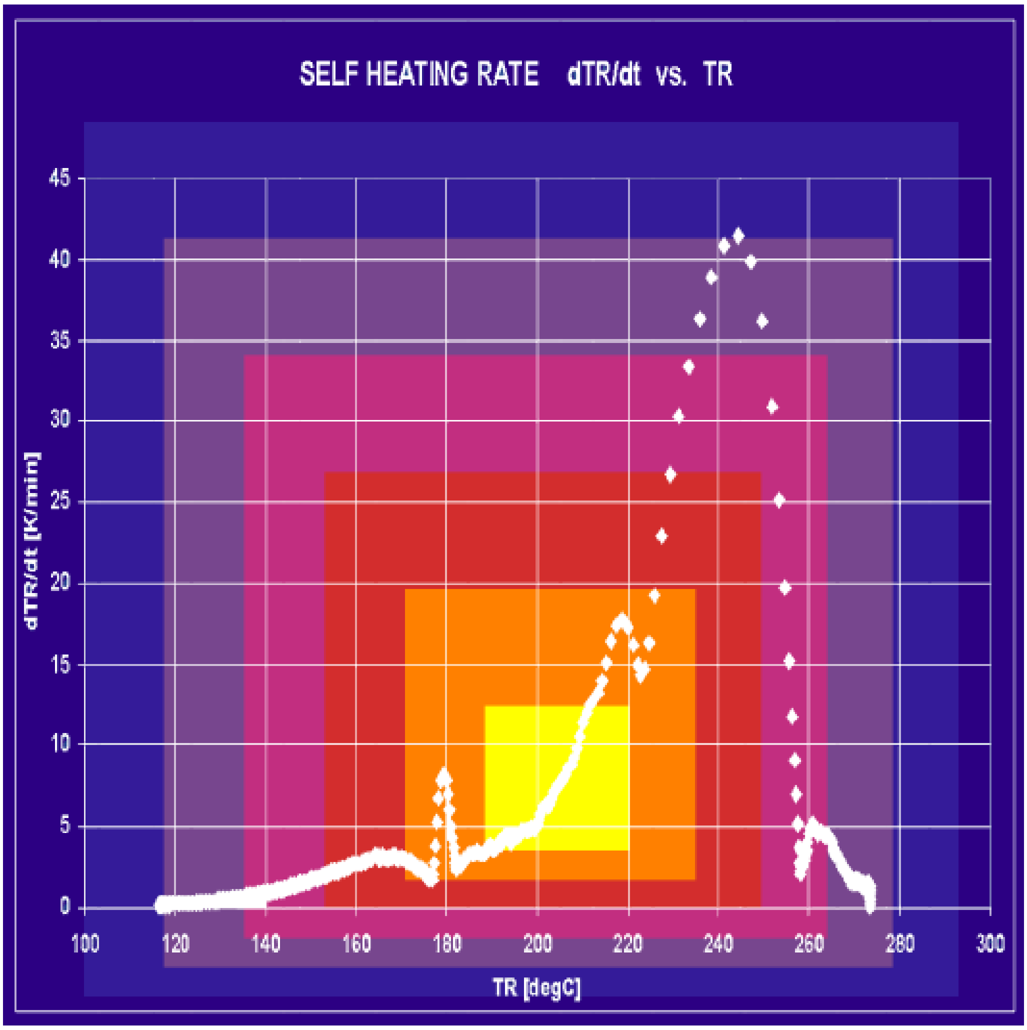
INFORMATION

Technical vade mecum for thermoanalysis



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Contents

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Vade mecum for thermoanalysis

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1 Purpose of SYSTAG's vade mecum for thermoanalysis

The current calorimetry offers such a wealth of equipment that even many experts have problems. How must a newly appointed safety expert feel, who is responsible for the company, but must first get acquainted with the work.

This vade mecum must offer a certain back-up support, but makes no claim to be complete in any shape or form. The variety of special knowledge which is needed is too large for us to presume that we can do that. The vade mecum must help the reader to obtain a somewhat ordered view of things, in order to enable him to better recognize his own needs.

In the first part we would like to give a specific overview of methods and equipment principles which are currently on the market. Subsequently we must address the needs, which are then further examined, mainly for thermal safety techniques, because this is SYSTAG's main area of activity.

Should you have further questions, please do not hesitate to contact us or our representatives in the appropriate country. We would like to advise you carefully, so that you will be completely satisfied with our response.

2 A multitude of different methods and equipment

Below follows a short list of many types of calorimeters. The list is not complete. A good aid is the book "Grundlagen der Kalorimetrie" [1] from which some examples have been taken.

2.1 List of some types of equipment

2.1.1 DSC (Differential Scanning Calorimeter) for small quantities

This is one of the most widely used pieces of equipment in the entire thermoanalysis. It offers no options however for inhomogenous tests, pressure measurement, gassing of test etc. They are fast and because of the small test quantities used, not very dangerous.

2.1.2 DTSC (Differential Temperature Scanning Calorimeter)

Heat conducting twin calorimeter with a scanning type operation, comparable to DSC.

2.1.3 DPSC (Difference Power Scanning Calorimeter)

Twin calorimeter used in a scanning type operation with electrical compensation as measurement principle (instead of temperature difference measurement).

2.1.4 DTA (Differential Thermal Analysis) for comparative tests

Method used for qualitative analysis of thermal processes through measurement of temperature difference between test and comparison sample with changing background temperature.

2.1.5 DTGA and TGA (Differential Thermal Gravimetric Analysis) for inclusion of weight loss

Like DTA, but with additional measurement of weight loss during the experiment.

2.1.6 ARC (Accelerating Rate Calorimeter) for adiabatic examination

Used for larger test quantities with isoperibol step search of the first, rational detectable exothermicity and subsequent adiabatic run. Also allows pressure measurement. Adiabatic run and pressure are pre-requisites for vent sizing.

2.1.7 VSP (Vent Size Package) Pressure Compensated Adiabatic Calorimeter PHI-TEC, APTAC...

In order to keep the Phi-factor-proportion of the heat capacity of Phi = (vessel + sample)/sample as small as possible a pressure compensated calorimeter for adiabatic experiments has been developed.

2.1.8 SIKAREX®, SEDEX® and RADEX® V5 for inhomogenous, larger test quantities; sequential DTA equipment

Combinatory equipment for several areas of use with large test quantities. Different measurement cells and different control systems allow many combinations, which can be used particularly for routine operations, but can also be used for scientific purposes in research.

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Functions such as DTA (but sequential; comparison test is first measured as calibration run), ARC, DPSC, all with or without pressure measurement are possible under different background conditions and with different test quantities. Tests can sometimes be stirred and gassed. Pressure ranges up to 200 bar or more are possible. Long-term isoperibol experiments (self heating experiments) are also provided for, as are pure adiabatic and over adiabatic experiments. Even wire basket experiments can be carried out in SEDEX.

2.2 Why so many pieces of equipment?

The question to be answered is not always the same and the measurement method is therefore different. We must always be aware that: ”Who measures measures rubbish!”. This stems from the disruption caused by the measurement and can never be eliminated.

For these reasons the different pieces of equipment have been developed. It needs to be said here that each has its use and delivers the best result in a certain situation, namely the situation for which it was developed.

Unfortunately all well intentioned ideas also have their drawbacks, which are not always obvious at first sight, because the physical laws can’t be compensated for.

Some examples:

Each pressure measurement is usually carried out outwards, because of high temperatures inside. This results in condensation. As a result test material is withdrawn from inside the system. Also, a ”heat-pipe” effect, which transports the permanent heat outwards, occurs at the front between hot and cold. With small reaction energies this can distort the picture greatly (example follows). Therefore *”Always only work with pressure measurement”* makes no sense.

With VSP the pressure must be compensated. Here there is therefore also a heat-pipe effect, but with large test sizes of approx. 100 ml to 1 litre the weight does not drop so significantly. In addition (because of the extremely thin wall of the reactor vessel) the external compensation pressure build-up must be set up in such a way that the temperature behaviour of the in flowing gasses does not disturb the adiabatic, which is difficult to manage in practice. Adiabatic run means, something happens in an unstable environment. More about that later.

Evaporation effects have two problem areas: on the one hand they can mask an exothermicity which occurs at this time; on the other hand the heat exchange area in a closed, but unfilled vessel is increased in the evaporation phase. This can be countered somewhat with good heat conducting vessel material, but it will never be perfect. All these small influences can add up to some 10%, so that quantitive measurements must always be interpreted very carefully and with a lot of experience.

Subsequently the non-linear characteristics of the heat conduction capability of the built-in ”measurement resistance” (e.g. air) aggravate the quantitive measurement, as do heat bridges, which are caused by mountings and contacts.

Also the Phi-factor is not constant across the temperature range and aggravates the exact calculations based on the measurements.

One can go on and on listing what needs to be taken into account.

3 What is needed where?

Thermoanalysis is a very large area of work. It is used for a wide variety of experiments.

A fundamental difference can already be seen from the required results:

1) Are you looking for a melting point and its enthalpy, or a glass conversion, or a weight loss at high temperatures or the reaction heat during a conversion or ....

--> because of substance data you are then destined for the classic and most used route.

2) If the question is how large the discharge lid on the reactor needs to be, or what the highest allowable working temperature is, or how long it takes for an explosion to occur at a specific temperature, or how high the pressure increase is or what the gas volume produced during a decomposition is ....

--> you want a thermal safety test.

If you can find your answer under 1), then unfortunately the vade mecum does not help you further. You must approach a supplier of the different DSC, DTA and TGA and associated equipment.

If your answer comes under 2) however then you should – no you must – definitely read on. This is SYSTAG’s main area of work and we – and obviously other manufacturers too – can help you further here.

3.1 Methods and equipment for determination of certain parameters

Sought after parameter	Methode No.	Test run method	**Ideal measurement cell** for optimum price-/performance ratio (in brackets: technically also possible)	**Ideal control equipment** for optimum price-/performance ratio (in brackets: technically also possible)
On-set temperature	1.1	Scanning, evaluation of temperature difference in relation to TJ	DSC for quick examinations and small test quantities	Indivisibly connected with measurement cell. Not available from SYSTAG!
	1.2.1 1.2.2 1.2.3		RADEX, typical 45 K/h (universal) SIKAREX, typical 30 K/h (very sensitive) SEDEX 30...60 K/h (for special sample vessel)	RADEX Solo RADEX Multi TSC 5000
	1.3	Isoperibol steps, evaluate temp. difference		
Time influence at different temperatures	2	Isoperibol long-term experiments (self-heating experiment) at different position temperatures, approx. 48 h. and longer	RADEX	RADEX Solo RADEX Multi (TSC 5000)
Self-heating test in wire basket	3	Sample keeping at 140°C for 24 h at isoperibol condition	SEDEX	RADEX Solo RADEX Multi (TSC 5000)
Pressure vs. temperature (the adiabatic run is most effective for vent sizing)	4.1	Scanning run	RADEX typical 45 K/h SIKAREX typical 30 K/h SEDEX 30...60 K/h	RADEX Solo RADEX Multi (up to 6 RADEX, but only 1 SIKAREX or 1 SEDEX or 1 RADEX V5) TSC 5000
	4.2	Adiabatic run	RADEX V5 SIKAREX (SEDEX)	TSC 5000
Gasflow vs. temperature (for reactions without pressure in open reactor)	5.1	Scanning run	RADEX typical 45 K/h SIKAREX typical 30 K/h SEDEX 30...60 K/h	FM4/4 with RADEX Solo RADEX Multi (up to 6 RADEX, but only 1 SIKAREX or 1 SEDEX or 1 RADEX V5) TSC 5000
	5.2	Isoperibol run, long-term or in steps	RADEX SIKAREX SEDEX	
	5.3	Adiabatic run	RADEX V5 SIKAREX (SEDEX)	FM4/4 with TSC 5000
Max. adiabatic increase	6.1	Direct start (only with calibration table, without immediate advance fine-tuning)	RADEX V5 SIKAREX (SEDEX)	TSC 5000 2 methods: a) evaluate in ThermoGraph after experiment with Phi-factor b) directly with SIKADIFF in the TSC 5000 SCIENCE
	6.2	Advance stabilizing 10...30°C below start temperature		
	6.3	Search on-set with isoperibol steps and start adiabatic automatically		
Max. temperature rate	7	--> see max. adiabatic increase (6.1 to 6.3)		
Time to maximum rate TMR	8	--> see max. adiabatic increase (6.1 to 6.3)		

Sought after parameter	Methode No.	Test run method	Ideal measurement cell for optimum price-/performance ratio (in brackets: technically also possible)	Ideal control equipment for optimum price-/performance ratio (in brackets: technically also possible)
Decomposition power vs. temperatur	9	Based on heat flow measurement in Scanning and Isoperibol	RADEX steel vessel 200 bar or all vessels, which must be measured. Glass vessels are dependent on level of filling!	TSC 5000 (with linearization tables in TR function)
Suppression of boiling points	10	In all types of experiments through pressure sealed (steel) vessel. With simultaneous pressure measurement losses through heat pipe effect.	All (ideal without pressure measurement)	All
Test for oxygen influence	11	Scanning Isoperibol in steps	RADEX: Glass open, pre-warmed gassed; steel closed, rinsed in advance with gas and filled	All
Test under inert gas	12	Scanning Isoperibol in steps	RADEX: Glass open, pre-warmed gassed; steel closed, rinsed in advance with gas and filled	All
Testing for catalytic converter effect	13	All For example steel filings or others, mix the medium affected in production and storage later with the experiment substance	All	All
Examination with gas dosage under high pressure	14	Scanning Isoperibol in steps	Steel vessel with special fittings for RADEX, SIKAREX and SEDEX	TSC 5000
Determination of decomposition energy (see also under 9)	15.1	Based on heat flow measurement with Scanning or Isoperibol	RADEX steel vessel 200 bar or all vessels, which must be measured. Glass vessels are dependent on level of filling!	TSC 5000 (with linearization tables in TR function)
	15.2	Can be calclulated with Phi-factor from adiabatic run	RADEX SIKAREX (SEDEX)	
Reaction's ordinal number n	16	Adiabatic run: a straight line in Arrhenius plot, when 1st order	RADEX SIKAREX (SEDEX)	TSC 5000
Dimension of discharge lids (vent sizing)	17	Adiabatic run: can be calculated from pressure and temperature rate with special mathematical package	RADEX SIKAREX (SEDEX)	TSC 5000

4 Basic principle behind RADEX, RADEX V5, SEDEX and SIKAREX equipment

The wealth of equipment can drive each safety representative to distraction. And with the multitude of equipment there are more demands on the budget. With regard to training, we come to the next hurdle, because each piece of equipment is operated differently and the results are evaluated differently. In the Seventies and Eighties this led to the former SANDOZ (now NOVARTIS) changing this by developing some systems for the practitioner which can be very meaningful in a few experiments. The knowledge needed for evaluation however can (still) not be built in. As before well trained personel is an essential and success determining factor for each company.

4.1 Instrumentation hierarchy with the new instruments:

DSC is used for fast determination with very little substance, also for dangerous tests.

RADEX® screening with 4…6 RADEX is used in parallel running Scanning Run with open, gassed and closed samples, mixable with steel filings (for example) as catalyst. Can also be inert, with and without pressure measurement.

RADEX® Isoperibol in steps with 4…6 RADEX is used in parallel running isoperibol step experiment with open, gassed and closed samples, also mixable with steel filings as catalyst. Can also be inert, with and without pressure measurement.

RADEX® for long-term studies (self-heating experiment over 2…6 days) is used at different temperatures with 4…6 RADEX ovens parallel, frequently in an open vessel (like normal storage).

RADEX® V5 is also used for adiabatic, screening and isoperibol (steps and long-term), multiple implementation (2…6 RADEX V5) only at three phase network with TSC-5000.

SIKAREX® is used for highest sensitivity and therefore highest stability for individual adiabatic experiments, also up to deflagration. Alternative: RADEX V5 for the same, but with a somewhat reduced sensitivity.

SEDEX® is used for example with steel wire basket experiments for transport tests (a UN recommendation). Special test vessels are also possible (Dewar can also be used). Can be stirred with a magnetic stirrer (built-in) and thanks to a window at the front can be viewed inside with the inside light. The inside can be inert. Dosages with pre-heating are possible. There is a real solid oven construction with discharge openings for example for an oxyhydrogen explosion inside the oven (SEDEX has been tested with this).

4.2 Types of experimental procedures for obtaining as much information as possible

SCANNING linear set-point value ramp of 50°C to 350°C for example in order to be able to make quick statements about exotherms. Typical ramps: 30 … 45 K/h.

ISOPERIBOLIC STEPS, alternative methods for searching for the occurrence of the first exotherm. The time induction already plays a (smaller) role here. Typical step values: 10 K.

ADIABATIC run for examination without heat exchange and projecting the actual maximum temperature increase with the Phi-factor. Further information which can be obtained is the Arrhenius plot (straight line with a reaction of the first order) and the TMR (Time to Maximum Rate), both naturally compensated with Phi.

The ARC combines the two previously mentioned experiments into one run. This is specific to ARC. As a result the first exotherm and the adiabatic behaviour are combined into one experiment. This is a very useful way of operating. Unfortunately other types of experiments cannot be carried out with the ARC.

The TSC-5000 makes such an **ISARC** run possible (Isoperibol Step with subsequent Accelerate Rate Calorimeter Run), because of the unique recipe control.

SYSTAG also offers **SIKADIFF®**, which can automatically compensate the water euqivalent. Expensive calibrations are needed for this however, so that in most cases a projection is simpler and also more accurate.

SYSTAG is the only company which also offers an **OAC® (Over Adiabatic Calorimetry)** run, with which a pre-defined, constant heat input can be carried out in the test. As a result an adiabatic run can be shortened. Consequently the system can be calibrated at heat capacity, when the heat conduction is known or vice versa (most used) when the heat conduction can be determined with known substance data (cp over the temperature range) from the measurement system.

Isoperibol self-heat equipment is used for examination of time induction at a certain temperature. Multiple equipment only is useful here. In the past the „Long-term bank“ was used here. Although this was simple, it was somewhat inaccurate. Today, with a multiple RADEX, this can be carried out much more precisely.

IPC (Isothermal Power Calorimetry) can also be used. This is most beneficial with small reaction performances and has a secondary use (scientific application), but is expensive for calibration. For that it is possible to measure quantitatively really accurately.

PSC (Power Scanning Calorimetry) is the implementation of the above principle on a scanning ramp. Not of great significance, see above.

Generally it can be stressed that methods 1 to 4 (SCANNING to ISARC) are the methods most often used.

The SYSTAG equipment family is specially designed for multiple application purposes. Consequently a large number of experiments can be carried out with a reasonable small investment. Newly developed hardware and software under Windows NT 4.0 massively increases the value of the entire family. Equally, old appliances can be easily upgraded. This is always worthwhile because it is known that SYSTAG equipment runs for at least a quarter of a century (much to SYSTAG's regret).

5 Different ovens' specialities

5.1 RADEX®

Can be used from room temperature up to 400°C. Test volumes 1.5 to 3 ml. Operates on the same principle as DTA (sequential).

Open glass vessels, gassed glass vessels with and without pressure measurement, closed glass vessels up to approx. 6 bar and pressure vessels with and without pressure measurement up to 200 bar can be used.

Small system, economical and robust, suitable for up to 6 systems with one control system. Operated in a fume cupboard.

Ventilator for fast cooling after successful experiment.

5.2 RADEX® V5

Can be used from room temperature up to 400°C. Test volumes 1.5 to 3 ml. Operates on the same principle as DTA (sequential).

Open glass vessels, gassed glass vessels with and without gasflow measurement, closed glass vessels up to approx. 6 bar, pressure vessels with and without pressure measurement up to 200 bar can be used.

Increased heating capacity and improved temperature distribution for adiabatic use. A parallel multiple use is only possible with TSC 5000 three phase control equipment. Operated in a fume cupboard.

Ventilator for fast cooling after successful experiment.

RADEX V5 is absolutely the universal measuring cell.

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5.3 SIKAREX®

Can be used from room temperature up to 400°C. Test volumes 3 to 30 ml. Works on the same principle as DTA (sequential). Extremely sensitive. Specially designed for examination of samples with smaller energies.

Especially strong oven construction, which allows a deflagration, without endangering personal. Operated in a fume cupboard.

Open glass vessels and pressure vessels with and without pressure measurement up to 150 bar can be used. Higher pressure vessels can be supplied on demand.

High heating capacity and excellent temperature distribution for adiabatic use. Parallel multiple use no longer possible.

Cooling hoses for fast cooling or continuous cooling during operation at room temperature is available.

5.4 SEDEX®

Can be used from room temperature up to 400°C. With an external cryostat it can be operated with the built-in cooling hose down to approx. minus 10°C. The oven space can be inert. Test volumes can be determined freely within the widest limits, depending on vessel type. Individual vessels can also be used. Typically 5 to 1000 ml. Works on the DTA (sequential) principle.

Sensitivity is dependent on the type of vessel and its isolation. Dewar vessels can also be used.

In accordance with UN recommendations, steel wire baskets up to 1 litre can be used for transport test.

Particularly safe oven construction prevents injury to personal due to discharge openings.

Operated in a fume cupboard.

Open glass vessels and pressure vessels with and without pressure measurements can be used up to 150 bar.

Viewing window with inside light is available.

Magnetic stirrer is built-in.

High heating capacity. Parallel multiple use is no longer possible.

6 Overview of test vessels which can be used

6.1 RADEX® vessels

Clockwise from top left: gassed glass vessel with output measurement, standard gassing, pressure vessel with bursting foils or bursting screw (30, 100 and 200 bar models), open glass vessel, all vessels approx. 3 ml (standard filling 2.5 ml).

Clockwise from top left: collet attachment (tool part) with pressure vessel (bottom part), torque wrench inset for bursting screw, pressure transmitter with connection parts and pressure vessel, torque wrench with pressure vessel cover (second part of assembling tool).

Gas flow meter FM4 for the smallest gas fluids with extremely low back pressure (approx. 1 .. 2 mbar). Measurement range FM4/4: 4l/h or FM4/60: 60 l/h. Has its application with all RADEX, RADEX V5, SEDEX and SIKAREX systems.

6.2 SIKAREX® vessels

From left to right: pressure vessel with 150 bar bursting disk, glass liner for pressure vessel, Pt-100 glass liner and PTFE lid, open glass vessel with standard taper-ground joint.

6.3 SEDEX® vessels

From left to right: double jacket vessel with magnetic stirrer rod, single jacket vessel with glass liner for Pt-100, 150 bar pressure vessel (front), adiabatic stabilising compartments for special experiments over very long times (back).

From left to right: simple wire baskets for different filling quantities for a self-heating test in SEDEX.

7 Selection of control equipment and software

7.1 RADEX® Solo

The RADEX Solo is an economic universal control system. An external controller for the RADEX, SIKAREX or SEDEX measurement cells, together with a PC and one interface card per controller can be put together into a simple system.

The accompanying DOS software (also runs under WIN 95 and NT 4.0 in DOS emulation mode) allows the control of the experiment run in a simple way. A calibration can be carried out with polynom. It allows the evaluations of on-set temperatures and calculation of heat power with automatic base line.

The system can be extended with further control equipment, interface cards (AT compatible slots necessary), software adapted to this and measurement cells up to a maximum of 4 places.

Scanning, isoperibol and isoperibol step experiments can be carried out. Pressure measurement and gas measurement are also possible, each with separate measurement converters.

We are dealing with a system which is adequate for a small safety laboratory which doesn't carry out too many tests in one week. An extension to Windows is not possible.

7.2 RADEX® Multi

The RADEX Multi is the most economic multiple control system with up to 6 RADEX measurement cells in parallel operation. An individual SIKAREX or SEDEX oven can also be operated with a separate insertion module. Controller and data recording are carried out with the PC. Two AT interface cards are needed in the PC.

The accompanying DOS software (runs also under WIN 95 and NT 4.0 in DOS emulation mode) allows an extremely simple experiment run control. A calibration run for scanning and isoperibol can be carried out automatically. With RadCalc up to 6 curves can be displayed for quick comparison. RADEX Multi, together with RadCalc, allows the evaluations of on-set temperatures and calculation of heat power with manual base line.

A PC extension to further RADEX Multi is not possible.

Scanning, isoperibol and isoperibol step experiments can be carried out. Pressure measurement and gas measurement are also possible, each with separate measurement conversions.

We are dealing with an outstanding system for a large safety laboratory which has to carry out a great number of tests per week. An extension to Windows is not possible.

7.3 TSC 5000

The TSC 5000 is the latest development and impresses with outstanding accuracy and the highest stability (0.01°C/year). This sytem is predestined for adiabatic experiments. Equipped with the latest process control software, it is the first and to date the only equipment on the market which allows recipe controls.

We are dealing with a single place system. Depending on the construction of the system, single place, 4 times or even 6 times applications are possible (see TSC 5000 Multi). Consequently all types of measurement cells can be operated. Pressure measurement and gas measurement are also possible, each with separate measurement converters.

The accompanying TSC 5000 STANDARD Windows software (runs under NT 4.0) allows the control of the experiment run in an extremely simple way. Manually controlled test experiments and automatic experiment runs with recipe can be carried out. A calibration run for scanning and isoperibol is carried out automatically. The on-set temperatures can be determined manually with the new Thermograph evaluation software. The heat power and heat energy against the calibration baseline can also be calculated and displayed. With adiabatic experiments the Arrhenius plot, the TMR (Time to Maximum Rate) and the maximum adiabatic increase can be displayed and printed.

In the TSC 5000 SCIENCE version SIKADIFF (compensation of water equivalent and Phi-factor), OAC (Over Adiabatic Calorimetry), IPC (Isothermal Power Calorimetry) and PSC (Power Scanning Calorimetry) can also be carried out. All these experiments demand an enormous calibration effort however, so that the test throughput drops. Not recommended for a routine laboratory.

We are dealing with an outstanding and universal system, which is suitable for a small and a large safety laboratory.

7.4 TSC 5000 Multi

In a way the new TSC 5000 Multi is a combination of TSC 5000 and the earlier RADEX Multi.

The whole construction is based on the TSC 5000. In contrast to the TSC 5000 however the measurement value recording and measurement cells power control can be extended. Up to 6 RADEX measurement cells can be connected in the one phase implementation. In the three phase implementation up to 6 RADEX V5, 3 SIKAREX or 3 SEDEX are possible in parallel operation (within the same experiment). All measurement cells can therefore be operated with this. Pressure measurement and gas measurement are also possible, each with separate measurement converters.

In parallel operation however only SCANNING, ISOPERIBOL STEPS and LONG-TERM ISOPERIBOL experiments are possible. All other experiments with TSC 5000 STANDARD or TSC 5000 SCIENCE are limited to one single measurement cell.

The accompanying TSC 5000 Multi Windows software (runs under NT 4.0) allows the control of the experiment run in an extremely simple way. Manually controlled test experiments and automatic experiment runs with recipe can be carried out. A calibration run for scanning and isoperibol is carried out automatically. With the ThermoGraph evaluation software up to 6 curves can be displayed for quick comparison. Consequently it is easy to determine the on-set temperatures manually. The heat power and the heat energy against the calibration baseline can also be calculated and displayed.

By combining the TSC 5000 STANDARD and TSC 5000 Multi an outstanding price/performance ratio has been reached for an enormous number of functions. Routine and demanding individual tests can be carried out. Thanks to the modern software, operation is child's play. Consequently it is also useful in a routine laboratory. With this combination everything can be carried out from Geigy-Kuehner to ARC – and an awful lot more!

Depending on the application you can start with a TSC 5000 Multi, which can be adapted later to TSC 5000 STANDARD or even TSC 5000 SCIENCE – or vice versa. Alternatively, with the same equipment one or other appliance can be conDiagramd in minutes by loading software. On the other hand the calibrations only need to be carried out when the vessel type, the measurement cell or a sensor changes.

8 Some curves examples from the TSC 5000 STANDARD thermo analysis

8.1 Calibration

The calibration is responsible for the compensation of the available sensor and temperature distribution error. Consequently the system’s errors will be compensated as best as possible. For this purpose the TR sensor is taken as reference and everything is referred to this. Through off-set and span comparison it can be calibrated separately with absolute accuracy in the TSC 5000. All other recordings are referred to this calibrated TR temperature and corrected accordingly.

In order to carry out the calibration as accurately as possible, the entire operating zone, for example 30°C to 400°C, must be recorded either continuously or in as many steps as possible. We have set the selection to approx. 5 .. 20 steps (freely selectable) and have achieved results which give deviations of only a tiny 1/100°C in the TSC 5000 across the entire temperature range.

The fundamental problem during the calibration is the use of an inert substance, which perhaps behaves in the same way as the test substance. Powder or even liquid would be ideal. The first one, for example glass powder, is possible. The second one on the other hand gives big problems: each liquid evaporates differently (depending on the vapour pressure and boiling point) and withdraws energy from the system. In each case therefore we have selected a very fine grained powder (for example Pyrex glass). Obviously other inert substances are also feasible.

In order to change anything the filling level must also be defined, because even in vessels with thin walls the heat exchange primarily takes place accross the substance surface during scanning and isoperibol operation, i.e. glass that sticks out is only partly effective. This is different for steel vessels with higher heat conductivity and wall strength. There practically the entire surface is involved in the heat exchange, i.e. there the level of filling is only an influencing factor for the Phi or the total reaction energy.

8.1.1 RADEX V5 isoperibol calibration

The **_ISOCAL** diagram shows the run (freely put together via recipe) of the TJ (J=jacket) and TR (R=reactor) temperatures (scale 0-400°C) and the difference (scale +/-20K). The isoperibol step size is 25K. The drift across the measurement range lies at approx. 10K. For correction purposes the individual deviations are now transferred into a linearization table and will effect the result in the next curve.

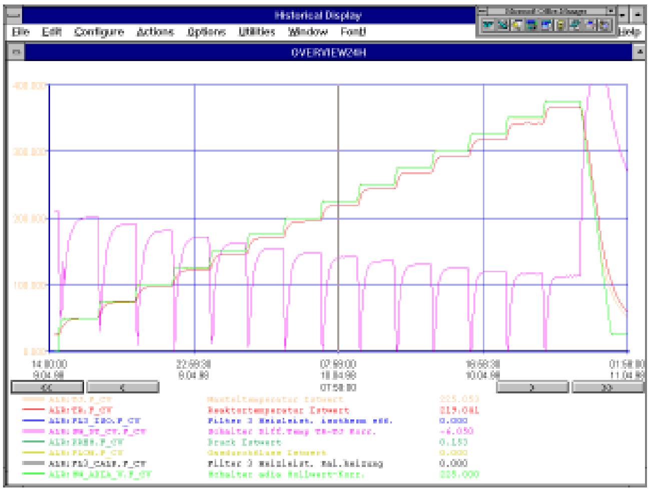


Diagram _ISOCAL: Isoperibol calibration

8.1.2 RADEX V5 isoperibol test run

The same experiment was subsequently carried out as **_ISORUN** with completed linearization table and it very nicely shows the correction effect with the temperature difference. The scales were retained.

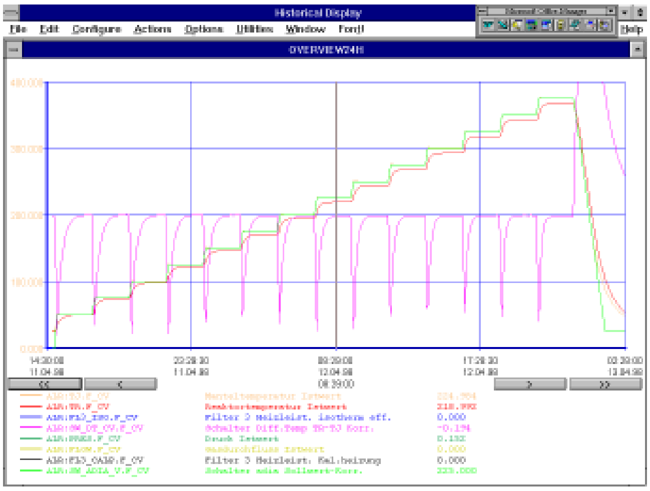


Diagram _ISORUN: Isoperibol test run

8.1.3 Scanning calibration

Using the same principle we can also calibrate a ramp (see **DTBPSCAL** diagram). In addition, the relatively large drift of approx. 7K, determined by the ramp, is compensated for. On the other hand this compensation is dependent on the cp value of the substance used. During a live experiment the zero line may therefore have to be moved again slightly. On the other hand all system errors are compensated for, as are the sensor errors. The next diagram shows this run with one peculiarity: a vessel which has already been used several times and which was not completely clean, is used. Shortly before 400°C a small exotherm can be determined which of course makes the calibration in this range unusable. For this reason there is a simultaneous control of the cleaning (see also a later chapter).

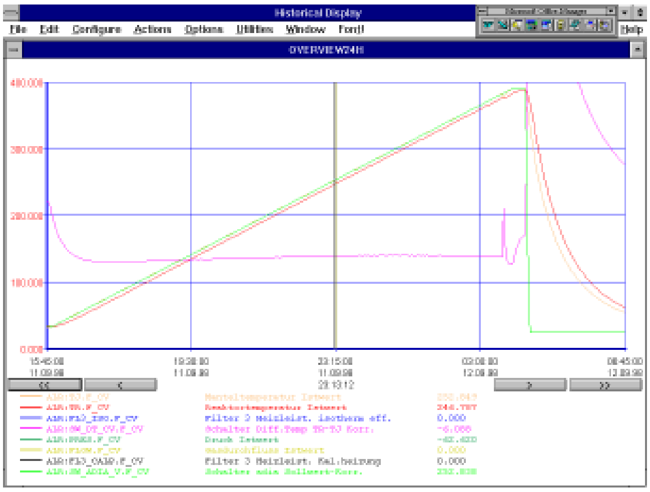


Diagram DTBPSCAL: Scanning calibration

8.1.4 RADEX V5 scanning run open vessel

The **RMSCRUN1** curve shows a scanning from 35 to 350°C after a calibration. The temperature difference curve very nicely shows the reaction and also the following exotherms. The scale is +/- 20K. The on-set point of approx. 117°C lies either immediately after the very slight endotherm or is presumable even masked by it. This small example very nicely shows how carefully an interpretation must be carried out and how it is never completely absolute. Based on the temperature (117°C) the assumption suggests itself that this weak endotherm might stem from water (humidity) connected with the chrystal structure. At the same time the example also shows how sensitively the system reacts. A careful interpretation must always be made by an expert who knows the actual chemistry and the particular measurement circumstances and can therefore interpret them.

Diagram RMSCRUN1: Scanning Experiment

8.1.5 Isoperibol steps in RADEX oven (self heating experiment)

This **J_ISRUN3** example very nicely shows how with a step increase (here around 10K) the behaviour of the substance can also be examined. This method is particularly sensitive at the start of the reaction, because a sufficiently long rest time is available. After the experiment we determine the highest temperature differences from the individual steps and enter these into an Excel table. A print-out of the points afterwards will very nicely show how the on-set temperature can be found. This method is very sensitive and where applicable binded water can be taken away.

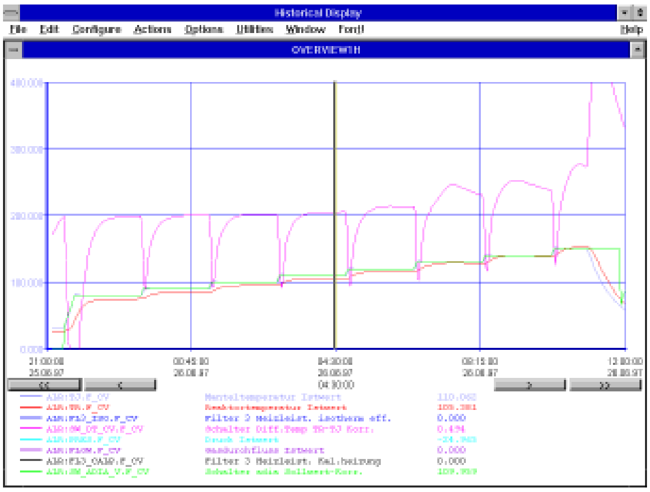


Diagram J_ISRUN3: Isoperibol steps

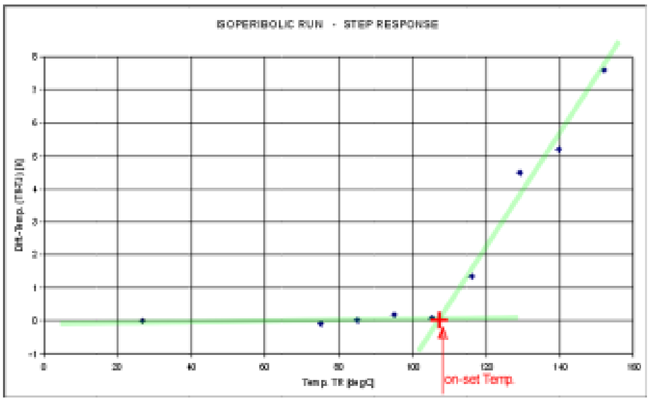


Diagram ISOSTEP.xls: Evaluation of on-set temperature

8.1.6 ISARC Isoperibol search steps & adiabatic run – RADEX V5 open vessel

With the **RMISARC1** heat build up experiment the occurence of the first exotherm is sought. and subsequently switched over to adiabatic. Consequently, at the same time you have found the approximate on-set temperature. The effective on-set temperature lies between the previous and the triggered isoperibol step. The adiabatic part is then used for the following evaluations: Arrhenius plot, Time to Maximum Rate (TMR) plot and adiabatic increase.

This experiment shows a very slight exotherm with a small adiabatic increase, because the mass in the glass vessel is really small. At the end everything has been reacted out and the temperature remains stable at the new level (still adiabatic conditions) until the programme is either broken off manually or breaks itself off automatically at a pre-selected time.

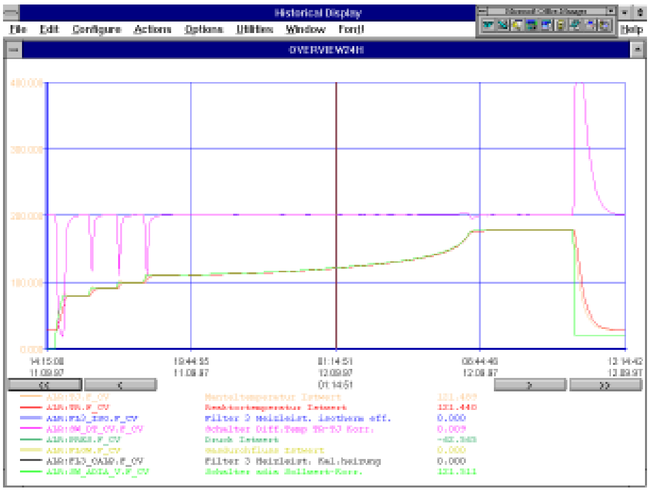


Diagram RMISARC1: adiabatic run

8.1.7 A few possibilities from adiabatic displays/evaluations

In the **'adiabatic run'** diagram you can see the rough display of the temperature run from another experiment. The black curve displays the TR temperature, the green one the TJ. The following diagrams show what information can effectively be drawn from this experiment.

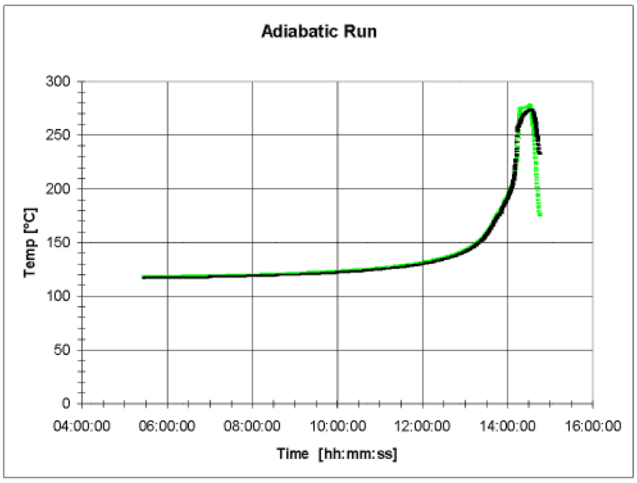


Diagram adiabatic run

The pressure is also measured and shown in the diagram **'pressure vs. TR'**. Even this pressure run alone indicates a more than complex decomposition reaction. The dotted section is run through extremely quickly, because the distance per measurement point is only 10 sec.

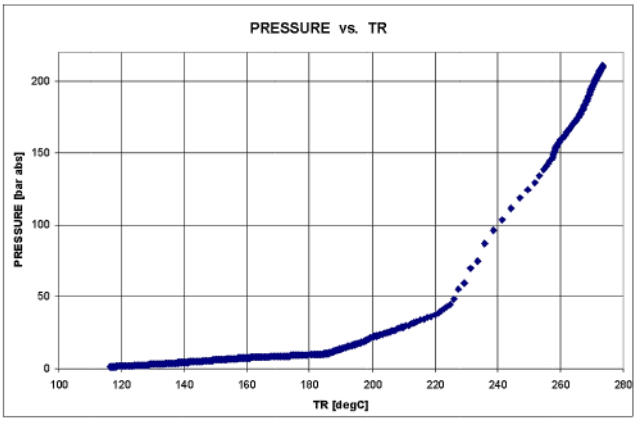


Diagram pressure vs. TR

In the **'self heating rate dTR/dt vs. TR'** diagram supplementary maxima, which indicate supplementary reactions, are shown in addition to the main maximum. An exact interpretation must always be left to the process chemist.

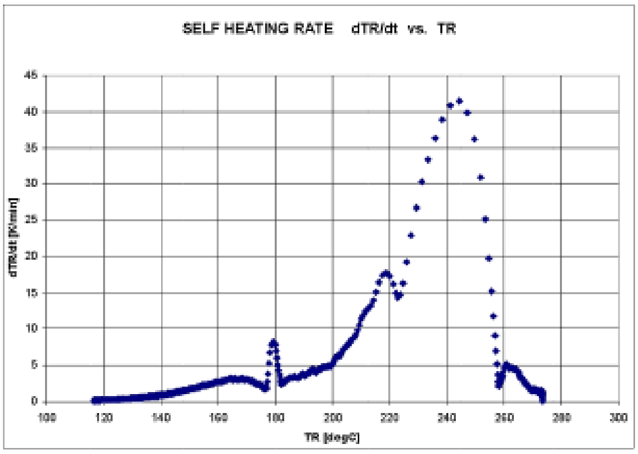


Diagram self heating rate dTR/dt vs. TR

Finally, the **'Arrhenius Plot'** shows a linear increase during the first part, whereby the drop indicates the use of educts. A second decomposition has been started spontaneously, which changes into a third one with a quasi linear increase, but only a quasi one, which is then brought to a standstill. Finally a fourth one has presented itself. All in all very complex.

A linear increase in the display 'In dTR/dt vs. 1/TR_{abs}' suggests a first order reaction.

Note: the rough data are only filtered lightly. Consequently a certain noise can be noted in the range 0.1 to 1 K/min. More about this in the next section.

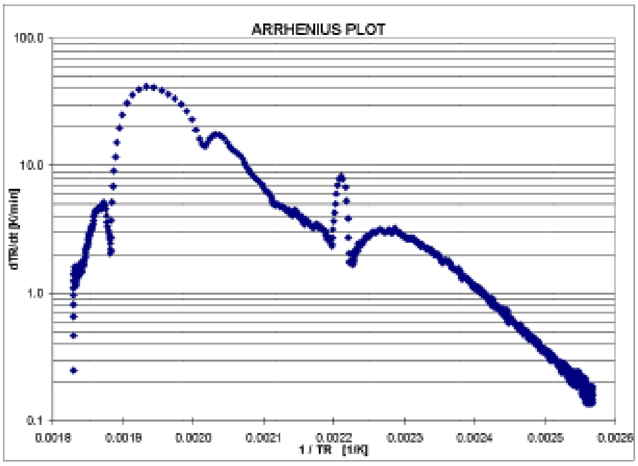


Diagram Arrhenius plot

Additionally, on the basis of the adiabatic run, the experimental **'Time to Maximum Rate TMR'** dependent on the TR temperature, can also be determined. This allows estimations in the danger potential.

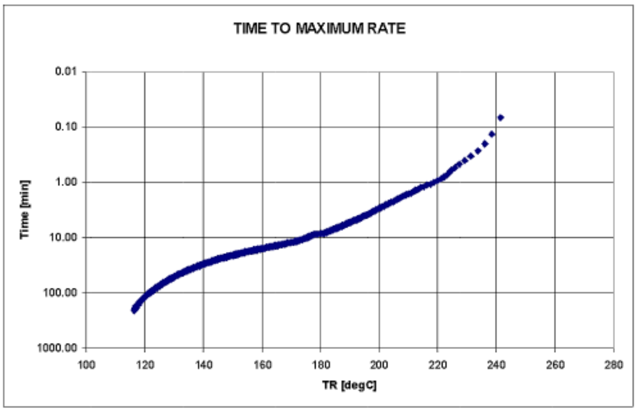


Diagram Time to Maximum Rate TMR

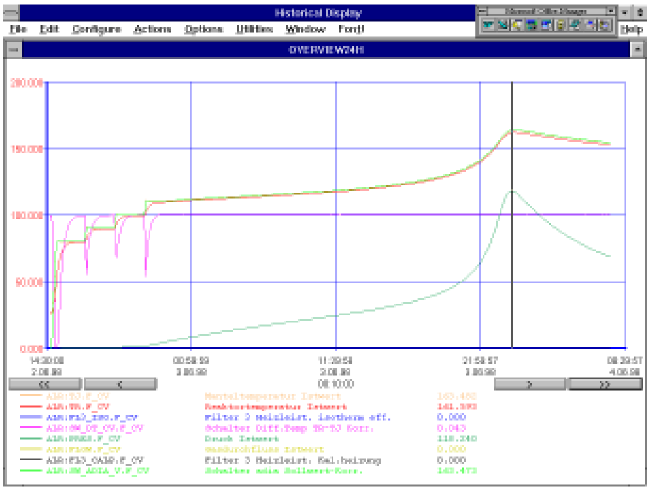
8.2 Selection from some special test experiments

The pressure measurement application is always demanded by many safety experts. Hereafter we show you from two examples that the pressure measurement can also be counter productive. It is therefore important to consider carefully when a pressure measurement should or should not be used. We also refer to the influence of the Phi factor, the temperature dependency of the entire system, the determination of the heat flow and its integration, the influence of previous cleaning of the vessel and specific points which concern the measurement noise.

8.3 Pressure measurements influences

8.3.1 ISARC with Di-t-butylperoxide (DTBP) with pressure measurement

This **R1ISARC** mode of experimental procedure with the weakly reacting Di-tert-butylperoxide in the 200 bar RADEX pressure vessel was tested in the ISARC mode (on-set search with self heating experiment in 10K steps, followed by automatic switch over to adiabatic). The pressure was measured simultaneously across a capillary. The maximum pressure was 118 bar.



AIR:TJ.F_CV	Manteltemperatur Istwert	163.402
AIR:TR.F_CV	Reaktortemperatur Istwert	161.393
AIR:FA2_ISO.F_CV	Filter 2 Heizleist. Isotherm eff.	0.000
AIR:SW_DT_CV.F_CV	Schalter Diff.Temp TR-TJ Korr.	0.043
AIR:PRES.F_CV	Druck Istwert	118.240
AIR:FLOW.F_CV	Gasdurchfluss Istwert	0.000
AIR:FA3_CALR.F_CV	Filter 3 Heizleist. Kal.heizung	0.000
AIR:SW_ADIA_V.F_CV	Schalter adia Sollwert-Korr.	163.473

Diagram R1ISARC: search of on-set & adiabatic run

There are three points which must be taken into account:

a) First of all, the starting point lies at 110°C and

b) Secondly, the adiabatic increase is 51.6 K. The cursor was moved to the maximum value and can be read below. The start is by definition 110°C, therefore 161.6°C – 110°C = 51.6°C.

c) Thirdly, a drop in the adiabatic temperature can be established after reacting out.

A discussion about this follows in the next section.

8.3.2 ISARC DTBP without pressure measurement

The next diagram **R3ISRAC** shows exactly the same experimental arrangement with the same substance and the same substance quantity. With this experiment the pressure connection is sealed with a cork when still in the heat zone. No pressure measurement is available. On the other hand, the result shows the following changes:

a) The starting point has dropped to 100°C.

b) The adiabatic increase is 58.7K.

c) After reacting out the adiabatic run is more or less flat.

What are the causes? It is solely the pressure measurement which effects this result. Because we are examining a liquid which evaporates (see previous pressure curve), the capillary is situated on the outside from the pressure transducer to a heat pipe, which efficiently draws off heat outside.

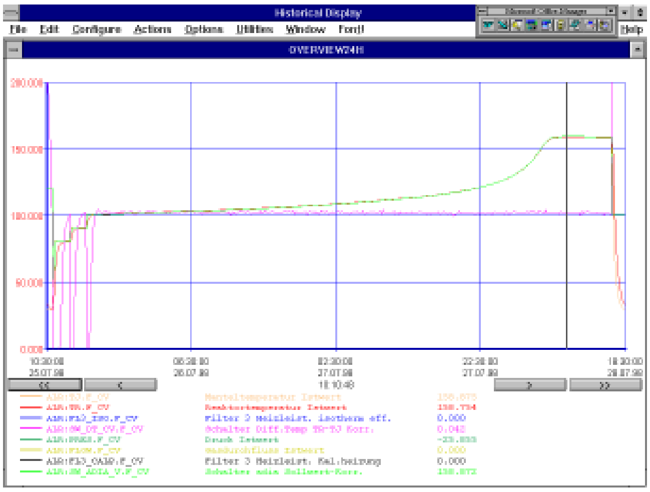


Diagram R3ISARC: identical run like R1ISARC, but *without* pressure measurement

The consequences are clear:

a) Starting point: because the pressure is already building up at 100°C, a draining away of heat has already begun, which postpones detection.

b) Adiabatic increase: because during the entire experiment the pressure measurement or the heat pipe is active, a part of the heat is drawn off. The result is a minor increase.

c) Adiabatic drop at the end: because even after the reaction has finished energy continues to be drained off via the heat pipe, it is essential that the reactor temperature drops in adiabatic operation.

These experiments show very clearly the pressure measurement influence. Each operator must therefore be clear about what he wants to obtain as measurement result – regardless of whether pressure measurement is used or not – and how the results could be distorted.

Reducing the capillaries in order to eliminate the influence suggests itself. The following experiments deal with this but also show how difficult using liquids is.

NOTE: For better results with on-set temperature and adiabatic increase a pressure measurement must be sacrificed in each case.

8.3.3 Adiabatic RADEX V5 heat pipe effect with PTFE isolated wires

Within the framework of heat flow numbers and water equivalent determinations (Phi factor) many different experiments were carried out. Amongst others an adiabatic experiment was carried out with closed steel vessels, filled with water, supplied however with an electric calibration heating. In the **ST_AD154** diagram the adiabatic run from 50°C to 140°C is displayed. It is broken off at that point in order to strain the heating wire seal (two component bond) neither thermally nor with excessive pressure. The supplies to the calibration heating consist of two very thin wires insulated with PTFE, which are stuck on. No pressure measurement was available. The connection was insulated. The system used was weighed before and after the experiment. No loss of material (water) was established.

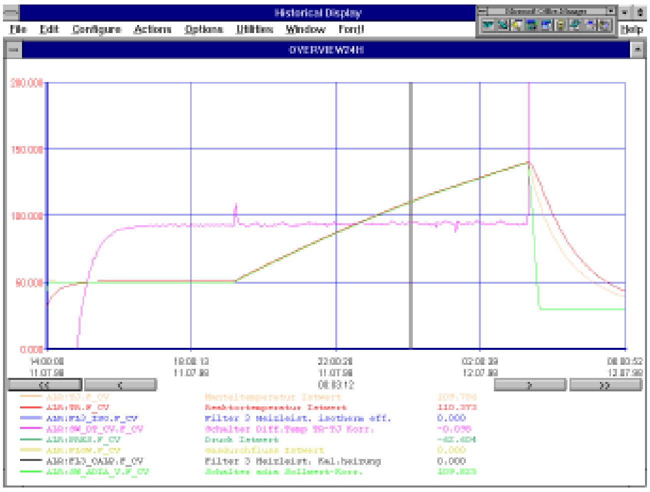


Diagram ST_AD154: adiabatic run with calibration heater in a sealed water test

The measurement result however shows a somewhat different diagram than expected. Firstly the temperature increased linearly, as expected. Later it levelled off, but with a bend. This lies at around 110°C, therefore slightly above the boiling point. Subsequently the increase is significantly flatter. Examinations show that more energy is lost than was necessary for the production of vapour.

Conclusion: as a result of the occurance of excessive pressure, together with the higher temperature, the with PTFE insulated wire acts as a mini heat pipe. Between insulation and wire finite evaporation quantities can be exchanged. This is already sufficient to put the brakes on the adiabatic increase with constant heat power. Because the system does not indicate any weight loss, the seal in the cold part is o.k.. The system is sealed therefore but a heat exchange nevertheless occurs!

8.3.4 OAC RADEX V5 pressure vessel with and without pressure measurement

Within the framework of determining the temperature dependency of heat flow and vessel capacity a defined heat input was simulated, amongst others through an OAC Run (Over Adiabatic Calorimetry) with a steel or glass vessel and through constant temperature difference (as with melting).

With the 2K temperature difference in the **OAC2_ST1** experiment a heat input of about 80 mW is produced. The sealed steel vessel was filled with 2.5 ml water and there was no pressure measurement. The experiment was started at 50°C and was continued to 150°C. The adiabatic temperature increase was very gradual. However, here also a small bend can be detected which lies at around 101°C. It is therefore easily possible that we are dealing here with the boiling point with the subsequent vapour production.

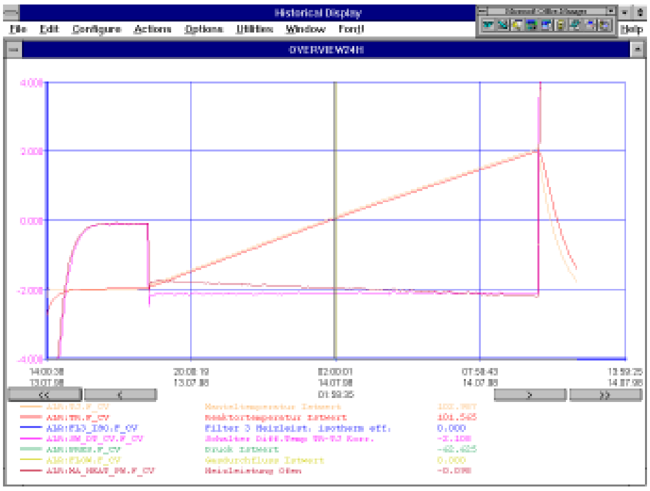


Diagram OAC2_ST1: over adiabaitc run with water

The same experiment is now carried out as **OAC2_ST2** with pressure measurement. The sealed steel vessel was filled with 2.5 ml water and has a capillary which leads to the outside to the pressure measurement transducer. The experiment was started at 50°C and must also be continued to 150°C.

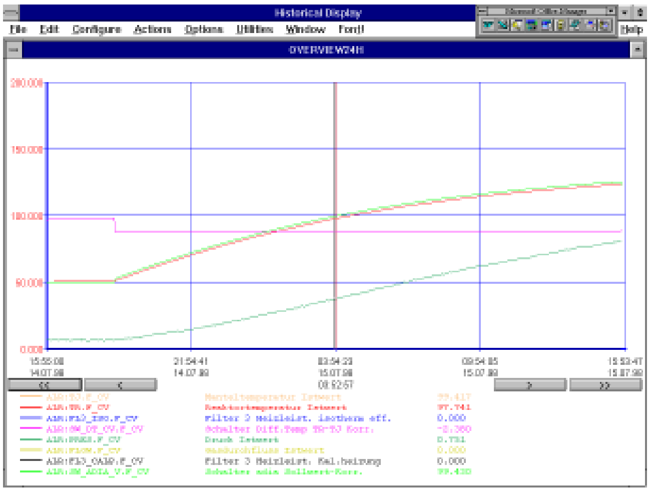


Diagram OAC2_ST2: over adiabatic run with pressure measurement of a water sampleasserprobe

The adiabatic temperature increase however levels off noticebly and does not reach the 150°C in the designated time. Even at approx. 110°C we have only half the increase, which results in a loss of around 40 mW. The higher the temperature rises, the higher the pressure and the heat pipe losses. These two experiments show very impressively the disadvantages of a pressure measurement.

Counter measures: The pressure measurement has to be carried out in the hot zone, which is basically possible with special sensors, but which is significantly more costly and expensive.

8.4 Temperature dependency on heat flow and heat capacity

8.4.1 Heat flow calibration RADEX V5 oven

It is best to determine heat flow numbers with electric calibration heaters. In **GO_ISO 154** an open RADEX vessel, filled with approx. 2 ml glass powder, was alternatively heated and paused with 154 mW. At the same time the surrounding area was continuously raised by 10K, from 50 to 150°C. The influence of the temperature is remarkable! An experienced user might assume that with the same heat power at 50 and 150°C the same temperature difference must result and not, as proven in the experiment, a change of 6.27K at 50°C to 4.64K at 150°C. This also indicates the difficulty in being able to execute calibrated measurements (can in principle also be transferred to DSC and other equipment!). For this reason both RADEX glass vessel open and 200 bar steel vessel measurement cells are calibrated in with a lot of effort. Thanks to these calibrations, power measurements and subsequent integrations for the total energy have become possible, but both with only moderate accuracy. All computer entries with measurements over xx.xx mW (more than two to three numbers) are pure eyewash. We are dealing here with errors of a few up to some ten percent.

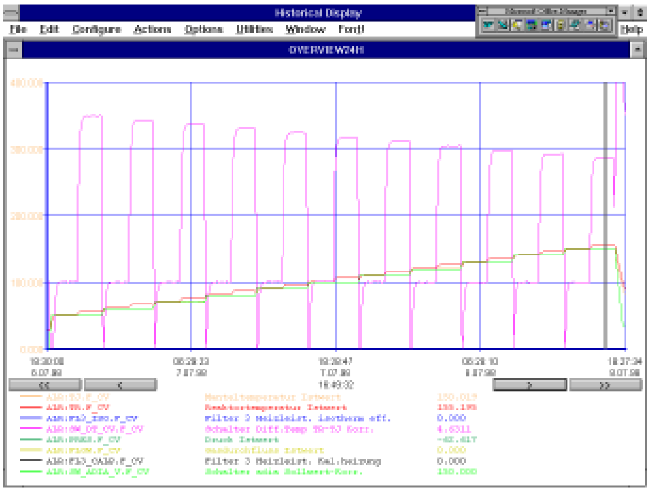


Diagram GO_ISO154: same heating power, increising ambient temperature --> decresaing difference temperature

Conclusion: *In order to obtain the highest possible accuracy, a calibration with a known melting point must be carried out at the expected experiment temperature.*

8.4.2 OAC RADEX V5 open steel vessel

Last but not least we would like to show the influence across the entire temperature range of heat transmission and heat capacity of a steel vessel filled with glass powder. With the **OAC10ST3** experiment an Over Adiabatic Calorimetry experiment was carried out from 50°C to 380°C. The approach is a constant 10K.

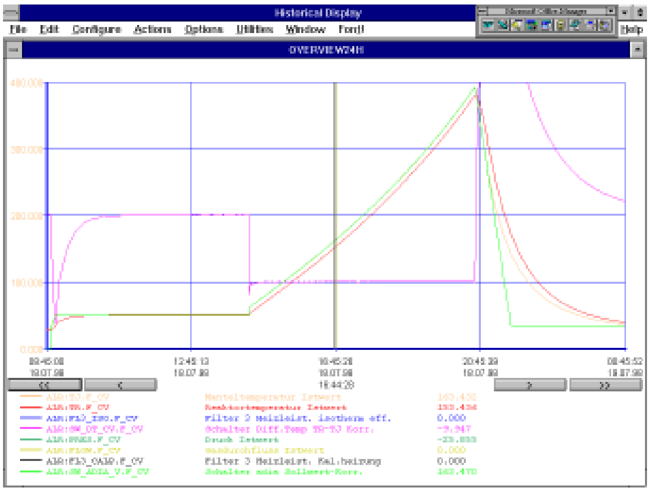


Diagram OAC10ST3: over adiabatic run with inert solids

The curve shows impressively that the influence from transmission and Cp value of vessel and filling increases positively, i.e. the curve is not linear but increases gradually. From this we may conclude that:

a) The heat transmission increases with higher temperatures (Brownian motion)

b) The heat capacity of the steel vessel and its filling changes also - it increases as well - but less strongly.

From this we conclude:

1) For a heat power measurement a function must be introduced which is dependent on TR and TJ.

2) For a projection of pure adiabatic results with Phi a temperature dependent Phi has to be introduced.

Both situations for the RADEX vessels are taken into account in the ThermoGraph (not in TSC 5000). For other vessels an experienced user can carry out the necessary determinations himself and enter them in the ThermoGraph programme.

8.4.3 Quantitative Scanning evaluation with RADEX V5 steel vessel and DTBP

In the previously calibrated RADEX V5 measurement system with controller equipment TSC 5000 with 200 bar steel vessel and closed with an airtight seal but without pressurement, a scanning experiment was carried out with Di-tert-butylperoxide (pure). The following diagram **DTBP_SCN** shows a pure experiment.

Just below 300°C the bursting foil is broken as a result of excessive pressure. This can be seen at the drop in temperature which the system has produced. A slight drift of the baseline can be seen after the successful reaction, despite a previous calibration.

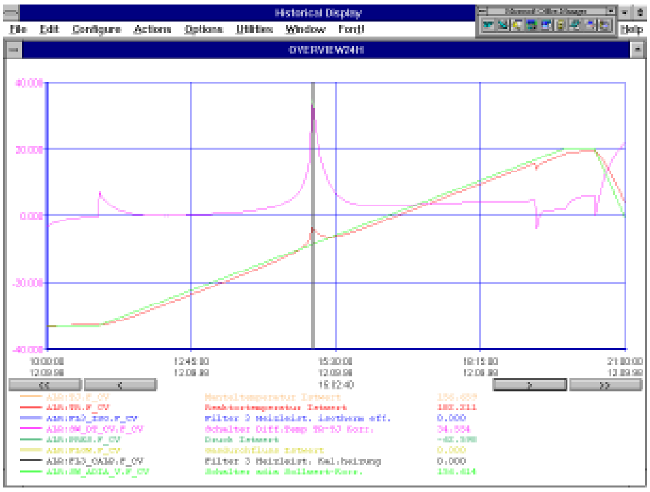
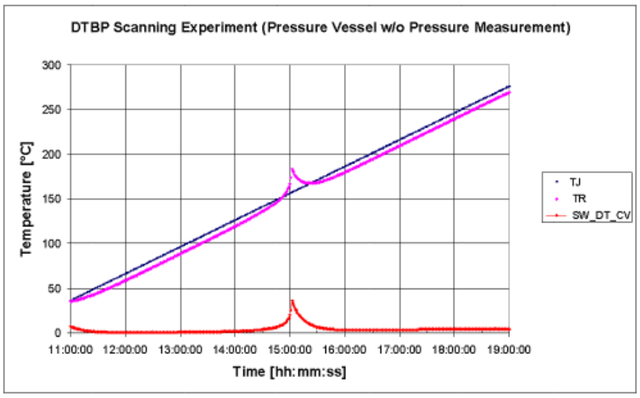


Diagram DTBP_SCN: Scanning Experiment with DTBP

After successful base line correction the following rough values can be seen:



Figuer DTBPeScn: run and corrected temp.-diff. curve (red)

With the help of the included heat flow calibration function of the pressure vessel, the power produced was subsequently calculated and through integration the total decomposition energy as well. The **DTBPeP_Q** graphic display shows the following experimental run with regard to TJ (see next page):

Result and comparisons:

RADEX V5	1240 J/g (DTBP pure)	SYSTAG
RADEX Solo	1201 J/g (20% DTBP in toluene)	[2]
DSC	1233 J/g (DTBP pure)	[3]
ARC	1191 J/g (20% DTBP in toluene)	[3]
ARC	1285 l/g (14.6% DTBP in mineral oil)	[4]
C80	1374 J/g (DTBP pure)	[5]

SYSTAG
automatically better

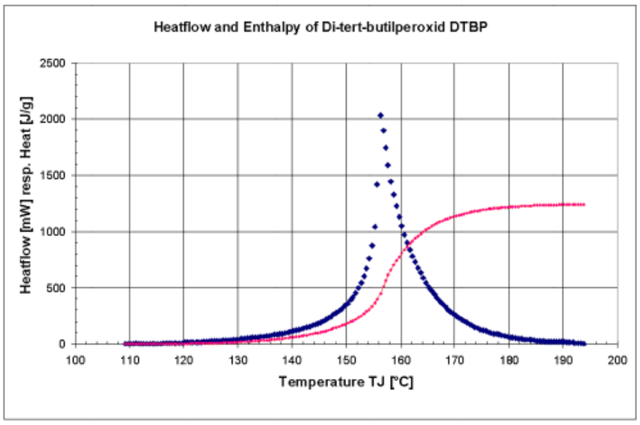


Diagram DTBPeP_Q: heat flow (blue) and energy (red)

The result therefore lies well within the spread area (arithmetic average value is 1254 J/g). At the same time this comparison shows that deviations of +/- 5 to 8 % are absolutely normal. In addition in the next chapter we will show the possible determinations in an adiabatic experiment. The result will be briefly anticipated here: the arithmetic spread range of the adiabatic experiment lies within the range 1225 to 1289 J/g (average value 1257 J/g.

These experiments are carried out with a 200 bar steel vessel, which has a high Phi factor but nevertheless – exactly because of that (!) – delivers accurate results! This discussion takes place in the next chapter.

8.5 Larger Phi Factor: Curse or blessing?

8.5.1 Definition of Phi Factor

Phi = (ms * cs + mv * cv) / (ms * cs),

whereby ms is the substance mass , mv is the mass of the vessel, cs the specific heat of the substance and cv the specific heat for the vessel.

In many discussions a larger Phi factor is always evaluated as negative. Especially during the experimental (not arithmetical) adiabatic increase this obviously plays an important part and reduces the measured increase remarkably. This was the basis which led to the development of equipment such as VSP, Phi-Tec or others. In retrospect this trend was not followed by all companies and many still make projections with a Phi which is too high.

SYSTAG has also selected this route, although in addition the SIKADIFF option is available. Making projections has the remarkable advantage that the weight of the main mass, the vessel, is very well known (can be determined by anyone by using the scales). The cv is also known, even across the entire temperature range. These values can in practice never be obtained from test substances.

If you are working with a Phi from 5...10 however, the following statement can be made: changes to the cs of 50% for example drop only approx. 5% in weight with a Phi factor of 10, i.e. 95% is defined exactly by the vessel. Consequently test calculations, even when the material data are not known exactly (cs), are only marginally distorted. For the measurement of the heat power and the projected determination of the enthalpy (integral of heat power over time) a vessel with a thick wall is much better suited. The heat generated inside, especially with a vessel which is only partly filled, is better distributed across the whole surface due to the higher strength of the wall and its considerably better heat conductivity. Consequently the measurement of the heat flow is remarkably accurate because of previous (works) calibration and delivers amazingly good results. With integration the varying cv and cs must of course again be taken into account. Because cs is hardly ever known but cv can be determined exactly, we have again the same effect as before: ignorance of the substance gives a remarkably small uncertainty in the calculation result, compared with equipment with a small Phi. This is carried out in an experimental example and displayed and briefly commented upon in the following curves.

8.5.2 Adiabatic increase

The **ADIRIS2** already shows the measured increase very nicely. By making a conversion with the corrected Phi, the 'real' increase occurred (put in inverted commas, because it is calculated and not really measured). The measurement takes place in a RADEX V5 with a 200 bar vessel, without a pressure measurement. The weighing in was 2g and the cs which was the basis for the calculation was 2.2 (no value was found at the time the evaluation was carried out). Consequently, the adiabatic increase was 586K. When a cs of only 1.4 is used as basis for the calculation however, the adiabatic increase changes to 888K, i.e. really considerably. This is of course because the connection is strictly reciprocal.

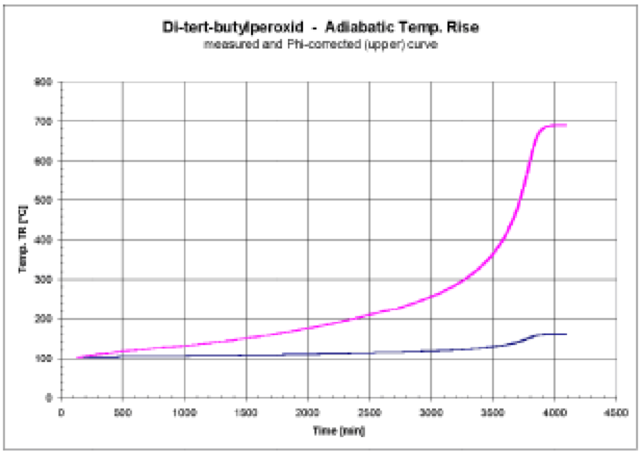


Diagram ADIRIS2: measured (blue) and calculated (red) adiabatic temperature increase

8.5.3 Calculation of enthalpy

The enthalpy calculation result, based on measurement results, looks different from the one with an adiabatic increase. Basically, two routes are practicable, although they are both based on the same principles (this explains the very close results):

a) Calculation from the adiabatic increase (Q = ms * cs * DTadia)

b) Integration of vessel heating (equivalent to heat flow), which is calculated with the help of the calibration of the temperature dependent cv.

Because with method b) the cs is entered into the calculation, a different result can be expected there.

The results in accordance with b):

Total heat with a cs of 2.2 J/g.K resulted in 1275 Joule/g.

Total heat with a cs of 1.4 J/g.K resulted in 1225 Joule/g, i.e. only a little less.

By comparison the results after a) with the adiabatic increase are:

Q = 2.2 J/g.K * 586 = 1289 Joule/g; or with the different increase Q = 1.4 J/g.K * 888 = 1243 Joule/g.

All four results lie very closely together, even though the calculation was at the one time calculated with 1.4 and at the other time with 2.2 J/g.K.

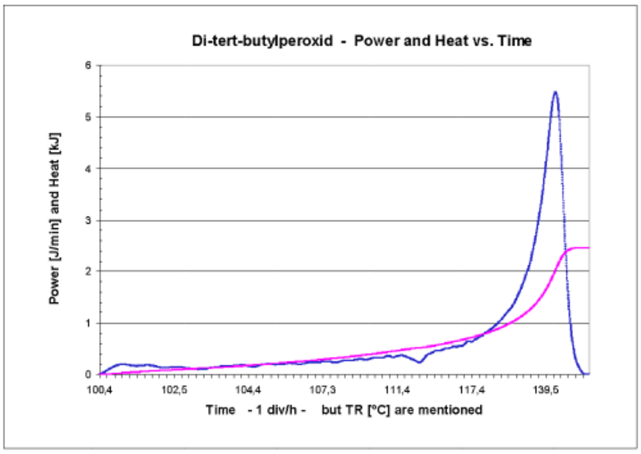


Diagram ENTHALPY: heatflow (blue) and integral (red)

Conclusion: with a larger Phi the enthalpy calculation turns out more favourably.

The maximum adiabatic temperature increase can only be calculated accurately with a known cp value.

With a larger Phi the heat flow measurement also improves.

Here we should also ask ourselves the question: what is the purpose of my examination? Only when this question has been answered can the appropriate procedure and consequently the appropriate equipment be determined.

8.5.4 Measurement and technical aspects of control of adiabatic experiments with a high Phi factor.

The adiabatic control is basically unstable! It would only be stable with infinitely good equipment. Why? The controller target value is the TR temperature for the test. When the sensor misses an excess of 0.1°C it exchanges it with more than is basically available. Consequently, the controller thinks that the surrounding area needs to be brought in line with this 0.1°C higher temperature. As soon as this is the case however, some heat flows from the outside into the test, the TR temperature in the test rises and the process continues. Consequently the temperature rises successively. With a negative error the temperature would drop. How quickly does the temperature rise or fall? Within the vessel system's tau time constant it rises by exactly the value which was measured inaccurately. If the time constant is small, the change is therefore faster than with a large time constant (= larger Phi).

8.5.5 What are the demands for a good adiabatic calorimeter

Based on the previous conclusions a good adiabatic calorimeter must be able to measure very accurately and with a high degree of stability! We are talking here of accuracies and stabilities in the 1/100°C range. Because this absolute measurement is not directly possible, a calibration must take care of the residual error compensation. On the other hand the system's stability must definitely lie in the 1/100°C range. In the TSC 5000 SYSTAG has developed a piece of equipment which indicates a drift of only approximately 1/100°C per year (!). The measurement resolution is 0.006 C. The noise is further reduced accordingly with filters. Consequently the TSC 5000 is the first highly accurate system which can be connected to any oven system and which allows adiabatic experiments.

The second part is the time constant. This has to be as large as possible, so that the drift decreases per time unit. When we have a vessel system with a high mass it obviously helps enormously to obtain a smaller drift. Consequently, the Arrhenius run, especially with rather low reaction temperatures becomes much more stable and much more accurate (this is really the crux of the matter!).

In the course of the reaction rise the TR temperature increases faster. The outside temperature must be able to follow this increase. When we have a high Phi this will use a high proportion of the energy needed to heat up the vessel. The dTR/dt gradient is therefore smaller by 1/Phi. Such gradients are technically easier to contain with the help of electrical control loops than very steep gradients. Consequently the picture across a longer portion of the total reaction time becomes significantly more accurate. For this purpose we must subsequently make a mathematical projection.

Conclusion: *With a higher Phi the adiabatic control becomes more stable.*

With a higher Phi a correct run can be followed for longer.

A very high measurement accuracy and an even higher stability are an indispensible requirement for stable adiabatic controls.

8.6 Influence of vessel cleaning on measurement results

8.6.1 RADEX Scanning pressure experiment with water

When examining several bursting disks and foils for burst pressure we have come accross a new phenomenon, which shows the user how tricky it is to obtain correct experiment results. We have filled a new vessel which has never been used with clean water and carried out a scanning experiment from room temperature to 390°C. The expectation was that a steadily increasing pressure curve be obtained, until the Berst foil breaks.

Diagram RSCPRa17: scanning with water, influence of disturbance

The result however was nothing like that! The **RSPRa17** has as y-axis 0-200 bar and 0-400°C. The pressure curve suddenly shows a sharp increase at around 298°C at a pressure of 73 bar. On the one hand the pressure is lower than with clean water (has to be 298°C at approx. 83 bar) and on the other hand no sudden change should occur in the behaviour up to approx. 370°C.

After having carried out the previous 16 experiments we have come to the conclusion that this change must be the result of contamination of a) previous experiments or b) lubricant residues from the production.

For this reason we have already changed the capillary and pressure transmitters, so that residues from previous experiments can't exert an influence. For this reason also we must determine that residues in the pressure transmitter – in the cold zone (!) – have an influence which should not be underestimated because of the heat pipe effect. Be therefore careful with cleaning!

After carefully cleaning all parts with alcohol after the RSPRa17 experiment, the same experiment is carried out again.

Diagram RSPRb18: scanning with water, pre-cleaned

The result is shown in **RSPRb18** diagram and shows a somewhat higher operating threshold for the bend in the pressure curve. In other words: part has been cleaned, but not everything. In the course of the experiment we have also changed the seals from graphite to copper. We have not established an influence as a result of this.

Conclusion: *New pressure vessels, capillaries and pressure transmitters must also be cleaned intensively, preferably immediately before they are being used!*

8.7 Influence of measurement contamination on the evaluation with the 1st derivative depending on time

8.7.1 Filtering of signals for the 1st dTR/dt derivative

Each derivative is obviously very sensitive to contamination. Consequently signals must be filtered accordingly. This noise can be almost completely eliminated in the ThermoGraph with an adaptive filter algorithm (slow changes are filtered more strongly) so that stable results of the 1st derivative up to <0.001 K/min (system limit) can be achieved. The effect of a normal, i.e. non adaptive filter can be seen in the following two diagrams.

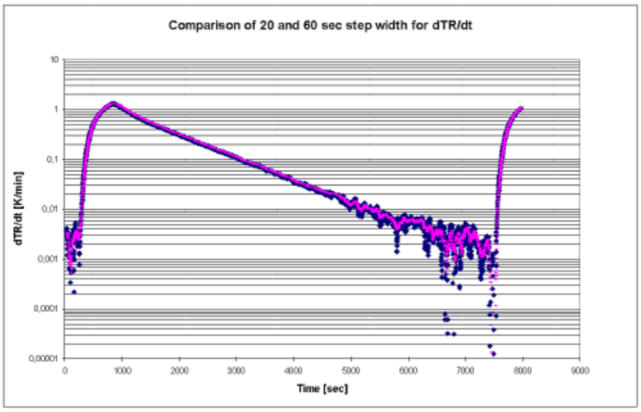


Diagram 7: noise of 1st derivative with short (blue) and long step width (red)

In **diagram 7** the rough values of the 1st derivative with two different step widths is displayed. In **diagram 10** the same one is displayed but filtered suitably constant (not adaptively). The filtering is obviously at the expense of the dynamics, but in most cases this can be justified. With the ThermoGraph the filtering can be determined by the user himself. As a result the best solutions are possible.

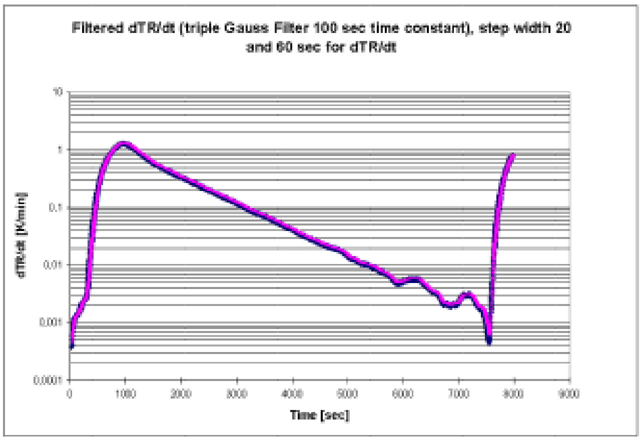


Diagram 10: 1st derivative of filtered signals with two different step widths (short=blue, long=red)

The last diagram also shows very clearly the high stability of the system. It can be stabilized to 0.001 K/min. The last tenth can only be achieved with a stabilized power supply (for the oven heating) or with a real power control (measurement of heating power with a True Watt Meter and control of this power). In addition the room temperature must be stabilized. Less than 0.001 K/min can then be achieved without problems and very cleanly.

As an option the TSC 5000 can be equipped with such a True Watt Meter control.

9 Closing Remarks

All the above explanations must now be weighed up carefully by the user. For this purpose a clear concept must be drawn up of what the company's fundamental objective is with regard to safety examinations.

Equally, it is essential to differentiate between routine and more in depth individual examinations as well as the scientific work.

Because so many influencing factors are pertinent when measuring, it is essential to decide on the basis of the objectives whether, for example, a higher Phi factor makes sense or not. Is it essential to measure adiabatically? Is it essential that the pressure measurement is carried out or is it necessary to obtain exact thermal reference values? These questions must be answered one by one.

The ones which give "either .... or" as objective, operate better with a somewhat more expensive basic variant, because all options are available, even when they do not need to be used at the beginnning.

Further information and curves can be seen in the TSC 5000 manual.

SYSTAG hopes to have helped you a step further with this brochure and will be pleased to actively advise you or even to win you as customers.

Literature index:

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[2] Carried out by ASI/USA
[3] Announced by ASI/USA
[4] ARC, Townsend, D.I. and J.C. Tou, Thermochemica Acta 37, 1-30 (1980)
[5] Entries SETARAM, Lyon, France

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10 About the author

As an academically trained engineer Peter E. Meier has been very familiar with calorimetry since the Sixties and with safety calorimetry since the Seventies. In the broadest sense calorimetry is a classic, inter disciplinary area of work. Physics and chemistry are closely linked to each other here. The author has most of all become an expert in the physical and technical measurement field and has always tried together with clients to integrate both fields as closely as possible. He is also the founder and head of SYSTAG.

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Notes