

Reaction Calorimetry

Hardness Test Calo 2000 Principle

Investigation into the suitability of heat flow and heat balance calorimeters in non-isothermal, homogenous and inhomogenous 2 phase systems (liquid/solids)

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Summary

The difficulties in reaction calorimetry occur above all with non-isothermal operation and especially in 2 phase systems. Particularly at risk however are the inhomogenous 2 phase systems. The transition from homogenous to inhomogenous however occurs in an insidious manner, so that until now it was extremely difficult to give reliable information about the measurement results.

The following report concerns itself with this topic using a crystallisation of DL mandelic acid as an example. This can explain more or less everything regarding the influences which need to be examined, depending on the control method (reactor/jacket), the ramp gradient and ramp direction, from the stirrer as well as the concentration.

Everything is examined in the new SYSTAG Calo 2100 combination reaction calorimeter, which simultaneously carries out a heat flow and a heat balance measurement.

The balance calorimetry proves itself as an uncomplicated, very robust but nevertheless sensitive method. With regard to kinetics, both systems give very good results as long as the measured system is somewhat homogenous. With inhomogenous systems balance calorimetry clearly has its nose in front.

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1 Introduction

Until now all measurement objects which change were a problem in the heat flow reaction calorimetry. In the first place this is because temperature changes the disturbing influence through the capacity change and through irradiation or emission, so that a correct measurement becomes difficult. Frequently changes in the stirrer velocity and/or viscosity are the worst enemies of an accurate heat flow measurement. This is simply because in such situations the measurement object suddenly becomes part of the measurement system (the U heat conducting co-efficient is changed!) and consequently an independent measurement becomes impossible. Furthermore, temperature changes cause variable evaporations, which influence the measurement directly. This is particularly critical with small reaction powers.

To date phase transfers have also presented an insurmountable problem. As example we use a batch reaction which is activated through heating and which is subsequently finished with a reflux. Such transfers can now finally be measured directly in Calo 2100.

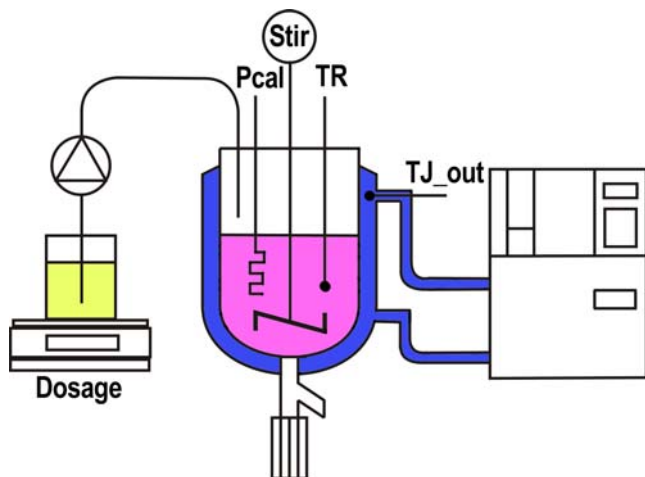
When adding a dosage during a semi batch reaction the variable surface A is an issue. Here the measurement object also suddenly becomes a part of the measurement system! Only when a surface change no longer has a direct influence on the measurement signal is the measurement object uncoupled from the measurement system. This is finally the case with heat balance calorimetry.

When changing an homogenous system to an 2 phase inhomogenous system new problems occur which have a direct influence on the evaluation through the model building. With an inhomogenous system an individual measurement point inside the reactor is no longer sufficient to describe the behaviour of the reaction sufficiently accurately for the model. Consequently it becomes obvious that this change influences both types of calorimetry: heat flow as well as heat balance calorimetry. This was also confirmed in the measurements which were carried out, which astonishingly shows up balance calorimetry as very robust and very meaningful, albeit with a somewhat reduced accuracy. Just as when we use statistical experiment planning however we rather accept a model with somewhat less accurate results as long as the confidence range is good!

2 Systems and concept definitions

2.1 Systems definition

2.1.1 Heat Flow Calorimetry → HFC



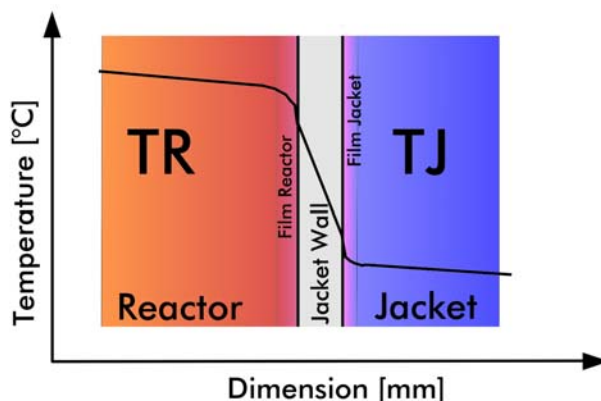
$$P_{HF} = (TR - TJ_{out}) * A * U \dots\dots(1)$$

[w]
[K]
[m²]
[W/m².K]

To date heat flow calorimetry is the most commonly used calorimetry and was developed in the sixties by Dr. Willy Regenass [1].

The **measurement** system consists of the thermal wall resistance between the reaction substance (called sample) and the thermostatically controlled jacket.

The sample is stirred and is normally homogenous. The rotation velocity returns to 0 m/s inside the film on the wall. Consequently this film becomes an additional part of the measurement system with its own heat conductivity.



A corresponding film can also be determined on the side of the heat-conducting medium. Because of the high rotational velocity however it is very thin, but nevertheless it also forms part of the measurement system.

It becomes obvious that with a change of the film, regardless of which side, the measurement system changes. The side of the heat conductor is clearly defined and can also be calibrated. The same applies to the heat flow number of the wall (for example glass or steel). On the other hand we now easily recognise the problem with HFC: the sample (in this article sample represents the reaction substance inside the reactor), which usually isn't known and which can change during a reaction, is to a smaller or larger extend directly part of the measurement system! That is the crux of the matter.

Consequently it is absolutely clear that only low viscosity, homogenous and single phase (fluid) samples lead to good results with HFC. Also, the stirrer velocity – or rather the sample velocity

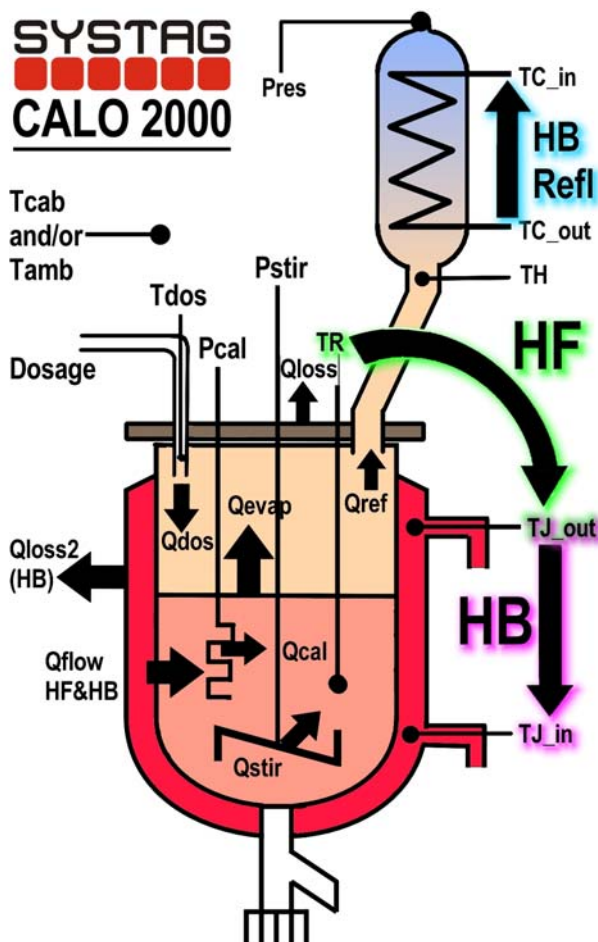
itself is not necessary.

Note 2:

With the heat balance calorimeter the sample is never part of the measurement system. It has therefore no influence on the measurement result. The system can also be calibrated through calibration heating.

2.1.3 Complete balance of a reaction calorimeter

The measurements in the reaction calorimeter involve temperature difference measurements which through the balance equation of the entire system lead to an effective reaction power. For this purpose we briefly give the balance equation followed by the concept definitions.



Concept definitions

Qflow	Heat flow, introduced via the wall and measured via HF or HB
Qreact	Reaction energy
Qwe	Energy for the water equivalent
Qloss	Losses against environment (with HFC and HBC)
Qloss2	Additional losses of jacket with HBC
Qcal	Calibration energy for calibration
Qstir	Stirrer energy
Qevap	Irradiation or evaporation energy
Qdos	Energy during dosing as a result of different supply dosage temperature against TR
Qref	Energy incurred in the reflux cooler
HF	Heat flow measurement
HB	Heat balance measurement
HB Refl	Heat balance measurement in the reflux cooler

The sum of all energies must be zero.

$$Q_{flow} + (Q_{react} + Q_{we}) + Q_{cal} + Q_{stir} + Q_{dos} + Q_{evap} + Q_{loss} + Q_{ref} = 0 \dots\dots\dots (3)$$

(Q_{react} + Q_{we}) are not displayed in the above diagram and represent the energies for the reaction and the water equivalent.

Q_{flow} represents the actual measurement via the HF heat flow or the HB heat balance.

Qref represents the HB measurement of the reflux condenser.
Qstir is calculated from the measured torque and speed.
Qloss can be determined in a system calibration as function $F(T_J, T_R, T_{cab}$ and/or $T_{amb})$
Qdos must be calculated on the basis of $cp \cdot m \cdot (T_R - T_{dos})$
Qcal is measured directly electrically

For Q_{react} this results in : $-Q_{react} = \sum Q_n$ (4)
 whereby n stands for all other indexes

2.1.4 Correlation between sample and water equivalent

In particular we must now concern ourselves with the term **Qreact + Qwe!** In the first approach we can assume that most losses of a certain size would be 'negligible' (for example low stirrer velocity, no dosage, working around the room temperature, low vapour pressure, no calibration heating switched on and no reflux). The system reduces itself to:

$$-Q_{flow} = Q_{react} + Q_{we} \dots\dots\dots (5)$$

or without integration (only the power) $-P_{flow} = P_{react} + P_{we} \dots\dots\dots (6)$

$$-P_{flow} = P_{mess} = dT/dt \cdot (m_s \cdot cp_s + cp_{we} \cdot m_{we}) \dots\dots\dots (7)$$

We must now try to define the **water equivalent (WE)** more accurately. The following basic principle applies:

WATER EQUIVALENT

All parts which are in thermal contact with the sample (also when only in partial contact) have a cp and a mass. The sum of all these parts can be summarised in the virtual expression $WE = cp_{we} \cdot m_{we}$.

Now a little bit about the history of the water value. The expression water value comes from earlier times when everything was mostly simulated with water. If for example 1 litre of water is heated from 20 to 21°C it needs 1000 cal or 4185 Ws or Joule. The factor 4.185 Ws/g.K corresponds with the cp for water. When we therefore introduce for example 41.85 Watt over 100 seconds into a reactor with 1 litre water and measure the temperature increase we do not get the expected 1.00°C (better K) but for example only 0.75 K. We must therefore use 0.25 K for all other parts.

When we calculate $Q_s = M_s \cdot c_{ps} \cdot \Delta T = 1000 \text{ g} \cdot 4.185 \text{ J/g.K} \cdot 0.75 \text{ K}$, we obtain only 3139 Ws instead of 4185. Where are the 1048 Ws now? These have flown into the 'water equivalent', which therefore represents simply $m_{we} = Q_{we} / (cp_{we} \cdot \Delta T) = 1046 \text{ [Ws]} / (4.185 \text{ [J/g.K]} \cdot 0.75 \text{ [K]}) = 333 \text{ g}$ water. In other words: the result looks as if we heated 1333 g water instead of only 1000 g. The 333 g are therefore the 'water equivalent'. If we use glass, for which the cp lies at approx. 1 J/g.K, then that would be approx. 1.4 kg glass, which corresponds to a 1 litre reactor.

2.1.5 cp Determinations

From the equation (7) we can easily see that we can determine either cp_s or cp_{we} , as long as one or the other is known. Here again applies: it is the small things that cause the problems! When we look at the behaviour of the cp_{we} via the temperature, we must determine that with glass this changes by approx. 30% from 20°C to 150°C. With the 1.4 kg glass (for a heat flow calorimeter

with 1 litre contents) the $cp_{WE} * m_{WE}$ term therefore varies by approx. 30%! When we now look at a typical content in a calorimeter of 2/3 litre of an organic solvent, for example methanol, we obtain the following results:

Methanol has a density of 0.795 g/ml and a cp of 2.547 J/g/K. 666ml are therefore 510 g.

We can now fill the equation (7) $P_{meas} = dT/dt * (m_S * cp_S + cp_{WE} * m_{WE})$:

$P_{meas} = dT/dt * (510 * 2.547 + 1 * 1400) = dT/dt * (1299 + 1400)$. The water equivalent is therefore slightly larger than the content itself. A change in the water value of +30% therefore automatically causes an error of the sample's cp of something more than -30% during the calculation!

Note 3:

It is clearly obvious that the water equivalent across the temperature must be known as well as possible in order to obtain sensible results for the sample! In general this applies to the reaction calorimetry as soon as it is no longer purely isothermal. In an isothermal case dT/dt becomes 0 and consequently everything becomes invalid!

Water equivalent and sample are always integrated with each other and can't be separated

2.1.6 Homogenous and inhomogenous systems

On the basis of our experience with such systems we must here carry out a careful differentiation. The definition of homogenous and inhomogenous depends purely the opinion of the calorimetry user! The following can be said:

During balancing of the system we need the information about the sample scope with the heat flow calorimeter as well as the heat balance calorimeter (this has nothing to do with the actual measurement procedure, but 'only' with the evaluation!). Because we normally only record the TR reaction temperature with a sensor, this balancing applies only to an homogenous system. By homogenous we mean: the same temperature distribution and if possible no temperature gradient in the entire sample scope (except for near the wall). This can be achieved with thorough mixing (needs an appropriately suitable stirrer), also with 2 phase systems, as long as the viscosity doesn't increase rapidly and nothing becomes lumpy or a crystallisation takes place in large blocks.

Classic inhomogenous systems are ones with a switched off stirrer. For each heat conduction therefore a correspondingly high temperature gradient is needed – dependent on the heat conductivity constant. Consequently the balancing of the entire reaction scope becomes almost impossible with only one temperature sensor! The same applies when part of the scope is available in a solid condition or even when a crystallisation takes place around the sensor. That gives a completely different dynamic picture of the system. It is therefore essential to establish where the two measurement types, HFC and HBC are with regard to toughness (confidence range of the measurement value). This is a topic for the following discussion.

Note 4:

Each inhomogeneity changes the reaction scope in such a way that only limited valid balances can be carried out as long as only an individual TR temperature measurement point is available.

This applies to the heat flow as well as the heat balance calorimetry.

If the measured system is independent of the measurement system (heat balance calorimeter), it is nevertheless still possible with the integral to give an indication about the entire time frame until everything is again in the balance, albeit with limited accuracy. This option is completely lost with the heat flow calorimeter.

2.2 Non-isothermal calorimetry

By non-isothermal calorimetry we mean any measurement which takes place between the start of the integration (for forming of Q_{react}) and the end of a change of the TR reaction temperature. The reason for these difficulties lies in the individual terms of equation (7) which is converted to the P power. We can explain this briefly:

$$P_{\text{flow}} + (P_{\text{react}} + P_{\text{we}}) + P_{\text{cal}} + P_{\text{stir}} + P_{\text{dos}} + P_{\text{evap}} + P_{\text{loss}} + P_{\text{ref}} = 0 \dots\dots\dots (8)$$

P_{flow} is the measured power (HF or HB principle), which flows across the wall to or from the sample

P_{react} is the sought after reaction power for which we make this big effort!

P_{we} is the water equivalent power which has already been discussed many times

P_{cal} is needed for calibration and can be measured very accurately (to say the least!)

P_{stir} is the entered stirrer power that is measured through torque and speed and which can be calculated

P_{dos} is the power entry through the dosage during a semi batch reaction. This can also be measured and calculated.

P_{evap} is the evaporation or vapour power, very critical and not easy to measure or to calculate!

P_{loss} is the power exchanged with the environment, for example through condensation on the lid!

P_{ref} is evaporation which flows to the reflux cooler and which is measured there as condensation power

2.2.1 Non isothermal influences on P_{we}

Above all here the behaviour of the temperature co-efficients of the cp plays an important part. We are mostly dealing with a mix factor between different materials, for example glass reactor, steel stirrer, PTFE bottom outlet valve etc. In addition the contents also partly have an influence, although generally this is marginal, for example 1 .. 2% of the total WE.

It is essential that the WE is measured live so that it can be compensated. It is thereby not important whether we know the sample's cp. If the sample's cp is not very well known the remaining difference is simply added to the water equivalent term. This always results in a good correction! The knowledge of the exact cp is therefore no longer necessary, except when you want to calculate the accurate adiabatic increase of the sample! The cp can be determined at any time via an experiment. Here also applies: the more accurately the WE is known, the more accurately the cp can be determined.

2.2.2 Non isothermal influences on Pstir

Each stir cycle must be stored somewhere. Each bearing has friction. With temperature changes friction also partly changes. The influence is marginal (approx. 0.5 to 1 Ncm).

2.2.3 Non isothermal influences on Pdos

This influence becomes more serious the greater the temperature difference is between supply dosage and sample. The basis for this is the correct recording of the supply dosage temperature, which normally is simple. Inserting a sensor somewhere is not the solution. The exact spot needs to be selected, only then can the compensation calculation take place. A further difficulty is the knowledge of the exact cp of the supply dosage. In many cases these powers regarding the actual reaction power are mostly slight, except with weak reactions, such as for example with a neutralisation.

2.2.4 Non isothermal influences on Pevap

This influence is very extreme during tests of small reaction powers such as crystallisation and can falsify the picture strongly. With increasing sample temperature the vapour pressure rises (typically doubling every 10°C). Slow ramps usually last many hours. During this time we not only loose substance but also a quantity of vapour energy! This can only be countered with an absolutely closed system, because the construction of a vapour pressure in the room only uses a few Joule. Also ventilation some times in between in order to adjust to the new temperature behaviour does much less damage than a not closed system.

2.2.5 Non isothermal influences on Ploss

This is a further factor which above all plays a big part in heat balance calorimetry and refluxes (→ heat balance measurement). With the heat flow calorimetry this influence is a bit smaller, because the jacket protects the measurement wall between the heat transfer fluid and the sample very well. The critical points are the heat flow from the lid in the wall, the heat flow from the installed probes, stirrer and baffles as well as from the bottom outlet valve. The influence can be indicated with approx. 0.2 W/K for the HFC and with 1 W/K for the HBC. This applies to a 1 litre glass reactor with vacuum jacket. If we work for example at +150°C, the temperature difference with the environment is approx. 125°C. This causes a heat flow of approx. 6W with heat flow calorimetry and 125 W with heat balance calorimetry. Approx. 80 .. 90% can be corrected mathematically with a model set-up and the rest can be eliminated through calibration. Certain non linearities and chronological answers are difficult to compensate. For high accuracy the environment must therefore always be brought to more or less the same temperature.

A further point represents the condensation on the lid. This shows itself as nothing other than a small reflux condenser, also below boiling point (!). In order to avoid such condensations the lid must have a higher temperature than the sample. This can be solved for example with a slightly increased environmental temperature.

2.2.6 Non isothermal influences on Pref

This gives further problems: the vapour supply is very sensitive. So is the reflux factor and the condenser itself. Apart from good vacuum isolation the appropriate compensation is also needed. Furthermore we need to remember that a reflux condenser also indicates a water equivalent which is known and which must be corrected for.

We have one advantage: during boiling there is at least an actual isothermal condition as far as boiling is concerned. Whether the environment is also isothermal remains to be seen.

Note 5:

For the non isothermal calorimetry all disturbing influences must be recorded meticulously, so that compensation becomes possible. We are dealing with two different influences:

Isothermal influences at different temperature levels.

Isothermal influences at different temperature levels.

For very accurate measurements we must therefore (just as before) carry out an isothermal calibration at two different temperature levels before and after the reaction as well as in addition inserting a reaction free ramp in the run for the dynamic calibration.

With homogenous, non isothermal systems with powers in a range of ≥ 50 W the Calo 2100 and 2200 already give an accuracy of approx. 10%, so that a calibration with calibration heating is only necessary for precision measurements. Consequently we can also measure reactions which do not tolerate a long calibration phase. On the other hand it is always sensible to calibrate all low energy experiments (for example crystallisation) as well, where ever the experimental process allows this.

3 Experimental arrangements, summary

DL-mandelic acid was used in 499 g water clear of minerals and tests were carried out with two different concentrations:

1. 17.2 % weight (103.9 g DL-mandelic acid) for a lower dissolution point and subsequently
2. 50 % weight (500 g DL-mandelic acid) for a higher dissolution point and especially to study non isotherm, inhomogenous systems.

In the following experiment discussion we would like to show the results of the heat flow calorimetry (HFC) and the heat balance calorimetry (HBC) in y-t diagrams, always next to each other. The integrator for Q was always immediately re-set to 0 directly before the start of the measurement (in the evaluation phase), i.e. for each calibration heating and before the actual measurement procedure.

Apart from the ramp direction we also have occasionally changed the ramp velocity. Usually we have gone from 65°C to 5°C and vice versa, whereby the ramp gradients were usually 5, 10 and 15 K/h. With a higher concentrated system the 10 K/h ramp led to very inhomogenous proportions. For the calibration each was heated at a higher and lower temperature in an isothermal phase over 60 minutes with 5.21 Watt (where it was at all possible).

In addition we also show the behaviour of both HFC and HBC methods during a reactor control and during a jacket control. Even in inhomogenous systems a reactor control can become critical, because the reactor control loop can be changed excessively and this can lead to severe error behaviour. For such cases jacket controls are usually better suited, whereby for safety reasons a monitoring of the inner temperature must never be forgotten!

As an exception a higher concentrated system was once even operated without an rotating stirrer, in order to examine an inhomogenous system in an extreme case on both calorimetry measurement and evaluation types.

Some photos also show the optical effect on the system as well as the change of the refractive index as a result of the concentration changes.

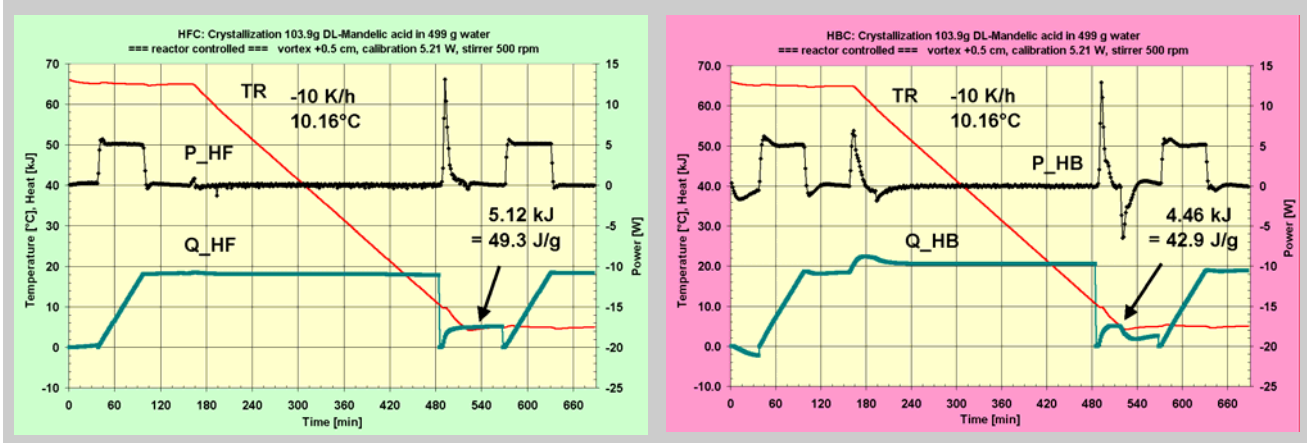
Each run has a number, i.e. run 9 has been carried out before run 10 and so on. If there is an 'a' after the run number that means that a strong inhomogeneity has been determined. We recognise this because the basic calibration value for the HFC is strongly disturbed and must be massively corrected. This concerns the correction of the changing U (heat conduction, wall strength). This is never the case with HBC. There usually only a 'fine-tuning' is needed.

All double diagrams shown hereafter, which are joined with a black edge, are taken from the same experiment: left the HFC and right the HBC result! Therefore 1 experiment with 2 measurement methods → our own co-operative test directly built in!

4 Discussion of experiment results

4.1 Non isothermal application, quasi homogenous sample

17% DL- mandelic acid, ramp 65°C – 5°C downwards, -10 K/h, reactor controlled



Heat flow calorimetry (HFC), run 04

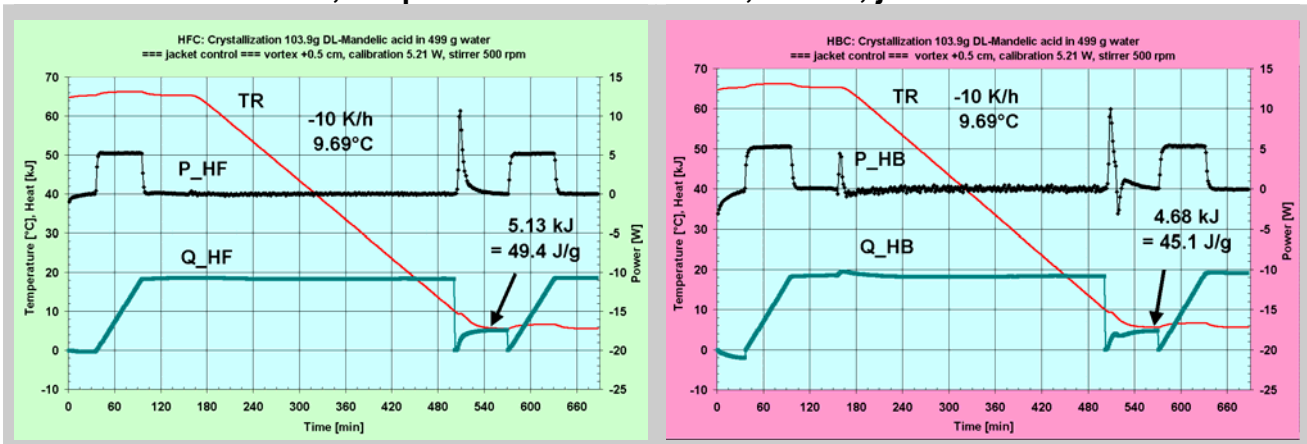
Heat balance calorimetry (HBC), run 04

Both systems work similarly, whereby the HFC gives smoother curve shapes. With the HFC the transfer (kink point) from TR at 65°C to the ramp especially gives rise to fewer difficulties. With the HBC this effects in the first place the 5x greater water equivalent and the imperfect model (which in the meantime has already been decreased by the factor 4).

The result of the dissolution heat is somewhat smaller with the HBC than with the HFC. This could be caused by the U-change which definitely does not behave linearly.

Because a very small concentration is available, obviously not everything crystallises. Up to 5°C we therefore only measure a part.

17% DL- mandelic acid, ramp 65°C – 5°C downwards, -10 K/h, jacket controlled.



Heat flow calorimetry (HFC), run 06

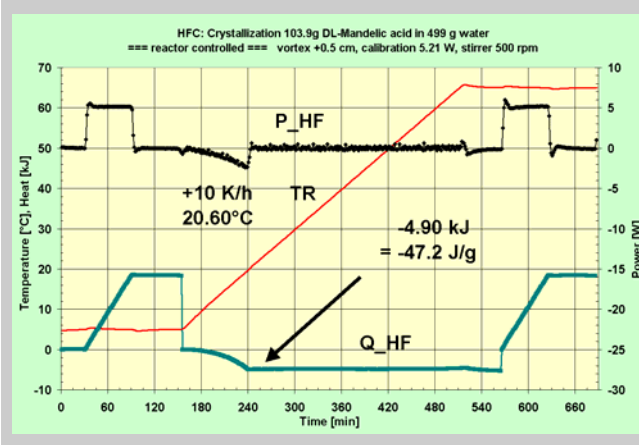
Heat balance calorimetry (HBC), run 06

The results are very similar to the reactor control, whereby the disruption influences with the ramp kink are somewhat less in both cases. This can also be explained in a simple way: a cascade control is more complex and is more inclined to oscillate than a simple jacket control.

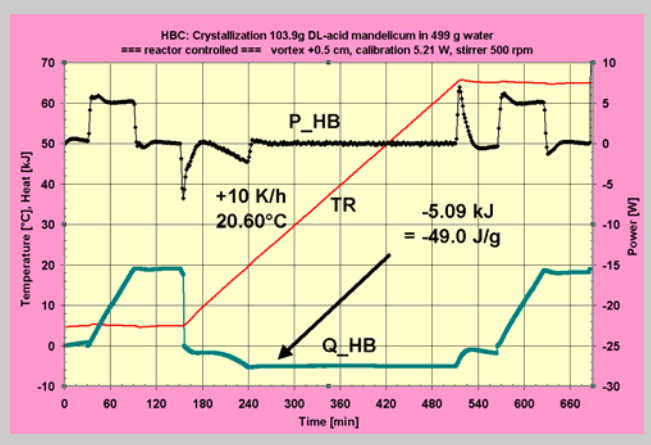
With a system controlled with a jacket we however must integrate longer, because the TR reactor

temperature only slowly aligns to the final temperature.

17% DL- mandelic acid, ramp 5°C - 65°C upwards, +10 K/h, reactor controlled



Heat flow calorimetry (HFC), run 05



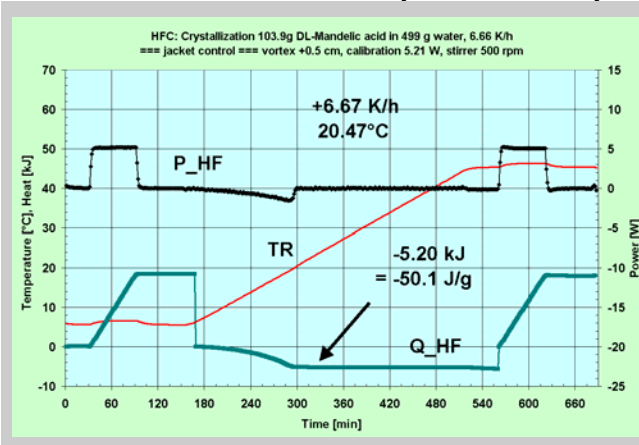
Heat balance calorimetry (HBC), run 05

As mentioned previously with run 4, with the rising HBC ramp the temperature kink incorporates the integration. Theoretically the surface integral of the integration phase must be zero, but it can't be ruled out that a small error occurs with the model calculation. It would be sensible therefore to start such measurements with integration, for example first from the stable condition, for example 8°C .. 10°C.

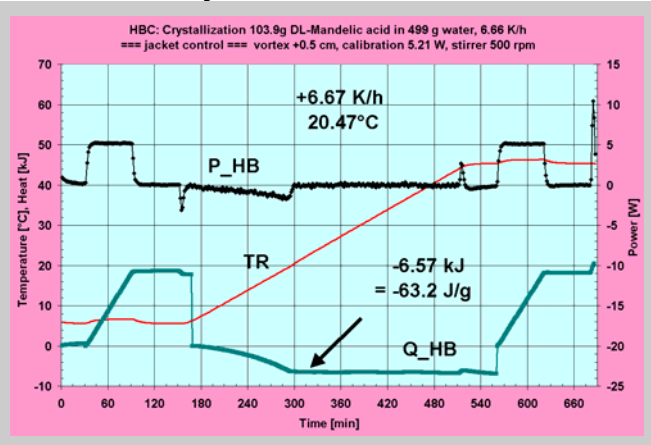
A sample must also be used at this time in order to determine the available remaining concentration. Consequently we obtain the weight for the part which still needs to be removed. Only this enables an accurate statement about the dissolution heat.

In general both behaviours and the result are very similar, so that there is a high credibility.

17% DL- mandelic acid, ramp 5°C - 45°C upwards, +6.67 K/h, jacket controlled



Heat flow calorimetry (HFC), run 07



Heat balance calorimetry (HBC), run 07

Warning: Here the gradient (from a recipe error) is only 6.67 K/h. Therefore the result can only partially be compared with the run of 10 K/h. The following is noticeable: the smaller the ramp gradient, the smaller the power. The error with the HBC appears to be somewhat larger through the over oscillation at the kink point. We are dealing with extremely small powers (between 0 ... max. 1.5 W) across a time frame of 2 hours. With such powers every small error inevitably leads to large errors percentage wise.

Conclusion of quasi homogenous systems:

A heat balance measurement is not absolutely essential but nevertheless gives a measure for agreement. From this a **measurement error** can be estimated, one for each measurement type and as a whole. Consequently the co-operative test is built in into a run!

The discussion about the measurement results follows in Chapter 5 'Discussion and summary'. **Fehler! Verweisquelle konnte nicht gefunden werden. 'Fehler! Verweisquelle konnte nicht gefunden werden.'**

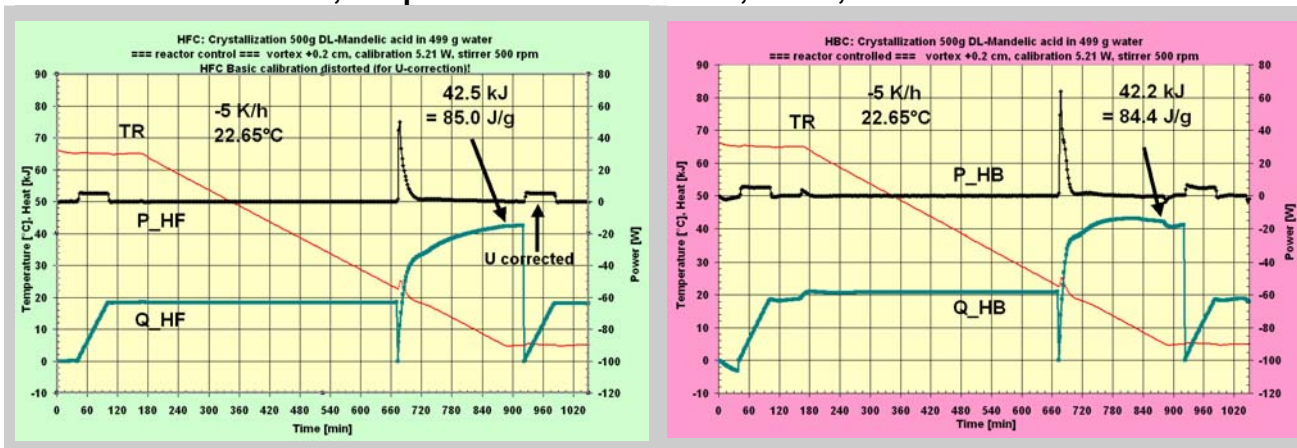
4.2 Non isothermal application with quasi homogenous and inhomogenous samples

4.2.1 Introduction

When working with 50 % weight DL-mandelic acid we have determined after a few experiments that we can expect certain surprises. Because an instinctive appraisal did not lead to a satisfactory result (as is so often the case!) we have decided to carry out a complete measurement sequence and only then to put this into a complete context. With the individual experimental results we therefore analyse the difference between both measurement methods and give some advice. The total overview follows later.

4.2.2 Ramp +/-5 K/h, propeller stirrer 500 rpm

50% DL- mandelic acid, ramp 65°C - 5°C downwards, -5 K/h, reactor controlled

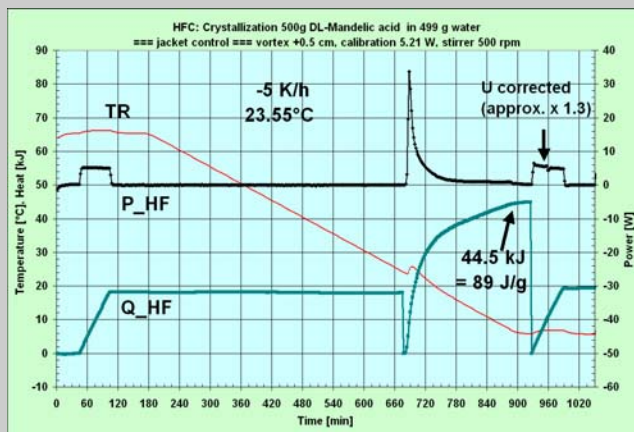


Heat flow calorimetry (HFC), run 14a

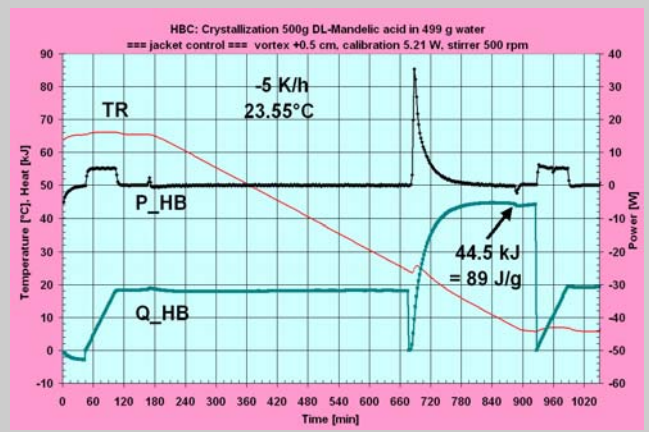
Heat balance calorimetry (HBC), run 14a

Because of the high concentration the spontaneous crystallisation occurs much earlier and runs over a longer time frame. With a higher concentration the danger of a strong change of the heat conductivity U with the heat flow calorimeter increases. This can be observed very easily here. Although U was corrected away with the second calibration with TR=5°C (a very strong change against the basic calibration of the system), the power run P with the HFC is different to the HBC. With the HBC it can be seen that the power goes to 0 more quickly.

50% DL- mandelic acid, ramp 65°C - 5°C downwards, -5 K/h, jacket controlled



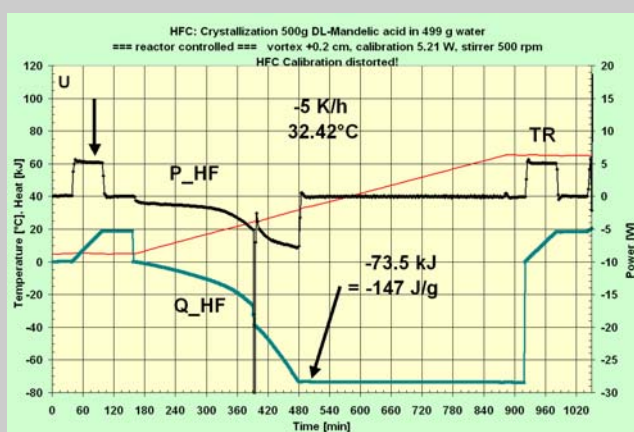
Heat flow calorimetry (HFC), run 16a



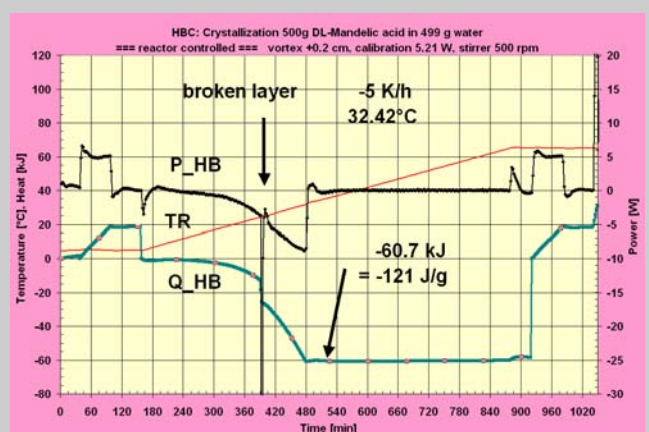
Heat balance calorimetry (HBC), run 16a

Observe the run of Q: with HBC the final value is reached considerably faster than with HFC. A distortion of P_HF results through the non linear U change.

50% DL- mandelic acid, ramp 5°C - 65°C upwards, +5 K/h, reactor controlled



Heat flow calorimetry (HFC), run 15a

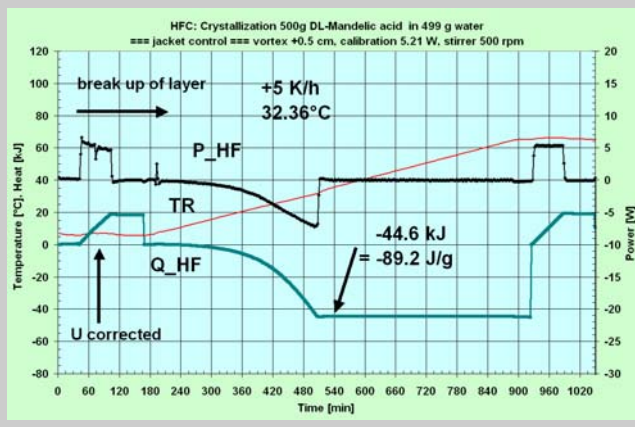


Heat balance calorimetry (HBC), run 15a

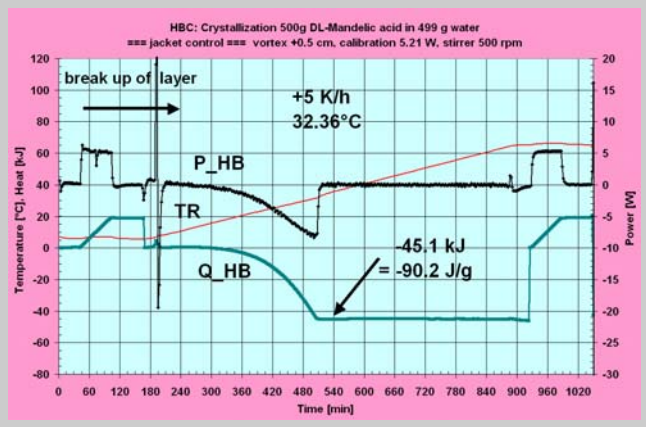
Here it becomes obvious that we are dealing with an inhomogenous system. During the dissolution process there is a sudden, strong disruption. The cause is the mutation of a crystal film, which was heated by the jacket and which exhibits an extremely high concentration. Because of the mutation (crystal layer was broken) the latent two phase mixture is mixed by the stirrer with the inner solution, which is still cooler. Consequently an intermediate crystallisation occurs again with an immediate dissolution following.

Through the previously long lasting dissolution in the HF signal the HF integral appears to become larger than that of the HB. Only after the break the dissolution starts smoothly.

50% DL- mandelic acid, ramp 5°C - 65°C upwards, +5 K/h, jacket controlled



Heat flow calorimetry (HFC), run 17a

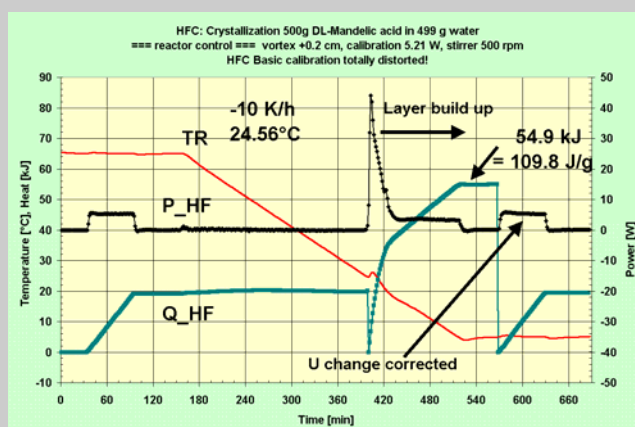


Heat balance calorimetry (HBC), run 17a

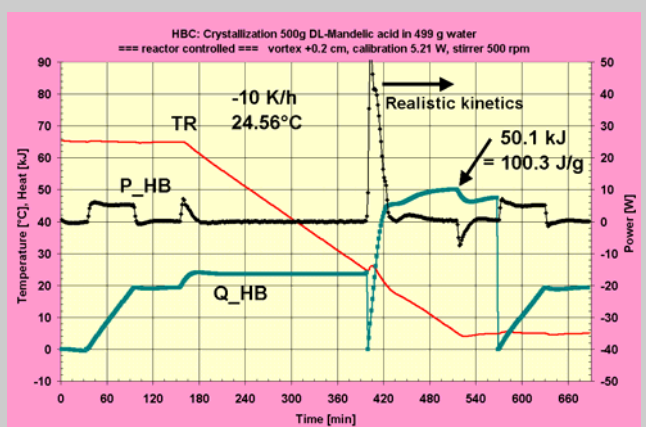
With this experiment the mutation in the crystal film (or part there off) appears to have taken place much earlier, so that the result of the integral in both cases is much cleverer and both results lie very close together, which may lead to a higher accuracy! This example again shows that the dissolution process is anything but regular and can not be predicted in advance.

4.2.3 Ramp +/-10 K/h, propeller stirrer 500 rpm

50% DL- mandelic acid, ramp 65°C - 5°C downwards, -10 K/h, reactor controlled



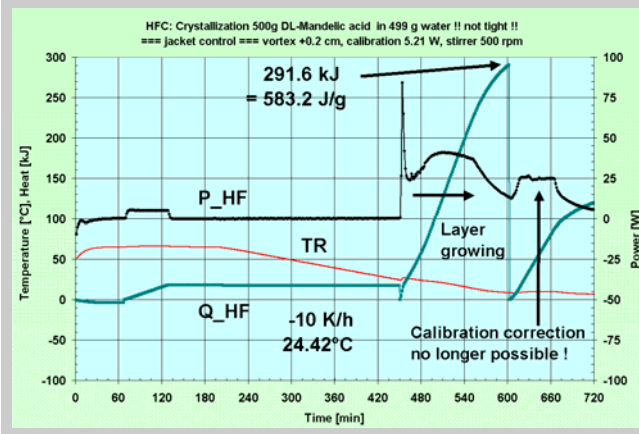
Heat flow calorimetry (HFC), run 10a



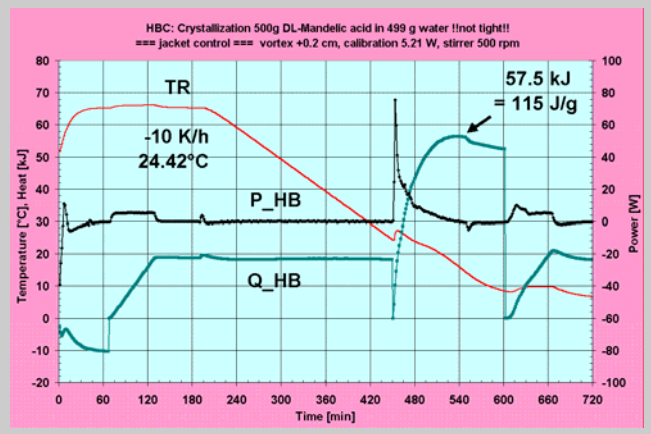
Heat balance calorimetry (HBC), run 10a

When we compare this diagram with the -5 K/h ramp, we determine that the difference between HFC and the HBC becomes more extreme. Also, both measurements [J/g] turned out to be higher. It is especially noticeable that in the <19°C range the P_HF is almost a 'constant' 3 Watt, even though the P_HB very quickly goes down to zero (with a small under oscillation after the spontaneous crystallisation power fades). This indicates a thickening of the wall and needs the essential, massive U correction.

50% DL- mandelic acid, ramp 65°C - 5°C downwards, -10 K/h, jacket controlled



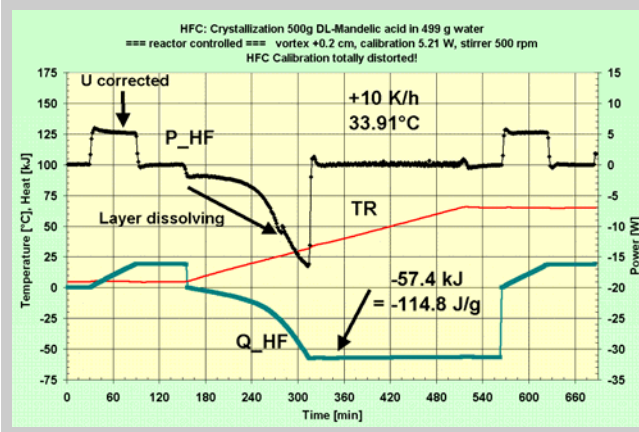
Heat flow calorimetry (HFC), run 08



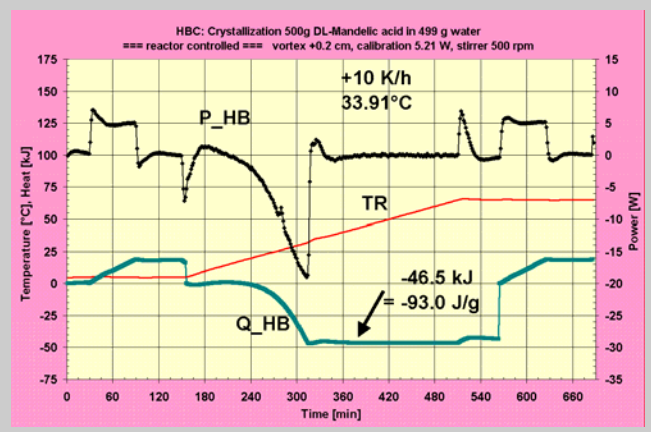
Heat balance calorimetry (HBC), run 08

With a jacket control with -10 K/h an extreme inhomogeneity has now occurred! It must have formed a thicker layer, which can be inferred on the basis of the P_HF run shortly after the spontaneous crystallisation. The power definitely no longer increases! If we look at the P_HB we actually see a relatively normal run, albeit a little stretched (because of higher TR). It is one which no longer decreases so quickly to zero, but which is still very complex. The result with 115 J/g is nevertheless a little higher, but not astronomically so. The main error with HBC is the faulty, inhomogenous model, possibly because the TR sensor already lies near or even inside the crystal layer.

50% DL- mandelic acid, ramp 5°C - 65°C upwards, +10 K/h, reactor controlled



Heat flow calorimetry (HFC), run 11a

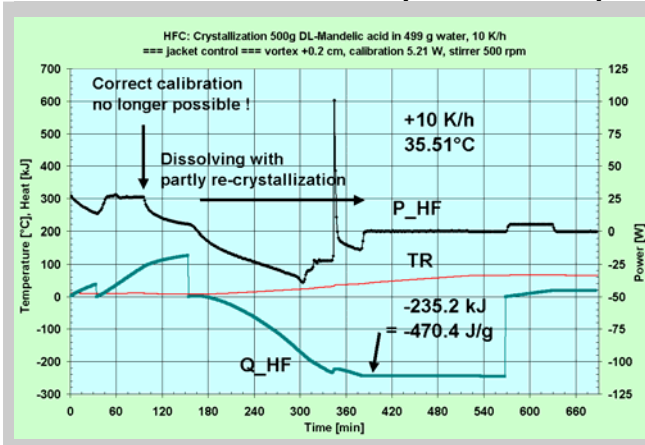


Heat balance calorimetry (HBC), run 11a

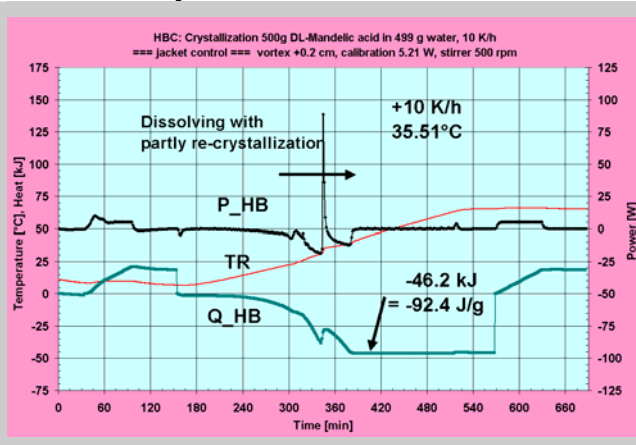
For general information: the first calibration here in run 11 is identical to the second in run 10!

The starting point for run 10 is still more or less o.k. It therefore appears that the dissolution process (generally always much more difficult) proceeds really well. Here also a break in the layer can be determined. This however takes place relatively late and therefore again gives a higher integral for the HFC.

50% DL- mandelic acid, ramp 5°C - 65°C upwards, +10 K/h, jacket controlled



Heat flow calorimetry (HFC), run 09

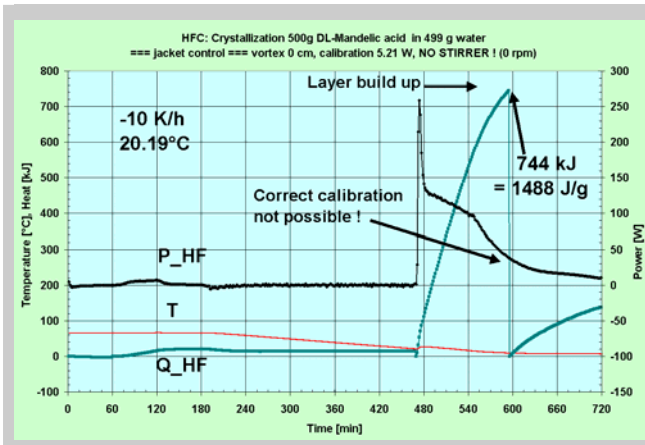


Heat balance calorimetry (HBC), run 09

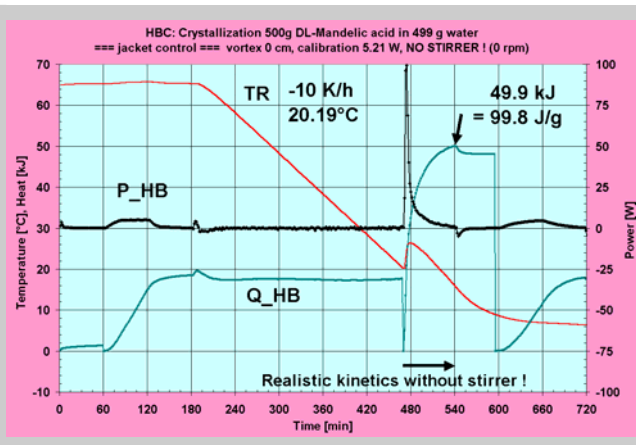
Run 8 with -10 K/h and an extremely thick wall layer is the basis here. Just as the others this is useable for the HFC. The problem therefore presents itself in the dissolution phase in the HFC. On the other hand, compared to the HFC, the HBC measurement gives a very good value. A break in the layer takes place here in two stages: first at the 300 min. time point, and then much stronger (or nearer to TR sensor!) at the 335 min. time point. Both are first an extremely brief crystallisation with subsequent longer duration dissolutions. This process has already been explained in more detail with Run 15.

4.2.4 Ramp +/-10 K/h, not stirred - 0 rpm !

50% DL-mandelic acid, ramp 65°C - 5°C downwards, -10 K/h, jacket controlled
NOT STIRRED!



Heat flow calorimetry (HFC), run 12



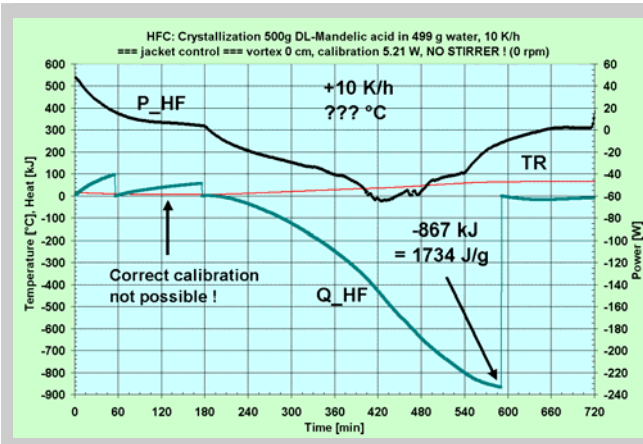
Heat balance calorimetry (HBC), run 12

This experiment is nothing other than a **limit value examination**. In practice you definitely never work like this (if need be with a Havarie estimation). For the comparison of the HFC with HBC however it is an interesting case. For safety reasons we have only examined the jacket control, because a reactor control would very probably cause freezing! It is obviously clear that in that case the HFC no longer functions. The HBC method on the other hand gives amazing results! The comparable, but stirred run 8 is not very different from this run. It appears that the result of

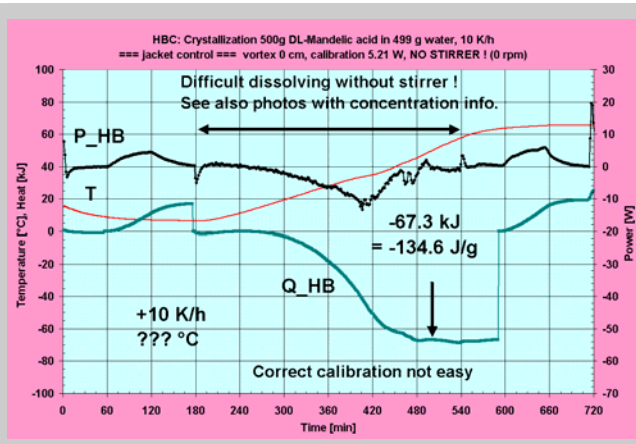
99.8 J/g is still better than the 115 J/g from run 8.

50% DL- mandelic acid, ramp 5°C - 65°C upwards, +10 K/h, jacket controlled

NOT STIRRED!



Heat flow calorimetry (HFC), run 13

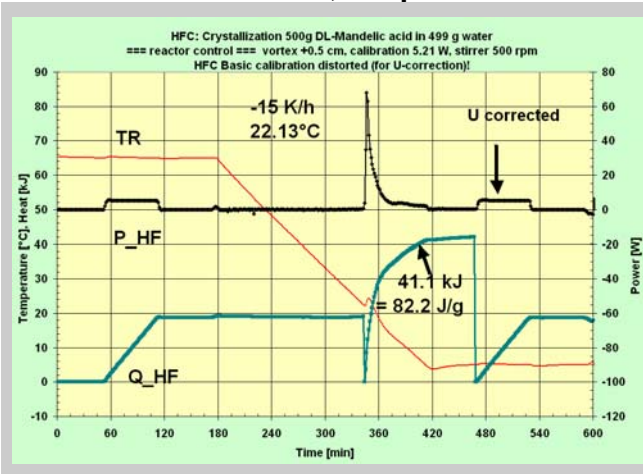


Heat balance calorimetry (HBC), run 13

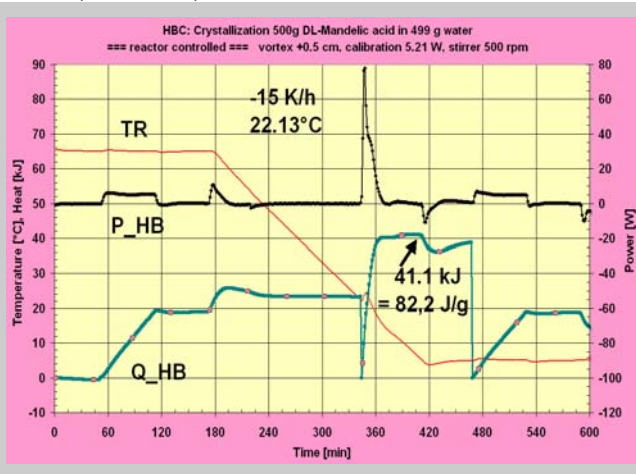
This is the worst of all inhomogenous situations which we have produced: a lump of mandelic acid in a reactor with concentrated fluid. In chapter '4.8 Photos' we have portrayed this situation again in order to obtain a picture of the inside of the reactor. The relative concentration can be recognised in the mutation (marked in the photographs with arrows). The dissolution in the unstirred condition is not just a temperature, but also a time function. +10 K/h is a much too steep gradient if everything develops as planned. We therefore can't carry out a precise calibration of the HBC system. The result of 134 J/g on the other hand is not worlds apart from the result compared to the 1734 J/g with the HFC. Both these experiments show the **sturdiness and reliability of the HBC** very clearly.

4.2.5 Ramp +/-15 K/h, propeller stirrer 500 rpm

50% DL- mandelic acid, ramp 65°C - 5°C downwards, -15 K/h, reactor controlled



Heat flow calorimetry (HFC), run 18a

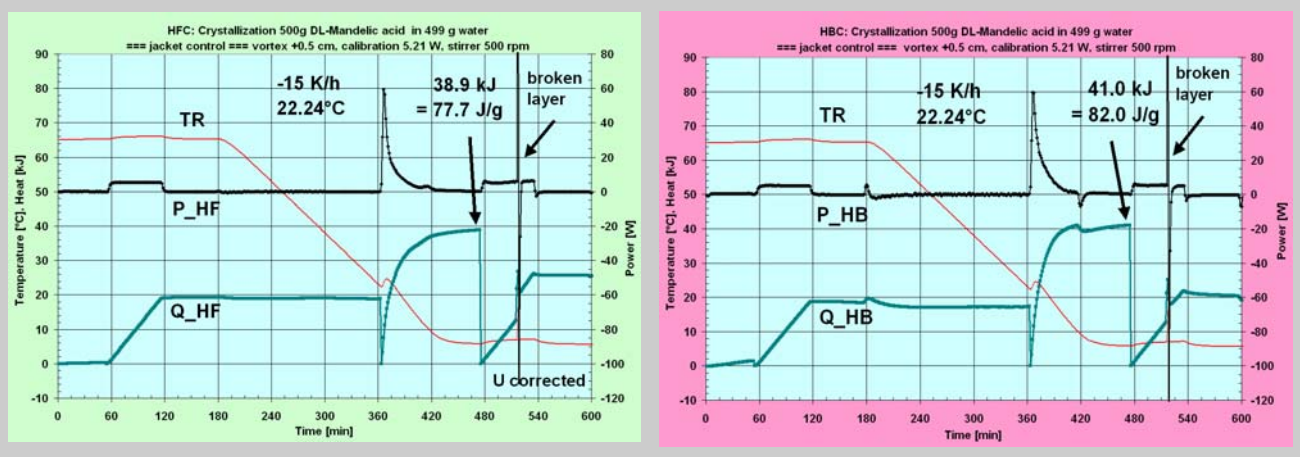


Heat balance calorimetry (HBC), run 18a

To take the bull by the horns: we had basically expected big problems with this fast gradient, because big differences occur when changing from 5 K/h to 10 K/h. Surprisingly the entire system

behaved with much greater stability than with 10 K/h! It is possibly more of a coincidence that both results are even similar, although the chronological behaviour is not identical. The under oscillation with the P_HB curve can also be traced back to a tendency for control oscillations with the reactor control. A slower levelling off with the P_HF curve on the other hand can be traced back to increased isolation (lower U).

50% DL- mandelic acid, ramp 65°C - 5°C downwards, -15 K/h, jacket controlled

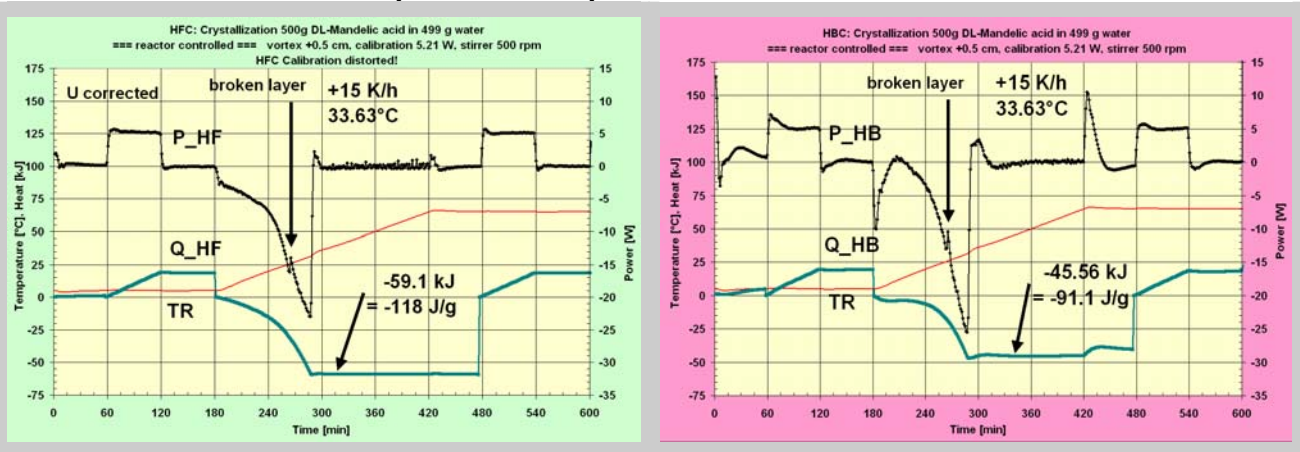


Heat flow calorimetry (HFC), run 20a

Heat balance calorimetry (HBC), run 20a

Here we determine – from somewhat smaller measurement values – an error behaviour (wall layer break) during the second calibration phase at 5°C. This makes a calibration more difficult and above all less accurate, which especially with the HFC can become a big problem. The HBC is basically extremely robust and therefore reacts much more gently to such problems.

50% DL- mandelic acid, ramp 5°C - 65°C upwards, +15 K/h, reactor controlled

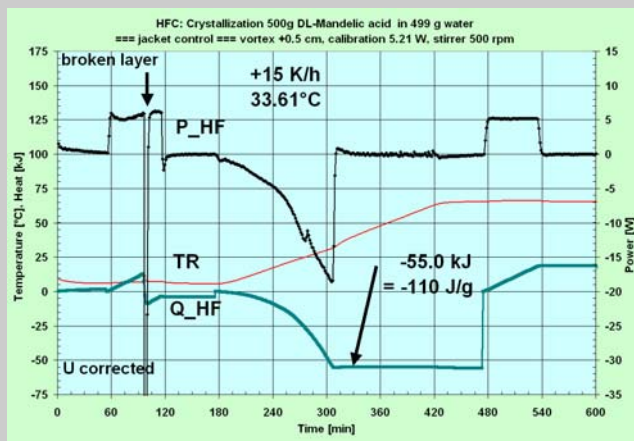


Heat flow calorimetry (HFC), run 19a

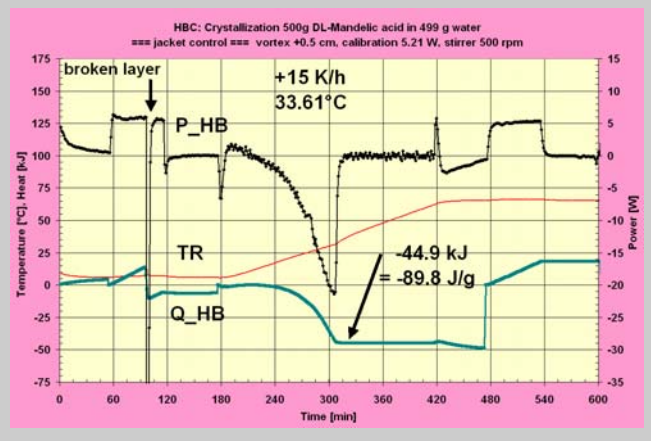
Heat balance calorimetry (HBC), run 19a

The previous run 18 also give a good starting point for this experiment, so that no large irregularities can be determined. A break in the wall layer can obviously again be recognised. The HFC results again lie higher than those of the HBC, because here also U must be corrected a lot.

50% DL- mandelic acid, ramp 5°C - 65°C upwards, +15K/h, jacket controlled



Heat flow calorimetry (HFC), run 21a



Heat balance calorimetry (HBC), run 21a

The forerunner was run 20. We therefore have the same problem (mutation in the wall layer) with the calibration phase at 5°C. The dissolution process here runs almost similarly to run 19. It therefore also gives very similar results.

4.3 Photos

Diagram 1 shows the suspension at around 20°C, stirred with 500 rpm. At higher temperatures the solution is clear (slightly yellowish) and is easy to stir and circulate, see diagram 2. Apart from a rotation, the propeller stirrer provides an excellent vertical circulation.



Diagram 1 20°C, stirred with 500 rpm

Diagram 2 60°C, stirred with 500 rpm, all dissolved.

The following diagrams show the dissolution process in an unstirred reactor. The temperatures indicated however are not meaningful on their own. The time, which leads to this result, must also be noted. That was omitted however. As a result more qualitative impressions are given here. Everything in one piece is really solid! With diagram 3 and 4 the stirrer cannot rotate. That happens only from diagram 5! There we have briefly rotated the stirrer a little bit by hand: correspondingly the concentration changes take place in stages. This can be recognised very well in the refraction profile (see arrows in photographs).

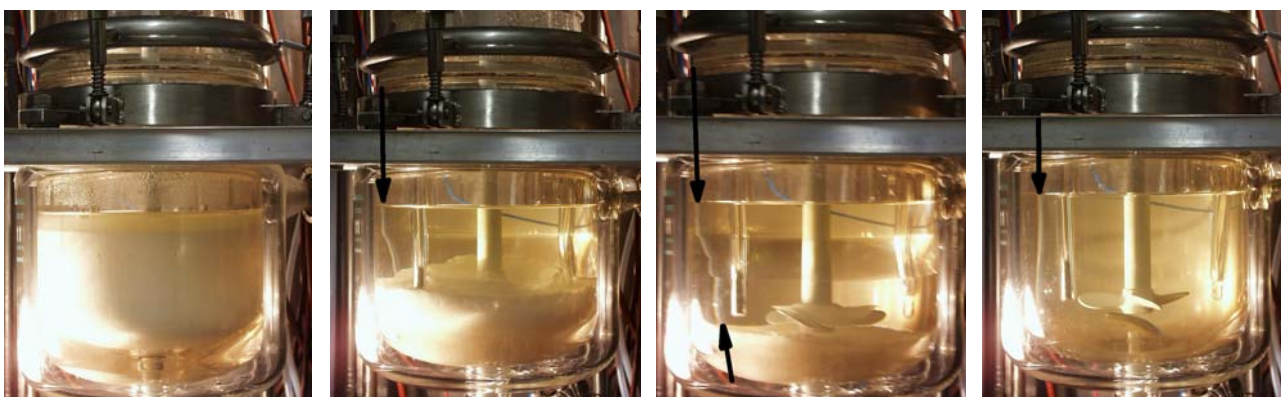


Diagram 3 5°C, unstirred, solids on the wall nearly up to the top level.

Diagram 4 42°C unstirred. The concentration change is clearly visible through the refraction profile (see arrow). At the top are weak and at the bottom are strong concentrations.

Diagram 5 58°C unstirred, but with the stirrer rotated by hand approx. 5 times however. The different concentrations are very clearly visible through the weak circulation in the refraction profile (see arrows).

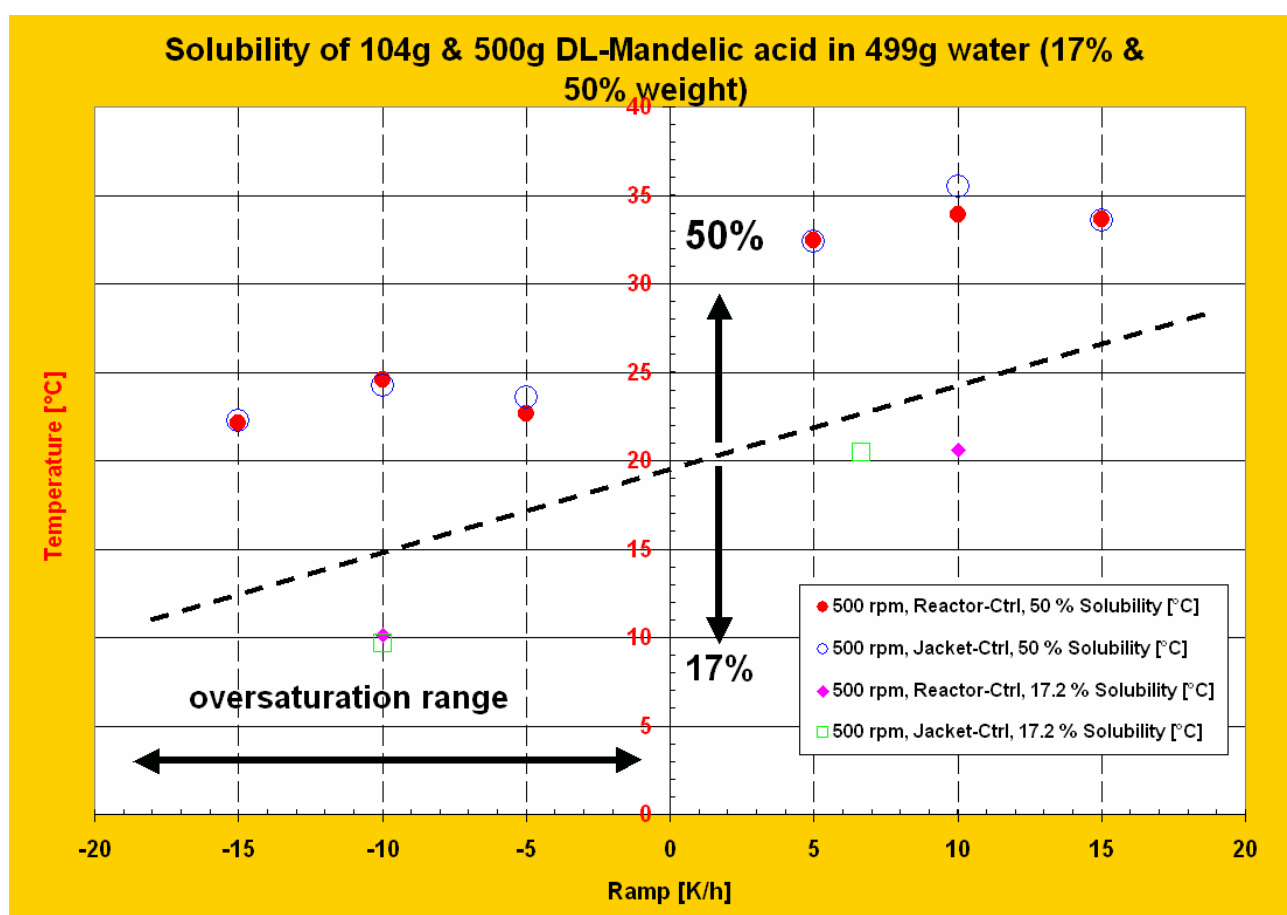
Diagram 6 60°C, briefly stirred in advance. Everything dissolved. The middle, increased and regular concentration is also clearly visible (see arrow), in contrast to the variations at 42°C.

5 Discussion and summary

The many measurements are very difficult to assess in one summary. We have therefore generated two diagrams, which should help to obtain a concentrated summary. We must immediately state the following: we are not crystallisation specialists and these are really necessary for a serious evaluation of the measurements! We can at best present hypotheses.

On the other hand we are reasonably clear that such processes can also take a significant place in reactions calorimetry, and generally also in inhomogenous systems, which cannot be ignored.

5.1 Search for dissolution temperature or the start of the crystallisation



Statistic 1: calorimetrically found dissolution temperatures at different ramps and with two concentrations.

In the previous experiments it was not the purpose to examine the crystallisation in itself, but the homogenous and inhomogenous systems under non isothermal conditions.

As a side effect however some results are now obtained from HFC and HBC for the crystallisation, which are displayed above.

At 17% concentration the HFC and HBC temperature values obtained lie very close together and are therefore credible.

The results at 50% concentration look different. What is amazing is the 10 K/h measurement value

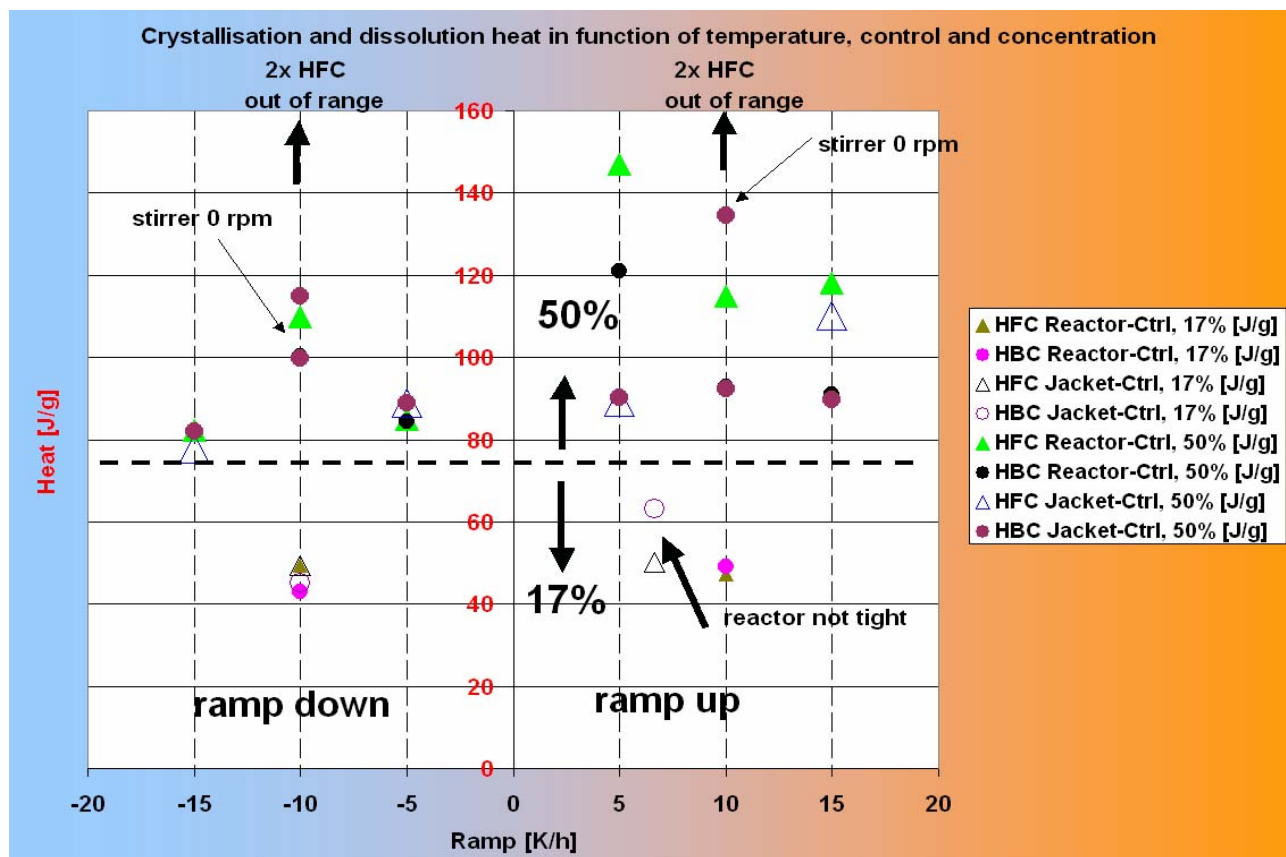
which springs out from the sequence, and in both ramp directions. With the dissolution process (increasing ramps) we really can expect a steadiness from high to low ramp gradients, so that the gradient can be concluded at 0 K/h. However this is obviously not the case. This is also covered by the previous conclusion, that most difficulties with regard to inhomogenous behaviour occur with 10 K/h ramps.

5.2 Measured dissolution heat in J/g as a function of concentration and ramp gradient, also unstirred

The following graphic summarises the previous measurement results with one point per measurement. The dissolution heat generated in the experiment is displayed in the ramp gradient function. Further information can be seen from the previous diagrams themselves.

We are aware that this measurement does not represent the effective dissolution heat, because the remaining concentration is not measured. This should be essential. In addition examinations with other substances also shows, that, as with a stationary temperature [4], the same behaviour does not necessarily occur in a ramp. We can also confirm these tests in accordance with [4] with KNO_3 in an earlier measurement carried out through HFC and HBC.

A further point with the HBC is the remaining disturbance power with an unsteady change from isotherm to ramp. This residual energy (determined by a not completely correct model and the very high water equivalent of approx. 5 kg glass) is compensated again at the end. However if only a measurement change was included, a small residual error occurs – even with very low energies (which we have reduced in the meantime by the factor 4!). It is therefore clear that for such evaluations only the ramp part (without the target value kink) should be evaluated (integration).



Statistic 2 Calorimetrically measured dissolution heat with different ramp gradients, directions and controls through HFC and HBC.

5.2.1 Discussion sample with 17% concentration

The measurements of both methods with negative ramp (-10 K/h) correspond very well with HF and HB in a reactor and a jacket control! The different reflection follows in the following table 1. Some advice: with the experiment with 6.67 K/h the reactor was unfortunately not closed and the measurement spreads more therefore (evaporation). Consequently the total picture deteriorates.

Statistical evaluation of non isothermal, quasi homogenous sample with 17% concentration DL-mandelic acid.

Number of experiments, evaluation	Ramp steepness t	Mean value	Standard deviation
4x Ramp downwards, each 1x reactor HF and HB and 1x jacket HF and HB	-10 K/h	46.68 J/g	6.0%
4x Rampe upwards, each 1x reactor HF and HB and 1x jacket HF and HB	+10 K/h reactor controlled +6.67 K/h jacket controlled	52.38 J/g	12.1%
4x HFC ramp downwards and upwards, jacket and reactor controlled	+/-10 K/h HFC (1x only 6.67 K/h)	49.00 J/g	2.2%
4x HBC ramp downwards and upwards, jacket and reactor controlled	+/-10 K/h HBC (1x only 6.67 K/h)	50.05 J/g	15.8%
All 8 exp. combined	+/-10 K/h	49.53	11.4

Table 1

5.2.2 Discussion of sample with 50% concentration

On the one hand we examine only ramps and on the other hand we examine methods, in order not to inflate the tables too much. Another examination is comprehensible on the basis of data at any time.

All cursive values contain unusable measurements.

Statistical evaluation of non isothermal, partly homogenous sample with 50% concentration DL-mandelic acid → HFC & HBC mixed.

Number of experiments, evaluation	Ramp steepness	Mean value	Standard deviation
HFC & HBC, reactor and jacket controlled	-15 K/h	86.5 J/g	2.5 %
	-10 K/h	227.1 J/g	→ 90.6 %
	-5 K/h	86.9 J/g	2.5 %
	+5 K/h	111.9 J/g	21.4 %
	+10 K/h	192.7 J/g	→ 83.4 %
	+15 K/h	102.2 J/g	11.9 %
	-10 K/h not stirred	793.9 J/g	→ 87.4 %
	+10 K/h not stirred	934.3 J/g	→ 85.6 %

Table 2

Here it is also noticeable that the +/-10 K/h ramp is a critical one. The unstirred version with this

ramp is therefore much more critical.

-5 K/h and -15 K/h have an extremely small standard deviation of only 2.5% in contrast to the +5 K/h and +15 K/h with 21.4% or 11.9%. With both these values the following is again noticeable: a higher ramp velocity results in a higher power and the standard deviation becomes more favourable.

Statistical evaluation of non isothermal, partly inhomogenous sample with 50% concentration DL-mandelic acid → +/- ramps mixed, divided into HFC & HBC

Number of experiments, evaluation	Ramp steepness	Mean value	Standard deviation
HFC Reactor and jacket controlled	+/-5 K/h	102.6 J/g	25.1 %
	+/-10 K/h	319.6 J/g	→ 66.0 %
	+/-15 K/h	102.6 J/g	25.1 %
HBC Reactor and jacket controlled	+/-5 K/h	96.2 J/g	15.1 %
	+/-10 K/h	100.2 J/g	9.1 %
	+/-15 K/h	86.3 J/g	4.9 %
HFC jacket controlled	-10 K/h not stirred	1611 J/g	→ 7.6 %
HBC jacket controlled	+10 K/h not stirred	117.2 J/g	14.8 %

Table 3

When we look at the composition with regard to HFC and HBC we can easily determine that the HBC does not indicate any significant peaks. Further characteristics are:

- 1) In general the HFC always lies somewhat higher, which can be traced back to the change of U and which gives a false indication despite a correction.
- 2) Quite extreme is the difference with an unstirred experiment (HFC cannot be used) but whose HBC values can still be viewed as very usable! When we assume typical values of 91.2 J/g (middle values from +/-5 K/h and +/- 15 K/h of HBC measurements) the measured 117.2 J/g are only just 30% too much, which can be seen as a very reasonable result.
- 3) Peculiarly the standard deviation decreases proportional with an increase of ramp velocity using HBC measurement:
 - +/-5 K/h → 15.1%
 - +/-10 K/h → 9.1%
 - +/-15 K/h → 4.9%

It looks like a linear correlation: the steeper it is the more accurate it is. This can be easily explained, because the signal to noise level increases correspondingly. The HFC on the other hand does not come off particularly well with 25%, 66% and 25%. This is not a cause of signal to noise level (which is already significantly better), but by the mix up of the measured system (sample) with the measurement system (HFC method)! Therefore no electronics which needs to be improved or anything like that are helpful here.

- 4) The evaluation of the two methods can obviously only be carried out seriously, when both results are available simultaneously, as was suggested in our report.
- 5) With this special experiment with DL-mandelic acid if necessary the special behaviour at 10 K/h should be examined more accurately, otherwise everything will run differently here than with 5 and 15 K/h. There are of course still other dependencies such as stirrer type and stirrer speed as well as possible further influences. It was not the aim of this investigation to find out about these.

6 Final conclusion

Combined HF/HB reaction calorimetry opens up completely new possibilities for isothermal and non isothermal calorimetry with homogenous, but above all also with inhomogeneous samples. Thanks to the comparison between both complementary HFC and HBC measurement methods, phenomenon which until now meant groping in the dark, can suddenly be recognised and explained. The assessment of the measurement quality through the comparison of both results is a further enormous advantage, because co-operative tests, which were used until now, are no longer needed to adjust the experimental runs and the evaluation methods.

7 Literature list

- [1] W. Regenass, 'The development of stirred tank heat flow calorimetry as a tool for process optimization and process safety', *Chimia* 1997, 5, p.189
- [2] L. Hub, 'Two calorimetric methods for investigating dangerous reactions', *I. Chem. E. symposium series no. 49*, p41
- [3] L. Hub and T. Kupr, 'Heat balance calorimetry and automation of testing procedures', *Symposium runaway chemical reaction hazards*, IBC December 2/3 1987, London
- [4] S. Taniewska-Osinska, Roman Logwinienko, 'Thermochemical investigation of aqueous KNO₃ dissolutions within a temperature range 5 - 25°C', *Acta Chimica*, vol 18, 1972

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