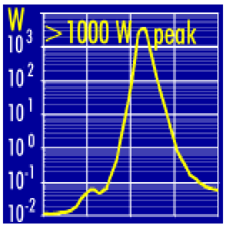
Non-isothermal with calibration



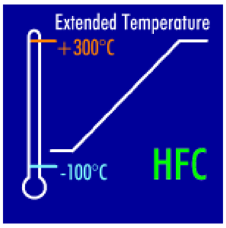
Excellent kinetics



Extreme dynamics

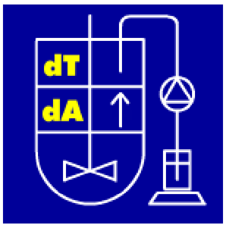


More extreme temperature range

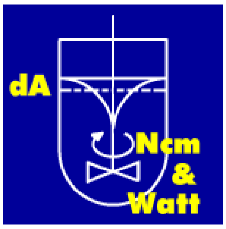


On-line guidelines with HFC: P & Q

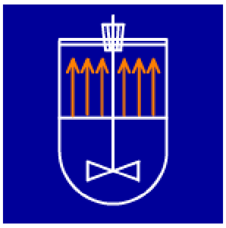
Complete corrections



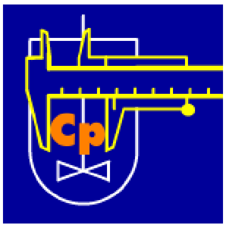
Vortex correction, torque and power



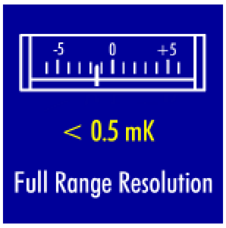
Closed system



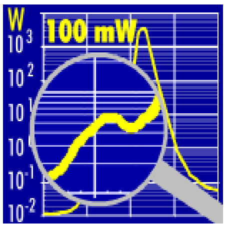
Automatic cp determination



Extreme measurement resolution



Very good sensitivity



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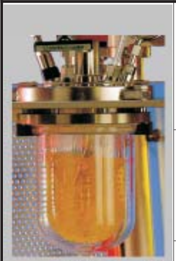
# OPTIONS Reactors and Thermostats



| **Reactors** | SysCalo SC1 | SysCalo SC2 2902 | SysCalo SC3 2903 | SysCalo SC4 2904 | Calo 2000 2100 | Calo 2000 2200 | Calo 2000 2300 | Calo 2000 2400 |
|---|---|---|---|---|---|---|---|---|
| **Double jacket glass reactors, cylindrical, 0-1300 mbar$_{abs}$**<br>100 ml, 250 ml, 500 ml, 1 l, 2 l, 3 l, 4 l (others on demand) | ● (1 l) | ● (2 l) | ○ | ○ | - | - | - | - |
| **Triple jacket glass reactor, cylindrical, 0-1300 mbar$_{abs}$**<br>1 l, 2 l, vacuum isolated (others on demand) | ○ | ○ | ○ | ○ | ● (1 l) | ● (1 l) | ● (1 l) | ● (1 l) |
| **Triple jacket glass reactor, conical, 0-1300 mbar$_{abs}$**<br>1 l, vacuum isolated (others on demand) | ○ | ○ | ● | ● | ○ | ○ | ○ | ○ |
| **Double jacket glass reactors, cylindrical, 0-6 bar**<br>1 l, 2 l (other volumes and pressures on demand) | ○ | ○ | ○ | ○ | ○ | ○ | ○ | ○ |
| **Double jacket steel reactors, cylindrical 0-60 bar**<br>0.3 l, 0.5 l, 1 l, 2 l (other volumes, pressures and material on demand) | ○ | ○ | ○ | ○ | ○ | ○ | ○ | ○ |
| **Large "chem reactor" double jacket glass reactors from Buchi**<br>25 l, 50 l, 100 l, 250 l (others on demand) | ○ | ○ | ○ | ○ | - | - | - | - |


| **Thermostats** | SysCalo SC1 | SysCalo SC2 2902 | SysCalo SC3 2903 | SysCalo SC4 2904 | Calo 2000 2100 | Calo 2000 2200 | Calo 2000 2300 | Calo 2000 2400 |
|---|---|---|---|---|---|---|---|---|
| **Unistat Tango -40°C to +200°C (generally standard)**<br>typ. process temperature in reactor approx. -10°C to +170°C in double jacket reactor 1..3 l and approx. -20°C to +180°C in triple jacket reactor 1 l and 2 l as well as smaller double jacket reactors 0.1 l to 0.5 l | ● | ● | ● | ● | ○ | ○ | ○ | ○ |
| **Unistat Tango HT -40°C to +300°C**<br>typ. process temperature in reactor approx. -10°C to +260°C in double jacket reactor 1..3 l and approx. -20°C to +275°C in triple jacket reactor 1 l and 2 l as well as smaller double jacket reactors 0.1 l to 0.5 l | ○ | ○ | ○ | ○ | ○ | ○ | ○ | ○ |
| **Unistat 360 HT -75°C to +300°C**<br>typ. process temperature in reactor approx. -40°C to +260°C in double jacket reactor 1..3 l and approx. -55°C to +275°C in triple jacket reactor 1 l and 2 l as well as smaller double jacket reactors 0.1 l to 0.5 l | ○ | ○ | ○ | ○ | ○ | ○ | ○ | ● |
| **Unistat 380 HT or 385 HT -80°C or -85°C to +300°C**<br>typ. process temperature in reactor approx. -50°C to +260°C in double jacket reactor 1..3 l and approx. -65°C to +270°C in triple jacket reactor 1 l and 2 l as well as smaller double jacket reactors 0.1 l to 0.5 l | ○ | ○ | ○ | ○ | ○ | ○ | ● | ○ |
| **Unistat Serie 160w for larger power -60°C to +200°C**<br>typ. process temperature in reactor approx. -45°C to +185°C in double jacket reactor 1..10 l and approx. -30°C to +170°C in double jacket reactor 25 l , larger reactor must be tested. | ○ | ○ | ○ | ○ | ● | ● | ○ | ○ |
| **Thermostats from Julabo, Lauda, Haake**<br>Condition: interface 4...20 mA or 0 - 10 VDC | ○ | ○ | ○ | ○ | - | - | - | - |
| **Water cooled high performance heating equipment and cryostats for "chem reactors"** on demand | ○ | ○ | ○ | ○ | - | - | - | - |

○ = can be ordered as option ● = already available as standard in the basic model ▪ = not available

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# OPTIONS Dosage, Distillation, Additional Controls

| | SysCalo | | | | Calo 2000 | | | |
|---|---|---|---|---|---|---|---|---|
| **Dosages, Stirrer, Reflux and Distillation** | SC1 | SC2 2902 | SC3 2903 | SC4 2904 | 2100 | 2200 | 2300 | 2400 |
| **Further gravimetric dosages (addition to basic equipment)** | | | | | | | | |
| a) with multi dosage adapter | ○ | ○ | - | - | - | - | - | - |
| b) with additional balance | ○ | ○ | tot. 2 | ○ | ○ | ○ | ○ | ○ |
| **For connection of specific types of balances** | | | | | | | | |
| a) Mettler | ○ | ○ | ○ | ○ | ○ | ○ | ○ | ○ |
| b) Sartorius | ○ | ○ | ○ | ○ | ○ | ○ | ○ | ○ |
| c) Denver, Chyo | ○ | ○ | - | - | - | - | - | - |
| **Volumetric dosages with Dosimat 665** | | | | | | | | |
| a) as controller device (such as pump) | ○ | ○ | ○ | ○ | ○ | ○ | ○ | ○ |
| b) remote control with complete function range | - | - | - | ○ | ○ | ○ | ○ | ○ |
| **Gas dosage with mass flow controller** | | | | | | | | |
| a) only 1 piece | - | ○ | ○ | ○ | ○ | ○ | ○ | ○ |
| b) Ratio control with 2 ore more | - | - | - | ○ | ○ | ○ | ○ | ○ |
| **Dosage of solids from balances** | - | ○ | ○ | ○ | - | - | ○ | ○ |
| **Stirrer-variants** | | | | | | | | |
| a) IKA Eurostar with manual set-ups (50-2000), only revolution measurement | ● | - | - | - | - | - | - | - |
| b) Heidolph (40-2000) with remote control and torque measurement | - | ● | ● | ● | ● | ● | ● | ● |
| c) Buchi revolution measurement, remote control and torque measurement | - | ○ | ○ | ○ | - | - | ○ | ○ |
| **Reflux condenser** | | | | | | | | |
| a) pure reflux condition | ○ | ● | ○ | ● | ● | ○ | ● | ● |
| b) with reflux separator for distillation | ○ | ● | ○ | ● | ● | ○ | ● | ● |
| c) silver coated and vacuum isolated | ○ | ○ | ○ | ● | ● | ○ | ● | ● |
| **Distillation cooler and receiver vessel** | ○ | ● | ○ | ● | ● | ○ | ● | ● |
| | SysCalo | | | | Calo 2000 | | | |
| **Vacuum, Pressure, Purging, pH, Turbidity etc.** | SC1 | SC2 2902 | SC3 2903 | SC4 2904 | 2100 | 2200 | 2300 | 2400 |
| **Vacuum measurement and control** | | | | | | | | |
| a) Measurement and 2-point control | ○ | ○ | - | - | - | - | - | - |
| b) PID-control | - | - | ● | ● | ● | ○ | ● | ● |
| **Pressure measurement and control** | | | | | | | | |
| a) Measurement and 2-point control | ○ | ○ | - | - | - | - | - | - |
| b) PID-control | - | - | ● | ● | ● | ● | ● | ● |
| **Purging by recipe** | - | ○ | ● | ● | ○ | ○ | ○ | ○ |
| **pH measurement** | ○ | ○ | ● | ● | ● | ○ | ● | ● |
| **non-linear pH control** | ○ | ○ | ● | ● | ○ | ○ | ○ | ○ |
| **Turbidity measurement (measurement of conductivity)** | ○ | ○ | ○ | ○ | ○ | ● | ○ | ○ |

○ = can be ordered as option ● = already available as standard in the basic model - = not available

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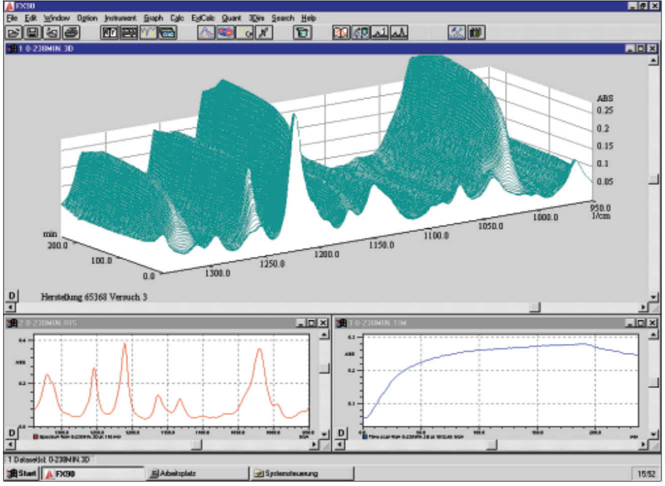
# OPTIONS Calorimetry and FTIR

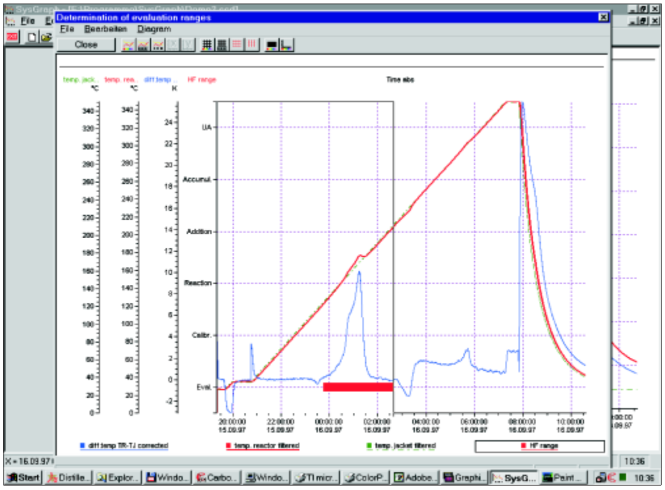
| Calorimetry, FTIR applications, Support | SysCalo | | | | Calo 2000 | | | |
|---|---|---|---|---|---|---|---|---|
| | SC1 | SC2<br>2902 | SC3<br>2903 | SC4<br>2904 | 2100 | 2200 | 2300 | 2400 |
| **HFC Heat flow calorimetry in the reactor**<br>The effect of manual dosage as well as from two automatic dosages can be taken into account. The measurement data and results can be put together freely and can be printed on a plotter or a printer. | ● | ● | ● | ● | ● | ● | ● | ● |
| **HBC Heat balance calorimetry in the reactor**<br>The effect of manual dosage as well as from two automatic dosages can be taken into account. The measurement data and results can be put together freely and can be printed on a plotter or a printer. | - | - | - | - | ● | ● | ● | - |
| **HBC Heat balance calorimetry in reflux cooler**<br>The effect of manual dosage as well as from two automatic dosages can be taken into account. The measurement data and results can be put together freely and can be printed on a plotter or a printer. | - | ● | - | ● | ● | ○ | ● | ● |
| **Calibration heaters - standard power** | 20 W | 40 W | 20 W | 20 W | 5 W | 5 W | 20 W | 20 W |
| **Calibration heater options for smaller or larger reactors**<br>5, 10, 20, 40, 75, 125, 250, 500 Watt<br>(up to 40W: 24VDC, >40W: 230VAC) | ○ | ○ | ○ | ○ | ○ | ○ | ○ | ○ |
| **Adiabatic base operation with system calibration** | - | - | - | ○ | ○ | ○ | ○ | ○ |
| **FTIR application (Analect/USA)**<br>a) with independent system | - | ○ | ○ | ○ | ○ | ○ | ○ | ○ |
| b) with data transfer into main system from at least 1 wavelength information | - | ○ | ○ | ○ | ○ | ○ | ○ | ○ |
| **SYSTAG remote support with modem and communication software** | - | ○ | ○ | ○ | ○ | ○ | ○ | ○ |

○ = can be ordered as option ● = already available as standard in the basic model - = not available

**FTIR 3D-display** of amplitude vs. time and wave length as well as 2 sub-diagrams vs. frequency- and time-axis (Analect/USA-System)



**KaloGraph** Display with non-isothermal reaction



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# 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] = (TJ_Out –TJ_In) [K] * cp [J/g.K] * r [g/ml] * F [ml/s]*

| | |
|---|---|
| *HB:* | *Heating power* |
| *TJ_In:* | *Jacket temperature at inlet* |
| *TJ_Out:* | *Jacket temperature at outlet* |
| *cp:* | *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.

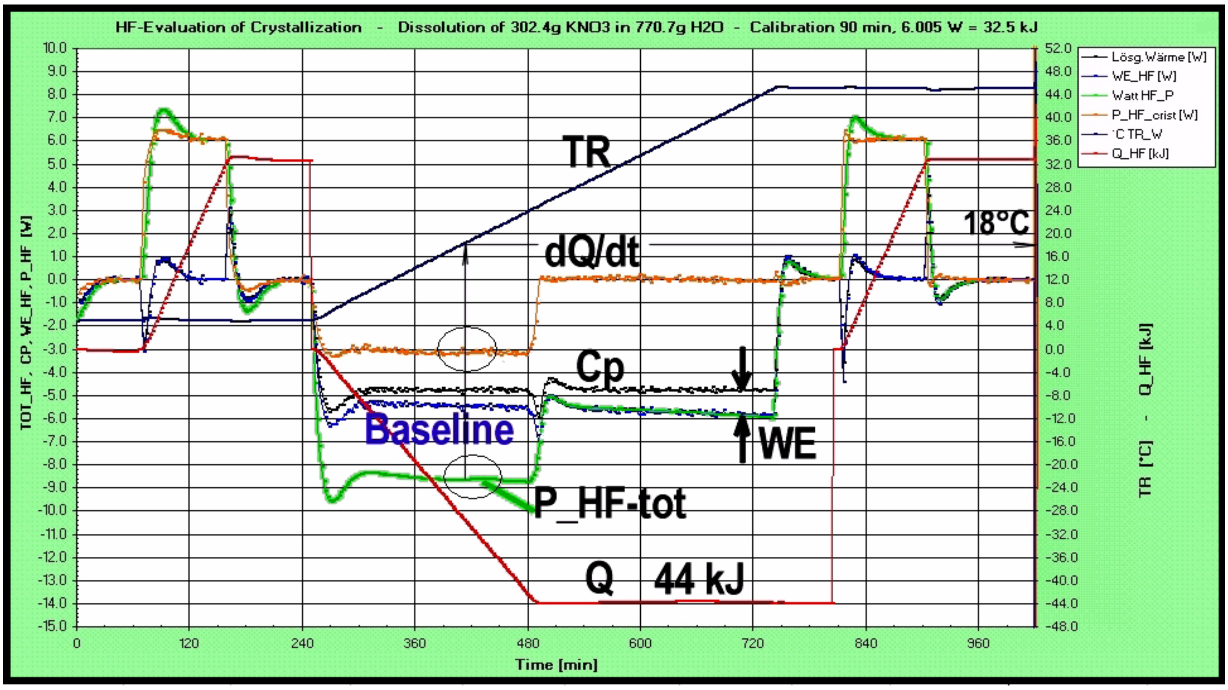
The hurdles to obtaining any conclusive results by means of HBC lie above all, however, in the considerable complexity of the instruments needed. The reasons for this are essentially as follows:

- ***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.

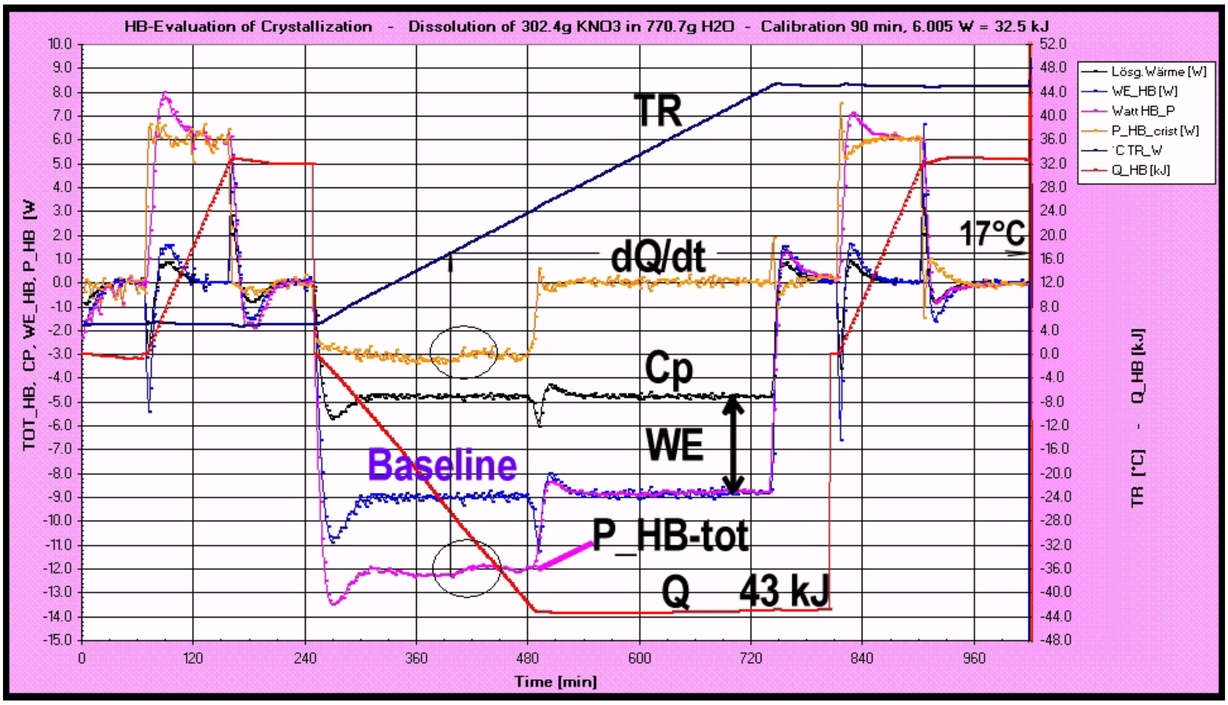
# Two simultaneous measurement principles in one experiment



*Dissolution heat of a supersaturated $KNO_3$-$H_2O$ 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)).*



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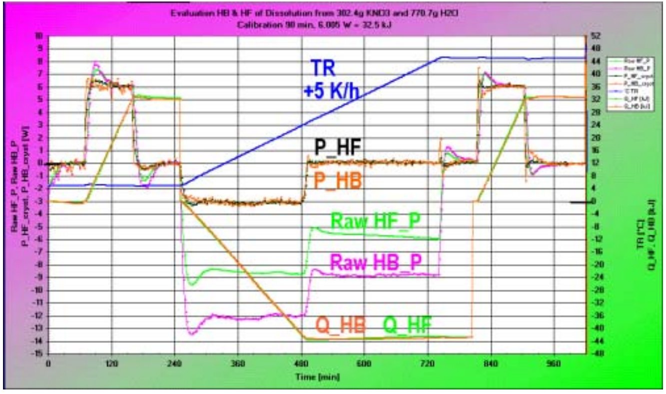
## Basic R & D report

# 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 $KNO_3$



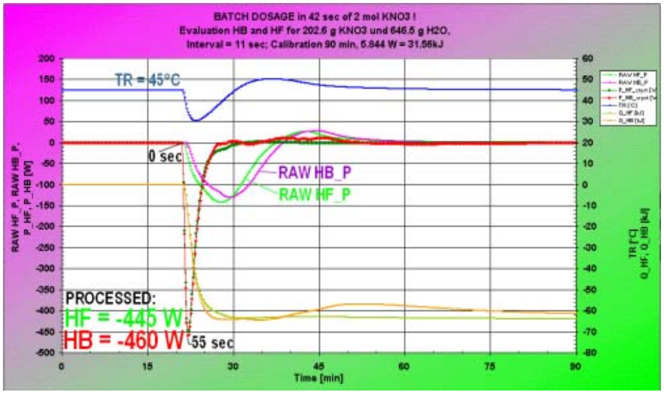
### Strong endothermic

2 mol $KNO_3$ 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.

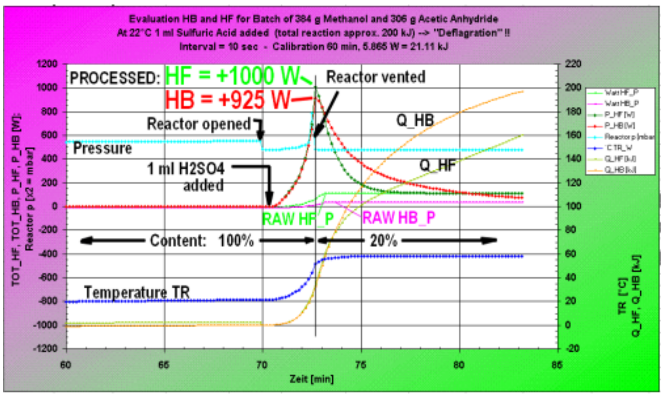
**Diagram 4** Strong exothermic during dissolution



### 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 and Q_HB. 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.

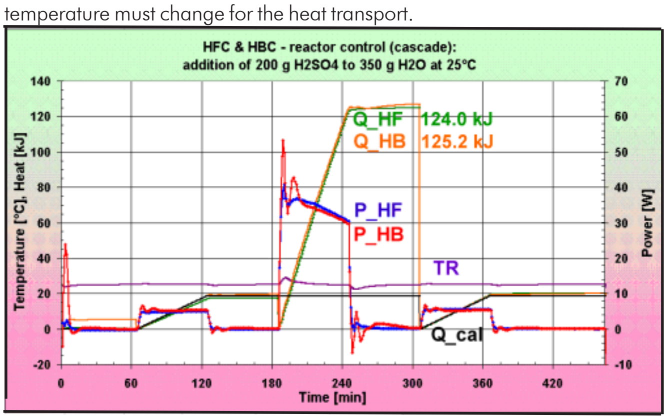
### Conclusion

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!**

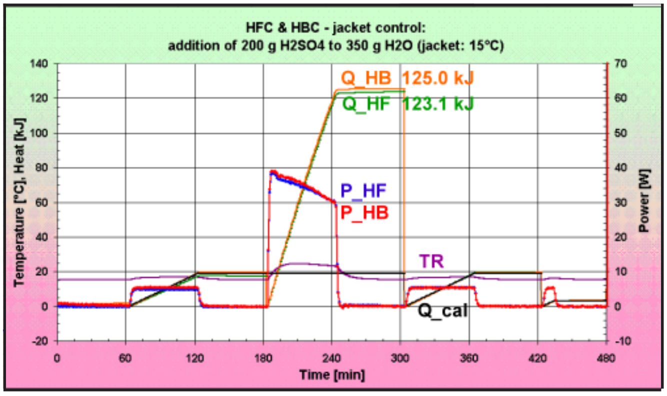
**Isotherm Fix-temperature**

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



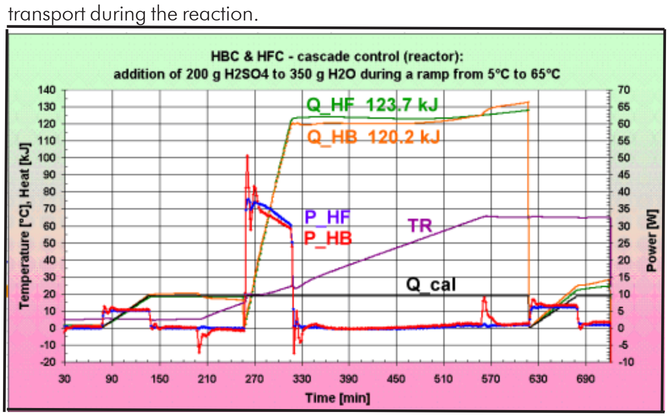
**Isoperibol Fix-temperature**

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



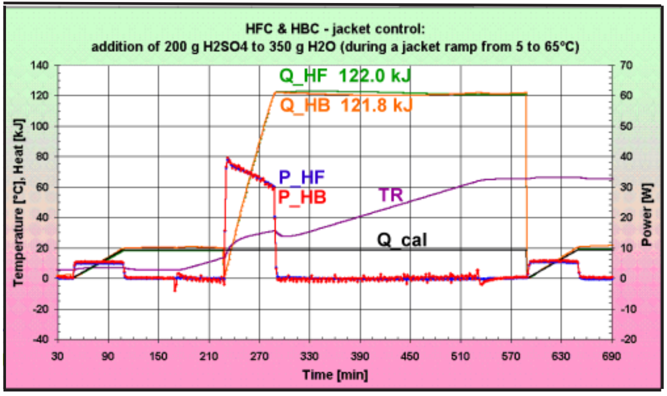
**"Isotherm" Ramp**

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.



**"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.



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## 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

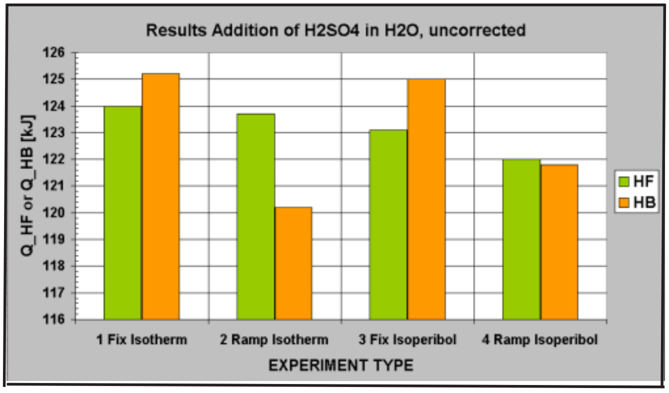
The average value was 68.18 kJ, and the standard deviation 1.92%, whereby the maximum peak deviations were –2.23% and +4.43%. For the theoretical reaction value of 67.9 kJ the average deviation was in addition +0.41%. When the somewhat high dosage (102.5 g. instead of 102.1 g.) is taken into account, 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.

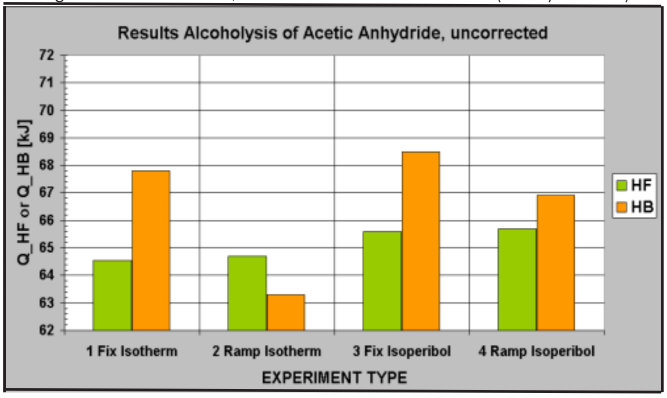
**Inorganic, water base: solution of H2SO4 in H2O, uncorrected, only with basic calibration**

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



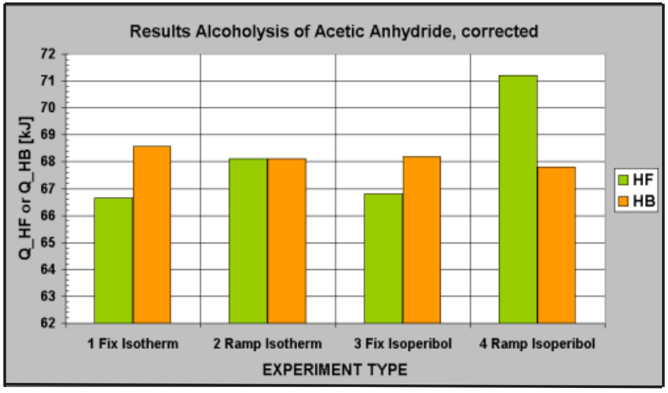
**Organic, methanol base: alcoholysis of acetic anhydride, uncorrected, only with basic calibration.**

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).



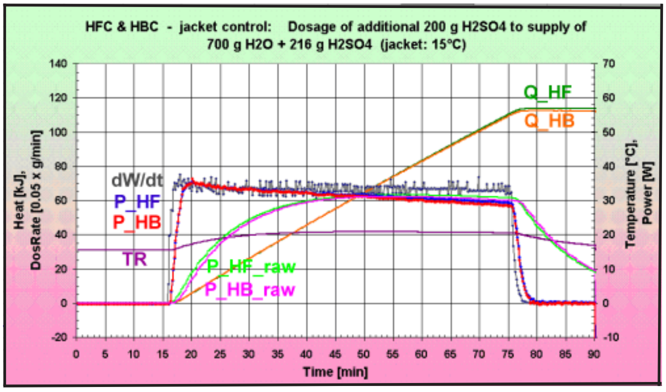
## R&D report no. 2:

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

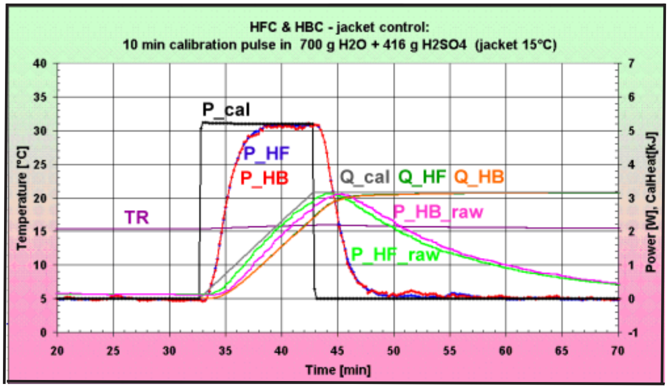
### Excellent dynamics

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.

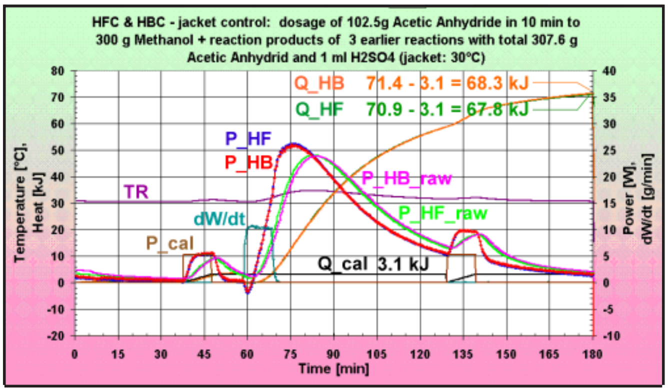
### Isoperibol creates the best dynamics!

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!

**Isoperibol 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.



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## FAQ – client asks, SYSTAG answers

# 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**

## FAQ – client asks, SYSTAG answers

# Common questions most frequently asked about the Calo 2000 system

**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 N2 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 $N_2$ 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.

## FAQ – client asks, SYSTAG answers

# Common questions most frequently asked about the Calo 2000 system

### 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 area (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!

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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

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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

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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?**

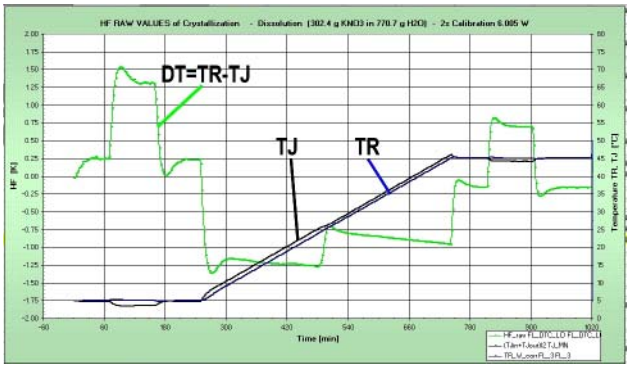
**Could you please clarify the technical background for us?**

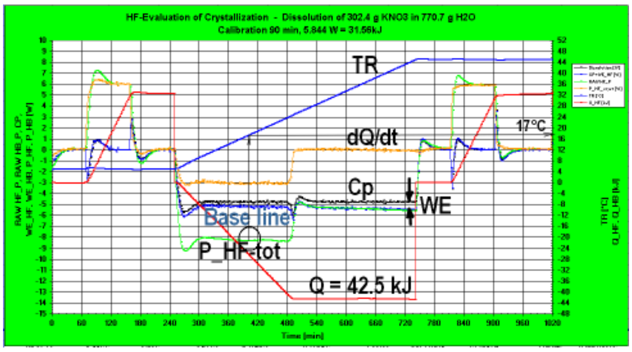
Some of these questions have already been clarified in some detail above. We don't want to go into any more detail, because that is not in the interest of SYSTAG (know-how divulgence).

### 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 $KNO_3$ 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.





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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)!

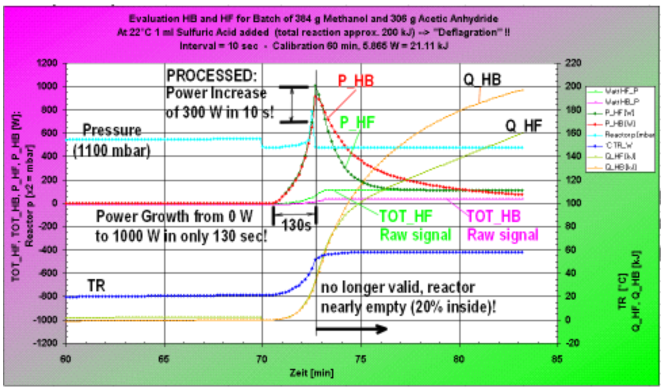
The residual error, which remains after that, such as unknown behaviour of the heat transfer fluid (HTF), cp and thickness as well as mix from steel, glass and PTFE in the system are calibrated in advance by SYSTAG across the entire process range with a calibration programme!

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 page 18 in part 1 of 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.*



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### 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?**

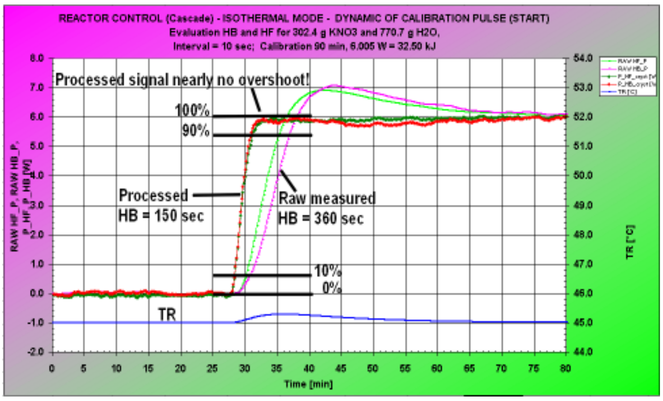
Depending on your version (active = reactor control, passive = jacket control) the experiment is carried out in the active mode. The system was immediately switched to the emergency off position after the popping and all consumers are switched off (danger of explosion!). The data recording however continues 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 g*2.52J/g.K+306g*2J/g.K) * (58-20 K) = 60 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 cp, 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 cp 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 Cp of the sensors etc., and the

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WE of the reactor and the measured Delta-T (TR – TJ_out for HF and TJ_out – TJ_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.

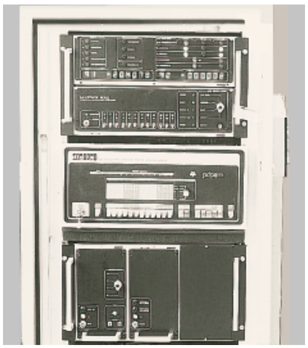
# The success is based on the history of SYSTAG's calorimetry

## 1966

### WFK-66

In 1966 the first heat flow calorimeter is produced in close co-operation with CIBA, Basle. The technology at the time already gives an accuracy of <0.001°C! The actual 2 l double jacket reactor system still needs a large room because of the large cooling and heating tanks used at the time.

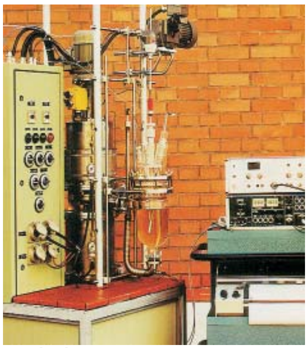
## 1974



### WFK-74/pdp8

Because of the good experience with the first calorimeters a larger computer project is started during the boom years 1973/74 which really increased the accuracy and the recording rate. Because of the oil crisis serial production however is no longer taken up.

## 1975



### WFK-75

Because of the oil crisis in 1975 the new, economical WFK-75 was developed for the first serial production of calorimeters. For the first time this is used in practice on a wider scale. This laid the foundation for a continuous expansion of the heat flow calorimeter.

## 1981

### BSC-81

In consequence SYSTAG then achieved – following the terminated serial production of the PDP-8 computer calorimeter – the new technology with the DEC computer LSI-11 in the BSC-81, which was again produced as a series.

## 1985

### PC-COMBILAB

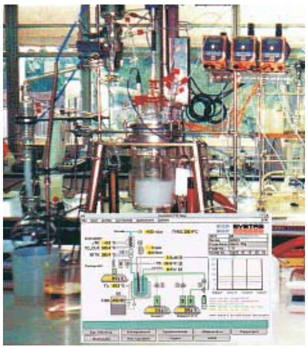
SYSTAG has to date developed for CIBA the most universal process control software with the simplest to operate batch recipe. These experiences resulted in the extremely flexible laboratory automation PC-COMBILAB, the ideal prerequisite for reaction calorimetry.

## 1991

### MIDILAB

Thanks to the growing use of PC-COMBILAB it is shown, that for simpler tasks, there is still an increasing need for, for example, low cost calorimeters. The MIDILAB equipment family with its 3 types for dosage, temperature and pH was therefore developed. These lie between a controller and a full automation.

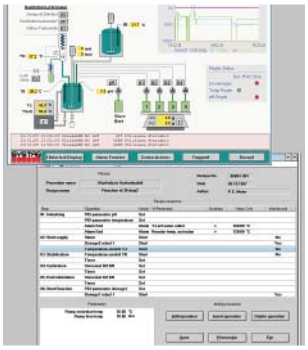
## 1993



### ALR

With the increased use of automation the requirement of a Windows interface became acute. Together with a new batch recipe editor, this modern automation which can be adapted to a multitude of problems – also with parallel recipes – was brought onto the market.

## 1996



### SYBAREX 3

The latest SYBAREX 3 recipe editor supported by databank is launched for automations with MIDILAB and SYNTALAB as the latest creation from the SYSTAG house. From all these building blocks the current family of SysCalo SC1 to SC4 reaction calorimeters emerged.

SYSTAG
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# Notes