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1 TC15 TA Controller

Content

Safety Notes

The instruments have been tested for the experiments and determinations documen-ted in the appropriate operating instructions. However, this does not absolve you from the responsibility of performing your own tests of the products supplied by us regard-ing their suitability for the methods and purposes you intend to use them for. You should therefore observe following safety measures.

Measures for your protection

– Ensure that you plug in the power cable supplied into a socket which is grounded! In absence of grounding, a technical default could have lethal consequences.
– Switch the instrument off and disconnect the power cable before you change blown fuses! An electrical shock could be lethal!
– Never open the housing of the TC15. There are no parts to be serviced by the user!

– Never work in a hazardous area! Explosion hazard through hot surfaces!

– Never switch off the TC15, when the cell temperature of the connected module is above approx. 300 °C. The cooling fan would no longer work and the surroundings of the cell could be heated unduly!

Measures for operational safety

– Before first setting up the equipment, check that the TC15 TAController is set to the correct mains voltage, otherwise the instrument could be damaged.
– Always keep all air vents clear for proper cooling!
– Always keep the TC15 away from any source of liquid!
– Avoid :
  - strong vibration
  - direct solar radiation
  - high humidity
  - temperatures under 5 °C and above 35 °C
  - strong electrical or magnetical fields

1 TC15 TA Controller

1.1 Introduction

The modules DSC20, DSC25, DSC27HP, DSC30, TMA40 and TG50 are used in the STARe System by means of the TC15 TA Controller. They are controlled by the Personal Computer in a very similar way to the modules DSC820/DSC821e and TGA850. You will find all necessary information concerning method, experiment, and evalu-ation in the Operating Instructions of the *STARe Software File* .

The TC15 TA Controller is the interface between the Personal Computer of the STARe System and the measuring cells DSC20, DSC25, DSC27HP, DSC30, TMA40 or TG50:

- The TA Controller receives the calibration data of the attached measuring cell from the data base of the Personal Computer.
- A method with its segments is sent from the Personal Computer to the TA Controller.
- The TA Controller keypad is used to start an experiment.
- The TA Controller controls the furnace temperature in the measuring cell.
- The TA Controller acquires and stores the curve data and sends them to the Personal Computer.

The TA Controller can be used to alternately operate the different measuring cells without recalibrating them. The calibration data are stored in the Personal Computer.

1.2 Installing the TC15 Controller

Before first setting up the equipment, check that the TC15 TA Controller is set to the correct mains voltage (yellow label or voltage selector above the mains plug with indication of mains voltage set)!

Location

All parts of the equipment must be set up so that they are not subjected to large fluctuations in temperature. Direct sunlight and draughts should also be avoided. The equipment will operate satisfactorily at humidities up to 85 %.

The TC15 can be connected to any plug (850 VA) provided that care is taken the voltage variations are not more than ± 10 % of the nominal value. To avoid unnecessary heating, the top of the TC15 should be kept free.

Power Supply

The power supply voltage must be set on the TC15 Controller. All other units (with the exception of the nitrogen evaporator of the DSC30) are supplied with power through the TC15.

The mains voltage for the TA Processor is set on the rear panel as follows:

(1) Disconnect power cable.

(2) Remove fuse holder in the center of the voltage selector with a screwdriver. You find the voltage selector above the mains switch.

(3) Rotate the voltage selector by means of a suitable coin until the arrow points to the required voltage.

(4) Check the fuse: 100…120 V / 10 AT, or 220…240 V / 6.3 AT

(5) Replace the fuse holder.

(6) Check whether the other two fuses match the specifications on the fuse labels. You'll find them under the mains switch and on the right of the voltage selector.

Using More than one Module with a TC15

Only one module at a time can be controlled by the TC15. When you intend to change from one to another module, the current module has to be disconnected from the TC15 and the next module connected. At the same time the Personal Computer needs the appropriate module controller. The TC110 Module switch box simplifies the modu-le change substantially.

Installing the TC110 Module Switch Box

The TC110 connected to a TC15 allows a fixed cable connection up to 3 measuring cells.

The power cable of the TC15 is loop wired over the module switch box to ensure that the switching is effected in the off-circuit condition (press the switch in for approx. 2 s).

It is essential to ensure that signal and power cables of a measuring cell are plugged into sockets with the same number.

Example: 1 = DSC25, 2 = DSC27, 3 = TG50. Paste the appropriate labels on respective switch positions.

(1) Install the required modules in the Personal Computer (see section Installation in the Operating Instructions of the *STARe Software File*).

Changing Module without TC110

(1) Switch off power of the TC15. Disconnect the module power cable with its round 7 pin plug from the socket at rear of the TC15. Disconnect the signal cable with its flat 15 pin plug from the socket. Connect the next module accordingly.

(2) **Important**: Make sure that the power and the signal cable of the same module are connected to the same TC15.

(3) Switch on power of TC15 and go to "Preparing the Personal Computer" below.

Changing Module with TC110

(1) Push in the TC110 switch and slowly turn it to the position of the next module. Release the switch and go to "Preparing the Personal Computer" below.

Preparing the Personal Computer

Without multimodule option

Disconnect any old module from COM1: Click the module in `Install/Port` and `Device` and confirm the question box with `Yes`. Click the empty COM1 box and select the new module from the list.

With multimodule option

Here each module can have its own port, e.g. port 1 = DSC25,

port 2 = DSC27, port 3 = TG50.

Thus remove the plug of the RS232 cable from the old multiport socket and insert it into the new socket.

1.3 The Keypad of the TC15

The keypad has four keys necessary to operate:

OK	to confirm, e.g. an error message or the request INSERT SAMPLE when done.
RESET	to abort a running experiment.
ROTATE	to change the display.
GAS	to switch the purge gas of the TG50 when adjusting the flow rates.

1.4 Operating the TC15 TA Controller

1.4.1 Switching On

Before switching on, make sure that a measuring module is properly connected to the TC15: power cable with the round 7 pin socket and signal cable with the flat 15 pin socket of the same module. TMA40 and TG50 have an additional data cable to be plugged in the round 5 pin balance plug.

For the communication with the Personal Computer a RS232 cable with 25 pin male for the TC15 and 25 pin female for the multiport is used. When connected to COM1 (or, if available, COM2) of the Personal Computer, it needs a 9 pin female plug.

When the TC15 is switched on, all segments of the display are illuminated during 1 s for test purposes. Then the display shows the connected cell type and the actual temperature:

DSC °C 25

module temp. unit temperature

Press ROTATE to check the software version that will be displayed on the left, e.g. V 2.00. At the same time you can read the identification number of your TC15, e.g. 0193:

V 200 0193 25

version Ident. no. temperature in °C

Note: When changing the software cartridge the identification number changes. In version 2.00 or higher, the identification number is displayed as a decimal figure.

COMM. TIME OUT

will be displayed alternating with the standby display when there is no communication with the Personal Computer (not connected, Personal Computer not switched on, DSC module not defined under `Install/Module` or not connected under `Install/Port and Device`, or RS232 cable not engaged in the appropriate port).

The Standby State

After switching on the TC15, the attached module is heated to the standby tempera-ture that has been defined under `Install/Module` in the Personal Computer (or the TC15 default standby temperature of 25°C when not connected to the Personal Computer).

After completion of an experiment, the TC15 returns to state defined by the Temperature End Behavior, TEB, of the experiment:

- controlling the insert temperature of the method
- controlling the standby temperature of the module defined under `Install/Module`

Note: "Heater power off" is not supported by the TC15. This state would be interpreted as standby temperature.

When controlling the insert temperature of the last method, the TC15 can be reset to the standby temperature at any time by the key RESET.

1.4.2 Performing an Experiment

- When an experiment has been sent to the TC15, the display INSERT SAMPLE reminds you to place the sample pan: Open the furnace cover of the module and place the sample carefully. Close the cell and start the measurement with OK. If a purge gas is needed, check the flow.
- At the end of the experiment, REMOVE SAMPLE indicates to open the cell and remove the sample. Confirm with OK and the cell goes to standby or to the insert temperature depending on the temperature end behavor, TEB.

1.4.3 Switching Off

Never switch off the TC15, when the cell temperature of the connected module is above approx. 300 °C. The cooling fan would no longer work and the surroundings of the cell could be heated unduly!

(1) Always remove the last sample before switching off. The mains switch is accessible at the rear panel from right. The order of switching off the Personal Computer and the TC15 is of no importance.

1.5 Error messages, warnings

Error	Cause
1	No module connected
2	Balance channel error
3	Experiment timeout, module temperature over 900 °C during one hour
31	RAM Check error
32	ROM Checksum error
41	Module code error

Warning	Cause
6	Balance channel error
20	Configuration parameter error
21...52	Internal software error
55	TAPID mismatch
57	Remote key overflow
58...64	Internal software error
65	Circulation buffer overflow
66...72	Internal software error
73	Warning buffer overflow

Using TC15 Software version 3.10

Please note the following points for using TC15 Software version 3.10:

1. The older STARe Modules (former TA4000 modules) do not have the same signal quality as the new STARe Modules DSC821e and TGA850.
2. Never use a forced start as long as the oven temperature is above the start temperature. A forced start would cause a shift in temperature.
3. Due to the temperature control of the TC11 the reproducability of the temperature during the cooling segments is not very good (errors of up to 5 °C can occur).
4. The settling time of the new software version is considerably longer (2 or 5 minutes or more depending on the difference between the current temperature and the start temperature).
5. ADSC measurements can be performed with the new software version but the quality of the results never reaches that of the DSC821e measurement results (the period should always be longer than 60 seconds).
6. The temperature control of the TC15 is not as fast as with the newer modules. For this reason you should always allow a period of at least 3 minutes to elapse before the first thermal effect.
7. **Calibration**

   When using the TC15 for the first time:

   – Carry out an ADC calibration first. The TC15 performs an internal calibration of the analog/digital converter (ADC calibration).

   The TC15 has no real 20 bit AD converter. Instead, a 14 bit DA and a 14 bit AD converter are used. These converters must be calibrated (ADC calibration).

   – Proceed with a total calibration (or a heat flow and Tau Lag calibration) with In/Zn.

   – Continue with a temperature calibration over the entire temperature range desired (with versions < 4.0, the temperature calibration is also used for the ADC calibration).

   The very last temperature calibration should cover the entire temperature range desired, for example:

   – desired temperature range: ambient temperature to 500 °C
   ⇒ In calibration from ambient temperature to 500 °C with a heating rate of 10 °C/min.

   – Change the start and end temperature of the method Calib DSC Temp...In/Zn to 25 and 500 °C, respectively. Use the same heating rate as in the measurements to be performed.
8. **Requirements for using the TC15 Software version 3.10**

You need at least STARe Software version 3.10 or TSW870 Software version V3.01 to use TC15 Software version 3.10.

9. STARe V3.10 program errors (does not concern TSW870 version 3.01)

For ADC calibration (temperature calibration)

- In the module controller, change the setting to WAIT FOR SAMPLE CHANGE OFF (the standard setting is ON).

  If this is not done the recalculated ADC parameters would not be transferred to the PC. On the next start of the PC the new ADC parameters stored in the TC15 would be overwritten by the old ADC values.

- For this reason press OK after the calibration and then press RESET.

- Only when this is completed, change the setting in the module controller back to WAIT FOR SAMPLE CHANGE ON (i.e. the standard setting).

10. TC11

Unfortunately, these software improvements cannot be used with the TC11!

11. Stray values, erroneous results

If you should receive stray values or erroneous results:

- Check all the procedures that may have been wrong:
  - What was the first measurement?
  - Did you choose the right pan and the right gas?
  - Was the oven lid really closed?
  - Did someone press the START button?
  - Did someone or something cause the module to shake?
- Switch off the TC15 so that it can be correctly started up with the PC again.

Never use a stray value for the calibration. Repeat the measurement!

2 The DSC20 Module in operation with the TC15 TA Controller

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Safety Notes

The instruments have been tested for the experiments and determinations documen-ted in the appropriate operating instructions. However, this does not absolve you from the responsibility of performing your own tests of the products supplied by us regard-ing their suitability for the methods and purposes you intend to use them for. You should therefore observe following safety measures.

Measures for Your Protection

- Ensure that you plug in the power cable supplied into a socket which is grounded! In absence of grounding, a technical default could have lethal consequences.
- Switch the instrument off, let the DSC20 furnace cool down and dis-connect the power cable before you open the housing or change blown fuses! An electrical shock could be lethal!

- Never work in a hazardous area! Explosion hazard through hot surfa-ces!
- Never use combustible gases or explosive gas mixtures to purge the sample chamber! An explosion could occur!

- Make sure that the power and the signal cable of the same module are connected to the same TC15. The measuring cell could melt, if only the power cable is connected!
- Never switch off the TC15 when the cell temperature is above 300 °C. The cooling fan would no longer work and the cell cover could be heated unduly!

- Never touch the furnace, the furnace lid or a sample just removed from the furnace! The temperature of the furnace can reach 600 °C.
- Open the furnace only when the temperature is lower than 100 °C! Always use tweezers to remove the lid or the crucible! Place hot items on the stainless steel area on the measuring module.
- Set up the instrument in a fume hood, if a sample may produce toxic gases during reaction.
- Never push objects of any kind through ventilation openings around the furnace!

Measures for operational reliability

- Always keep all air vents clear for proper cooling!
- Always keep the hardware away from any source of liquid!
- When you measure samples with corrosive decomposition products (e.g. HCl split off from PVC), always use a purge gas (50…80 ml). If possible, stop the measurement after the start up of the reaction. With the option *Conditional Experiment Termination* you may create a method with automatic termination!
- Never use corrosive or combustible gases to purge the sample chamber!
- Follow the instructions regarding electrical interferences in section 2.2.

2 The DSC20 Module in operation with the TC15 TA Controller

2.1 Introduction to the DSC20 Module

The DSC20 allows DSC measurements from ambient to 600 °C. When the DSC20 is placed in a deep freezer, measurements from -20 °C are possible. The measurement is based on the Boersma or heat flux principle.

The DSC20 cell is equipped with the glass sensor with a time constant of 7 s. The ceramic sensor can also be used, but a prerequisite is a silver furnace with a flat and clean heater plate.

The experiment parameters are composed in the Personal Computer and sent to the TC15 where the segments of the temperature program are controlled.

The purge gas is adjusted by the needle valve of a flow meter.

During a measurement, the data are transferred to the Personal Computer for the on-line curve in the module control window. At the same time they are available on the fluorescent display of the TC15. Scroll through the lines of the display by ROTATE.

At the TC15 display you also get messages such as INSERT SAMPLE. On the keypad of the TC15 you confirm the message by the OK key or you may abort the running experiment by the RESET key.

2.2 Installing the DSC20

Location

The DSC20 is a sensitive calorimeter. Today there is a certain electromagnetic noise field everywhere. It can disturb the sensitive measuring signal causing artefacts.

Please note the requirements concerning EMC (electro magnetic compatibility):

- There should be no rising mains, motors, or the like in proximity of the DSC20. Mind the neighbouring rooms, too!
- There are the minimum distances between the DSC20 with its TC15 and, e.g.:
  - the Personal Computer or a personal computer with CRT screen: 0.5 m
  - a printer or a plotter with a power transformer: 0.5 m
  - a cryostat: 0.5 m
  - any lamp with fluorescent tube: 0.5 m
  - a refrigerator or a deep freezer [1]) : 2.0 m
- All other electric equipment are noise sources and should therefore be kept away from the DSC20.
- During measurements do not use a wireless phone or walkie-talkie.

Also protect the DSC20 from even small mechanical shocks: the same measures may be taken as for micro balances or for a TMA. An individual sturdy table carrying the DSC20 may be sufficient.

The DSC20 operates trouble-free at room temperatures of +10 [1]) ... +32 °C and at relative humidity of 20 … 80%.

[1]) Accept reduced specifications when running the DSC20 in a deep freezer.

Measurement Below Room Temperature

The entire module can be placed in a commercial top loading freezer. It will reach –20 °C after about 1 h. The module should be placed in the freezer with operating fan at a minimum distance from the back wall of 10 cm. For prolonged measurements at higher temperatures, it should be checked that the freezer is not unduly heated.

Connecting the DSC20 to the TC15

Connect the power cable with its round 7 pin plug to the appropriate socket at rear of the TC15. Connect the signal cable with its flat 15 pin plug to the flat socket.

Make sure that the power and the signal cable of the same module are connected to the same TC15, if you have several modules or several TC15s.

Note: When using the TC110 Module Switch box, check that the signal and the power cables of the DSC20 are plugged into sockets with the same number.

Connect your purge gas to the purge gas inlet at rear of the DSC20. The gas connector opens when the appropriate nipple is engaged. Adjust the flow rate to approx. 50 ml/min.

Check the color of the code plug through the small round window at the bottom of the DSC20:

Green when using the yellowish glass sensor

Blue when using the blue ceramic sensor.

The amplification is defined by the orientation of the code plug. Through the small round window the following word is visible:

Medium normal amplifier setting for DSC signals of ± 60 mW

High high amplification (3.5 times higher than medium) for small signals (± 20 mW) and reduced signal noise.

Preparing the Personal Computer for the DSC20

Follow instructions given in the Operation Instructions of the STARe Software File for the install procedure. Ensure proper selection of the actual amplification (High or Medium) under `Install/Topic/Sensor and Gain`.

Preparing the DSC20 for Experiments

Prior to the first measurement, a temperature calibration has to be performed once. This is not needed if another module connected to the same TC15 was calibrated in the temperature range of interest.

To avoid artefacts on DSC curves, check the following points:

(1) Check the DSC sensor position. Is it in the center of the furnace? If not, move it towards the center by tweezers (or with the centring gauge of the DSC820) and heat the furnace 20 minutes at 600 °C without crucibles. Create a method from 25 to 600 °C with 50 °C/min and 20 min isotherm at 600 °C, use pan type `No Pan` .

(2) Check initial deflection and blank curve :

- A clean DSC measuring cell with a correctly inserted glass DSC sensor should give an initial deflection of not more than 1 mW with 2 empty standard aluminum pans (difference between starting point and stabilized signal at 10 K/min). A larger deflection can often be corrected by slight horizontal movement or rotation of the DSC sensor.
- The blank curve of the DSC cell with the glass sensor (DSC curve with 2 empty pans) should be constant within a range of 1 mW for a heating rate of 10 K/min up to 500 °C. It must be free from peaks and discontinuities greater than 0.1 mW. Otherwise, the DSC cell should be cleaned by heating for 30 minutes at 500 °C, if possible with oxygen or air (50 ml/min) as purge gas. Subsequently a new blank curve is measured. If necessary, the measuring cell should be cleaned as described under maintenance.
- With the ceramic sensor the tolerances are wider: Initial deflection ± 2 mW, drift 50...500 °C within a range of 2 mW.

(3) Run the `Check DSC ^exo In` when using the sign rule exothermal to the top or `Check DSC ^endo In` with endothermal to the top. You'll find details in the Operation Instructions of the STARe Software File.

2.3 Operating the DSC20

Switching On

There are no switches at the DSC20, please refer to chapter 1.4 (TC15 TA Controller).

Performing an Experiment

(1) Consult section 6 regarding sample preparation, choice of crucibles and furnace atmosphere (purge gas).

(2) If a purge gas is needed, ensure the appropriate gas is connected to the cell and check the flow. The usual flow rate is 50 ml/min.

(3) When an experiment has been sent to the TC15, the display INSERT SAMPLE reminds you to place the sample pan:

- Open the furnace cover.
- With tweezers remove the silver lid and place it on the stainless steel area behind the furnace.
- Place the pan carefully on the left pan position of the DSC sensor and ensure there is a (empty) reference pan on the right. When using pans without centering pin, check the position visually.
- Carefully place the silver lid on the furnace.
- Put the cover back. Ensure proper engaging.
- Start the measurement with OK.

(4) At the end of the experiment, REMOVE SAMPLE indicates to open the cell and remove the sample. Confirm with OK, and the cell goes to the insert temperature.

Note: In order to save cooling time, a water cooled cooling device (see section 2.5) is inserted into the DSC cell.

Switching Off

Never switch off the TC15 when the cell temperature is above 300 °C. The cooling fan would no longer work and the cell cover could be heated unduly.

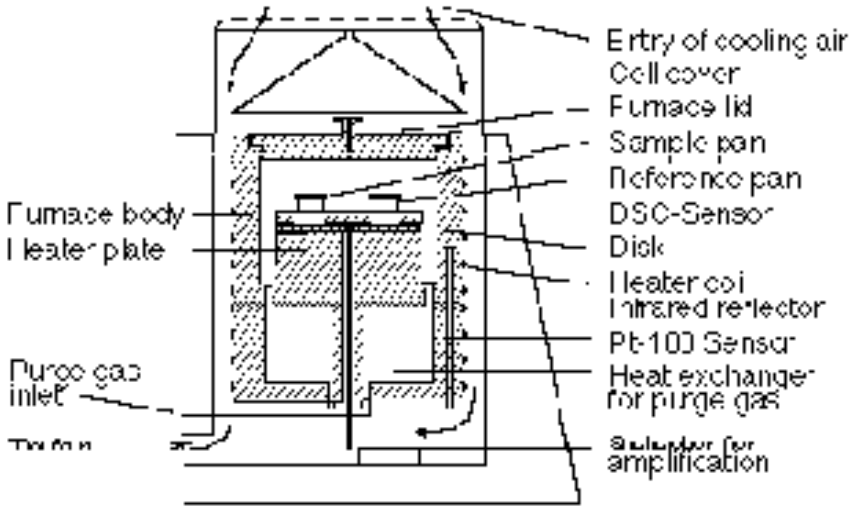
- Always remove the last sample pan before switching off. The order of switching off the Personal Computer and the TC15 is of no importance.

2.4 Description of the DSC20

The DSC furnace made of pure silver is heated by means of a coaxial heater coil. A temperature sensor, Pt100, generates the temperature signal. The DSC sensor with the 5 fold Au/Ni thermopile on a glass substrate is placed on a sapphire disk that is in direct thermal contact with the heater plate of the silver furnace.

Note: The optional ceramic sensor (14 Au/Au-Pd thermopile on a ceramic substrate) needs a ceramic disc instead of the sapphire disk. The ceramic sensor has a long life time even when exposed to corrosive decomposition products that would attack the glass censor.

The purge gas inlet guides the gas - usually 50 ml/min - to the bottom of the furnace body. Here it is heated to the cell temperature and enters into the sample chamber. It finally escapes through the center hole of the lid. Cooling is provided by cooling air flowing through the gap between the silver furnace and the infrared reflector to a fan.



Schematic cross section through the DSC20 cell. The DSC Sensor heats sample and reference pan. The obtained DSC signal is amplified and converted to digital in the TC15. A code plug appropriate to the installed DSC sensor is used to select the amplification (medium or high). The code plug with the actual setting is visible through a small window in the base plate of the DSC module.

3 The DSC25 Module in operation with the TC15 TA Controller

Content

Safety Notes

The instruments have been tested for the experiments and determinations documen-ted in the appropriate operating instructions. However, this does not absolve you from the responsibility of performing your own tests of the products supplied by us regard-ing their suitability for the methods and purposes you intend to use them for. You should therefore observe following safety measures.

Measures for Your Protection

- Ensure that you plug in the power cable supplied into a socket which is grounded! In absence of grounding, a technical default could have lethal consequences.
- Let the DSC25 furnace cool down and disconnect the module from the mains before you open the housing. Switch the instrument off and disconnect the power cable before you open the housing or change blown fuses! An electrical shock could be lethal!

- Never work in a hazardous area! Explosion hazard through hot surfaces!
- Never use combustible gases or explosive gas mixtures to purge the sample chamber! An explosion could occur!

- Make sure that the power and the signal cable of the same module are connected to the same TC15. The measuring cell could melt, if only the power cable is connected!
- Never switch off the TC15 when the cell temperature is above 300 °C. The cooling fan would no longer work and the cell cover could be heated unduly!

- Never touch the furnace, the furnace lid or a sample just removed from the furnace! The temperature of the furnace can reach 750 °C.
- Open the furnace only when the temperature is lower than 100 °C! Always use tweezers to remove the lid or the crucible! Place hot items on the stainless steel area on the measuring module.

- Set up the instrument in a fume hood, if a sample may produce toxic gases during reaction.
- Never push objects of any kind through ventilation openings around the furnace!

Measures for operational reliability

- Always keep all air vents clear for proper cooling!
- Always keep the hardware away from any source of liquid!
- When you measure samples with corrosive decomposition products (e.g. HCl split off from PVC), always use a purge gas (50…80 ml). If possible, stop the measurement after the start up of the reaction. With the option *Conditional Experiment Termination* you may create a method with automatic termination!
- Never use corrosive or combustible gases to purge the sample chamber!
- Follow the instructions regarding electrical interferences in section 3.2.

3 The DSC25 Module in operation with the TC15 TA Controller

3.1 Introduction to the DSC25 Module

The DSC25 allows DSC measurements from ambient to 750 °C. When the DSC25 is placed in a deep freezer, measurements from -20 °C are possible. The measurement is based on the Boersma or heat flux principle.

The DSC25 cell is equipped with the corrosion prove ceramic sensor of the short time constant of 3 s.

The experiment parameters are composed in the Personal Computer and sent to the TC15 where the segments of the temperature program are controlled.

The purge gas is adjusted by the needle valve of a flow meter.

During a measurement, the data are transferred to the Personal Computer for the online curve in the module control window. At the same time they are available on the fluorescent display of the TC15. Scroll through the lines of the display by ROTATE.

At the TC15 display you also get messages such as INSERT SAMPLE. On the keypad of the TC15 you confirm the message by the OK key or you may abort the running experiment by the RESET key.

3.2 Installing the DSC25

Location

The DSC25 is a sensitive calorimeter. Today there is a certain electromagnetic noise field everywhere. It can disturb the sensitive measuring signal causing artefacts.

Please note the requirements concerning EMC (electro magnetic compatibility):

- There should be no rising mains, motors, or the like in proximity of the DSC25. Mind the neighbouring rooms, too!
- There are the minimum distances between the DSC25 with its TC15 and, e.g.:
  - the Personal Computer or a personal computer with CRT screen: 0.5 m
  - a printer or a plotter with a power transformer: 0.5 m
  - a cryostat: 0.5 m
  - any lamp with fluorescent tube: 0.5 m
  - a refrigerator or a deep freezer [1]) : 2.0 m
- All other electric equipment are noise sources and should therefore be kept away from the DSC25.
- During measurements do not use a wireless phone or walkie-talkie.

Also protect the DSC25 from even small mechanical shocks: the same measures may be taken as for micro balances or for a TMA. An individual sturdy table carrying the DSC25 may be sufficient.

The DSC25 operates trouble-free at room temperatures of +10 [1]) ... +32 °C and at relative humidity of 20 … 80%.

Measurement Below Room Temperature

The entire module can be placed in a commercial top loading freezer. It will reach –20 °C after about 2 h. The module should be placed in the freezer with operating fan at a minimum distance from the back wall of 10 cm. For prolonged measurements at higher temperatures, it should be checked that the freezer is not unduly heated.

[1]) Accept reduced specifications when running the DSC25 in a deep freezer.

Connecting the DSC25 to the TC15

Connect the power cable with its round 7 pin plug to the appropriate socket at rear of the TC15. Connect the signal cable with its flat 15 pin plug to the flat socket.

Make sure that the power and the signal cable of the same module are connected to the same TC15. The measuring cell could melt, if only the power cable is connected!

Note: When using the TC110 Module Switch box, check that the signal and the power cables of the DSC25 are plugged into sockets with the same number.

Connect your purge gas to the purge gas inlet at rear of the DSC25. The gas connector opens when the appropriate nipple is engaged. Adjust the flow rate to approx. 50 ml/min.

Check the color of the code plug through the small round window at the bottom of the DSC25: Blue is correct for the blue ceramic sensor.

The amplification is defined by the orientation of the code plug. Through the small round window the following word is visible:

Medium normal amplifier setting for DSC signals of ± 60 mW

High high amplification (3.5 times higher than medium) for small signals (± 20 mW) and reduced signal noise.

Preparing the Personal Computer for the DSC25

Follow the instructions in the Operating Instructions of the *STARe Software File* for the install procedure. Ensure proper selection of the actual amplification (High or Medium) under `Install/Topic/Sensor and Gain`.

Preparing the DSC25 for Experiments

Prior to the first measurement, a temperature calibration has to be performed once. This is not needed if another module connected to the same TC15 was calibrated in the temperature range of interest.

To avoid artefacts on DSC curves, check the following points:

(1) Check the cover assembly:

- Remove the silver lid that is visible when the cover assembly has been opened. Make sure that the lid is cold. Move it upwards to get it out.
- Place a thin paper sheet over the furnace opening and firmly close the cover assembly. Open the cover and investigate the paper:
- The cover assembly is OK when there a ring shaped indentation of 49 mm diameter caused by the tube of the cover that engages to the infrared reflector of the furnace.
- The cover assembly needs to be centred when the paper remained flat:
- Remove cover plate at rear of the cover assembly.
- Loosen the two 7 mm screws that are now visible.
- Move the cover assembly until the tube of the cover engages to the infrared reflector of the furnace.
- Fix the two 7 mm screws.
- Do the paper check again. When OK fix the cover plate.
- Carefully place the lid back into the lid holder and check its free movement. If need be move the spring upwards before engaging the lid.

(2) Check the DSC sensor position. Is it in the center of the furnace? If not, move it towards the center by tweezers (or with the centring gauge of the DSC820) and heat the furnace 20 minutes at 700 °C without crucibles. Create a method from 25 to 700 °C with 50 °C/min and 20 min isotherm at 700 °C, use pan type `No Pan` .

(3) Check initial deflection and blank curve after installation:

- A clean DSC measuring cell with a correctly inserted ceramic DSC sensor should give an initial deflection of not more than 2 mW with 2 empty standard aluminum pans (difference between starting point and stabilized signal at 10 K/min). A larger deflection can often be corrected by slight horizontal movement or rotation of the DSC sensor.
- The blank curve of the DSC cell (DSC curve with 2 empty pans) should be constant within a range of 2 mW for a heating rate of 10 K/min up to 500 °C. It must be free from peaks and discontinuities greater than 0.1 mW. Otherwise, the DSC cell should be cleaned by heating for 30 minutes at 600 °C, if possible with oxygen or air (50 ml/min) as purge gas. Subsequently a new blank curve is measured. If necessary, the measuring cell should be cleaned as described under maintenance.

(4) Run the `Check DSC ^exo In` when using the sign rule exothermal to the top or `Check DSC ^endo In` with endothermal to the top. You'll find details in the Operating Instructions STARe Software File.

3.3 Operating the DSC25

Switching On

There are no switches at the DSC25, please refer to chapter 1.4 (TC15 TA Controller).

Performing an Experiment

(1) Consult section 6 regarding sample preparation, choice of crucibles and furnace atmosphere (purge gas).

(2) If a purge gas is needed, ensure the appropriate gas is connected to the cell and check the flow. The usual flow rate is 50 ml/min.

(3) When an experiment has been sent to the TC15, the display INSERT SAMPLE reminds you to place the sample pan:

- Open the cover assembly.
- Place the pan carefully on the left pan position of the DSC sensor and ensure there is a (empty) reference pan on the right. When using pans without centering pin, check position visually.
- Carefully close the cover assembly. Ensure proper engaging.
- Start the measurement with OK.

(4) At the end of the experiment, REMOVE SAMPLE indicates to open the cell and remove the sample. Confirm with OK, and the cell goes to the insert temperature.

Note: In order to save cooling time, a water cooled cooling device (see section 3.5) is inserted into the DSC cell.

Switching Off

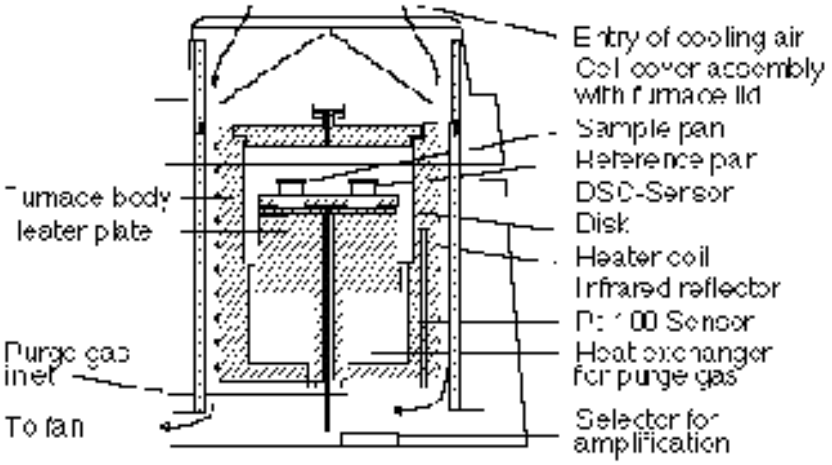
Never switch off the TC15 when the cell temperature is above 300 °C. The cooling fan would no longer work and the cell cover could be heated unduly.

- Always remove the last sample pan before switching off. The order of switching off the Personal Computer and the TC15 is of no importance.

3.4 Description of the DSC25

The DSC furnace made of pure silver is heated by means of a coaxial heater coil. A temperature sensor, Pt100, generates the temperature signal. The DSC sensor with the 14 fold Au/Au-Pd thermopile on a ceramic substrate is placed on a ceramic disk that is in direct thermal contact with the heater plate of the silver furnace.

The purge gas inlet guides the gas - usually 50 ml/min - to the bottom of the furnace body. Here it is heated to the cell temperature and enters into the sample chamber. It finally escapes through the center hole of the lid. Cooling is provided by cooling air flowing through the gap between the silver furnace and the infrared reflector to a fan.



Schematic cross section through the DSC25 cell. The DSC Sensor heats sample and reference pan. The obtained DSC signal is amplified and converted to digital in the TC15. A code plug appropriate to the installed DSC sensor is used to select the amplification (medium or high). The code plug with the actual setting is visible through a small window in the base plate of the DSC module.

3.5 Accessories

4 The DSC27HP High Pressure Measuring Cell in operation with the TC15 TA Controller

Content

Safety Notes

The instruments have been tested for the experiments and determinations documen-ted in the appropriate operating instructions. However, this does not absolve you from the responsibility of performing your own tests of the products supplied by us regard-ing their suitability for the methods and purposes you intend to use them for. You should therefore observe following safety measures.

Remark: The DSC27HP has been tested by EMPA (Swiss Federal Institute for Materials Testing and Research). The test showed that your safety is assured in operations with the pressure cell if you comply with the pressure limits and use nonhazardous gases.

Measures for Your Protection

– Use the pressure measuring cell only for experiments for which it has been manufactured in regard to maximum working pressure, corrosion resistance and max. temperature (see section 4.7: *Specification*:).

– The maximum working pressure must not be higher than 7 MPa!
The built-in safety rupture disc responds at a pressure of 9.6 to 11 MPa.

– Never use corrosive gases for the pressure buildup or purging!
With time, corrosive gases attack the materials of the parts under pressure: material weakness can lead to an explosion or to leaks in the pressure measuring cell.

• Never use gases that produce an explosive mixture (e.g. air with hydrogen)!
With such types of reaction, an additional pressure builds up so rapidly that even a ruptured rupture disc can not allow gas discharge: The measuring cell explodes!

– Make sure that the power and the signal cable of the same module are connected to the same TC15. The measuring cell could melt, if only the power cable is connected!

– In the use of toxic and flammable gases, place the pressure measuring cell in a fume hood! Burners or open flames must never be in the vicinity! Before applying a flammable gas, fill the pressure system twice with nitrogen to get rid of the oxygen.

– When using reactive gases, connect gas outlet and safety rupture disc to lines that lead off the gas for proper disposal!

– Always ensure cooling water flow (20…30 °C)!
  Pressure cylinder and cover would otherwise become so hot that you could burn yourself!
– The cooling assembly must not be wet. If you position it on the hot furnace, any water vaporizes in an explosive manner. You could burn yourself.

Measures for operational reliability

– Use only gas sources with a pressure regulator and a check valve!
  Never set the pressure at the regulator higher than 7 MPa (maximum operating pressure)! The gas source may become contaminated in the absence of a check valve.
– Never remove the pressure cylinder for measurements at ambient pressure!
– Always set the pressure buildup via GAS IN with the INLET valve!

Explosion limits and properties of lab gases

The following Table provides a rapid overview for several gases,

– that you must never use: **corrosive** gases, **explosible mixtures**.
– that you can use if you take the required safety precautions: **flammable** and **toxic** gases.
– that you can use under the maximum working pressure without restriction.

* **Explosion limits** = lower and upper limit concentration of a flammable gas in a mixture with air or another gas containing oxygen between which the gas-air mixture can explode through heating or sparks. These limits depend on temperature and pressure and are given here for initial conditions of 0.1 MPa and 20 °C. (Source: MERCK catalog 1990/91)

Gas	Explosion limits* in vol%	Corrosive	Flammable	Toxic
Ammonia	15 - 28	**x**	**x**	**x**
Argon	–	–	–	–
Carbon dioxide	–	–	–	–
Ethylene	2.7 - 34	–	**x**	–
Helium	–	–	**–**	–
Hydrogen	4.0 - 75.6	–	**x**	–
Nitrogen	–	–	**–**	–
Oxygen	–	–	**–**	–
Propene	2 - 11.7	–	**x**	–

4 The DSC27HP High Pressure Measuring Cell in operation with the TC15 TA Controller

4.1 Introduction to the DSC27HP

The DSC27HP* is a pressure cell that allows measurements up to a maximum wor-king pressure of 7 MPa (70 bar) from room temperature up to 600 °C.

The DSC27HP comprises a stainless steel pressure cylinder containing the furnace and the DSC measuring sensor and fittings for the gas inflow and outflow. A pressure gage shows the pressure and a built-in safety rupture disc protects the cell against excessive pressure.

The pressure cell with the TC15 TA Controller is part of the STARe Thermal Analysis System.

* High Pressure Differential Scanning Calorimeter

4.2 Installing the DSC27HP

4.2.1 Location

You should position the TC15 and the pressure measuring cell on a firm support near to water and gas connections.

The DSC27HP is a sensitive calorimeter. Today there is a certain electromagnetic noise field everywhere. It can disturb the sensitive measuring signal causing artefacts.

Please note the requirements concerning EMC (electro magnetic compatibility):

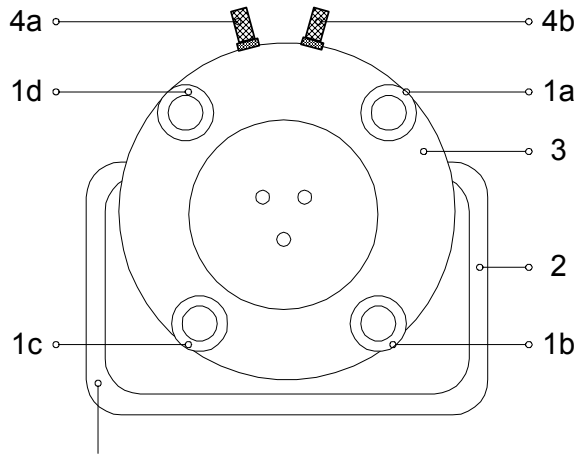
- There should be no rising mains, motors, or the like in proximity of the DSC27HP. Mind the neighbouring rooms, too!
- There are the minimum distances between the DSC27HP with its TC15 and, e.g.:
  - the Personal Computer or a personal computer with CRT screen: 0.5 m
  - a printer or a plotter with a power transformer: 0.5 m
  - a cryostat: 0.5 m
  - any lamp with fluorescent tube: 0.5 m
  - a refrigerator or a deep freezer : 2.0 m
- All other electric equipment are noise sources and should therefore be kept away from the DSC27HP.
- During measurements do not use a wireless phone or walkie-talkie.

Also protect the DSC27HP from even small mechanical shocks: the same measures may be taken as for micro balances or for a TMA. An individual sturdy table carrying the DSC27HP may be sufficient.

The DSC27HP operates trouble-free at room temperatures of +10 ... +32 °C and at relative humidity of 20 … 80%.

4.2.2 Setting up

On delivery, the instrument is screwed together, the furnace lids, the protective cover of the measuring cell and the ceramic mat for the pressure cylinder cover are individually packed (high furnace lid for normal crucibles, flat furnace lid for tall crucibles).



(1) Loosen the 4 nuts (1a - 1d) by hand and remove.

(2) Lift up bracket (2) and remove pressure cylinder cover (3).

(3) Place the ceramic mat packed in a plastic bag in the pressure cylinder cover and press down.

(4) Remove yellow plastic sleeve and foam filling from the furnace.

(5) Attach the connections for water inlet and outlet (4a, 4b) to the water line and a drain using tubing.

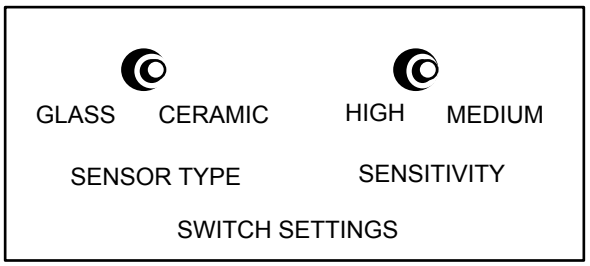
(6) Connect the DSC27HP to the TC15.

(7) Switch on the TC15.

Sensors

There are two types of sensor available for the pressure measuring cell:

- Ceramic sensors with a 14-fold Au-AuPd thermopile built in as standard with moderate amplification (sensitivity).
- Glass sensors with a 5-fold Au-Ni thermopile.



The built-in DSC sensor model and the desired amplification (sensitivity) are communicated to the TC15 by the switch setting at the rear of the pressure measuring cell.

Attaching gas source(s)

Always use a gas source (cylinder or line) that has a relief and a check valve! Set the pressure at the reducing valve to the desired measuring cell pressure.

The tubes that link the gas source(s) and the pressure cell must match the reduced pressure requirements of the gas source(s).

The gas connections are designed for tubes with an external diameter of 1/8 inch:

- Connection GAS IN for the pressure buildup.
- Connection AUX IN for the purge gas.

(1) Push the pipeline into the gas connection up to the stop and tighten the nut by hand.

(2) Then tighten the nut with an engineer's wrench by 11/4 turns.

(3) Attach the tube to the gas source and perform the leak test (see section 4.3.1).

Note: a) You can always remove and reattach the tubes.

b) If you do not have any suitable tubes, you can order the appropriate adapters from the local HOKE distributor.

4.2.3 Connecting the DSC27HP to the TC15

Connect the power cable with its round 7 pin plug to the appropriate socket at rear of the TC15. Connect the signal cable with its flat 15 pin plug to the flat socket.

Make sure that the power and the signal cable of the DSC27HP are connected to the same TC15. The measuring cell could melt, if only the power cable is connected.

Note: When using the TC110 Module Switch box check that the signal and the power cables of the DSC27HP are plugged into sockets with the same number.

Ensure the SENSOR TYPE switch is correct for the ceramic sensor (the switch is at rear of the DSC27HP base plate) .

The amplification is defined by the switch SENSITIVITY:

Medium normal amplifier setting for DSC signals of ± 60 mW

High high amplification (3.5 times higher than medium) for small signals (± 20 mW) and reduced signal noise.

4.3 Operating the DSC27HP

4.3.1 Leak test

Before you perform the first measurement under pressure, you should test the cell for leaks with an inert gas, e.g. nitrogen.

Always use a gas source (cylinder or line) that has a check valve and a reducing valve! Set the pressure at the reducing valve to the desired measuring cell pressure.

(1) Close the valves OUTLET, INLET and AUX.

(2) Attach the gas source to inlet GAS IN (see section 4.2.2).

(3) Set the pressure of the gas source with the reducing valve to 7 MPa and open gas source.

(4) Open INLET valve: The pressure should increase at a maximum rate of 0.1 MPa/s.

(5) Build up a pressure of 7 MPa.

(6) Close INLET valve and observe pressure gage.

The pressure drop in the cell should be less than 0.2 MPa/30 min. If this is not the case, several malfunctions can be the cause (see section 4.6: *Malfunctions*).

(7) After the test, open the OUTLET valve: the gas flows out of the GAS OUT outlet.

4.3.2 The safety rupture disc

The built-in safety rupture disc is intended to prevent an excessive pressure load on the pressure cell. It ruptures when its response pressure is exceeded.

The nominal bursting pressure of the rupture disc is between 9.6 and 11 MPa. The attainable pressure in dynamic measurements should therefore not be higher than 7 MPa (see section 4.3.4: *Pressure: not controlled*).

As soon as a leak has been found at the outlet of the rupture disc, you must change the rupture disc! (see section 4.5.1).

Install only a rupture disc supplied by METTLER TOLEDO that responds at the required response pressure! (see section 4.8: *Optional accessories)*.

A wrong rupture disc may not respond until the pressure is too high, in other words the pressure cell could explode!

4.3.3 Preparing an Experiment

(1) Attach the gas source for the pressure buildup to the inlet GAS IN.

(2) If necessary, connect a gas supply for purging the measuring cell to inlet AUX IN (see section 4.3.5).

(3) As appropriate, attach the tubing connection at outlet GAS OUT and connect tubing to lead off the outflowing gas (see section 4.8.: *Accessories*).

(4) Attach the tubing connection to the safety rupture disc and connect to pressure tubing
(Ø 14 mm) (fasten with clamp!) so that if the rupture disc bursts the escaping gas at that point will be led off.

Crucibles - without lid or with perforated lid

Depending on the application, you can work with a crucible without a lid, e.g. in the measurement of oils to determine their oxidative stability.

For enthalpy determinations, you should perforate the crucible lid once with the needle in the crucible set.

For determinations of boiling temperatures, perforate the crucible lid, e.g. on a hard support with a compass point (hole diameter: approx. 50 µm).

Note: Don't use a hermetically sealed crucible: it would collapse (pressure > 1 MPa)!

4.3.4 Performing an Experiment

When you have inserted the sample and reference crucibles in the measuring cell,

(1) Put on the furnace lid (if possible, always the high lid) and the protective cover.

(2) Mount the pressure cylinder cover and tighten the four nuts by hand. This suffices to seal the system.

(3) Set the flow rate of the cooling water to approx. 30 l/h.

(4) Close the OUTLET, INLET and AUX IN valves.

(5) Open the gas inlet for the pressure buildup.

(6) Open the INLET valve.

Note: The closed cell needs a relatively long time to cool down to room temperature after a measurement. To accelerate the process, you can use the cooling device (see section 4.8.: Accessories).

Note: If you need a pure gas atmosphere, fill (up to approx. 2 MPa) and empty (close INLET valve, open OUTLET valve) the pressure cell three times with gas before you fill the cell with gas for the measurement.

(7) When the pressure is reached, close the INLET valve.

(8) Start the measurement.

(9) When it is finished, open the OUTLET valve slowly to release the pressure.

(10) When the pressure gauge shows no pressure, open the valve fully to be certain that the cell is definitely at atmospheric pressure.

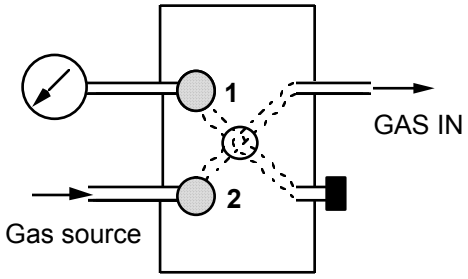
(11) Unscrew the nuts by hand. If this is not possible, use the engineer's wrench.

Do not unscrew the nuts until the measuring cell is at atmospheric pressure! Before removing one nut, unscrew all 4 nuts by one turn!

Note: a) If you need a more accurate pressure reading for your measurements, you can attach an additional pressure gauge to the inlet (or outlet) not in use.

If both inlets and the outlet are in use, you can attach a gas distributor to, e.g. the GAS IN inlet (see section 4.8: *Optional acces-sories*):

(12) After the pressure buildup, close valve 2, open valve 1.



Note: b) The closed cell needs a relatively long time to cool down to room temperature after a measurement. The cooling proceeds faster if the cell is under pressure, it is fastest if you use the cooling assembly (see section 4.8: *Optional accessories*):

(13) Remove the pressure cylinder cover, the protective cover and the furnace lid.

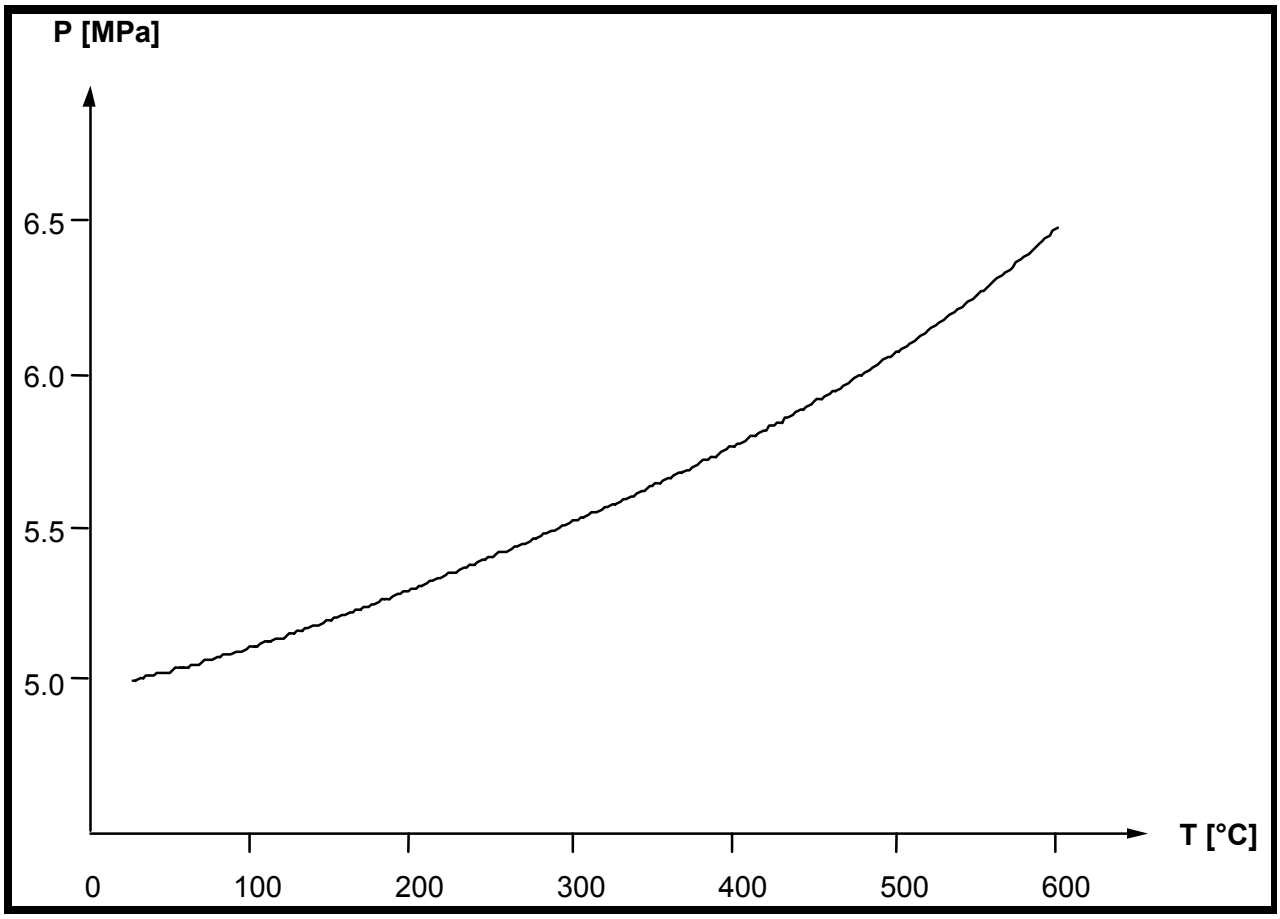
(14) Place the cooling assembly.

The cooling assembly must not be wet. If you position it on the hot furnace, any water vaporizes in an explosive manner. You could be injured.

Pressure: not controlled

When you perform isothermal measurements, you can set the required pressure at the desired temperature. The pressure does not change during the measurement.
In dynamic measurements, the pressure increases with the temperature in a manner which depends on the cooling of the pressure cylinder.

Pressure-temperature curve (heating rate: 10 °C/min, gas: nitrogen, cooling water: T ≈ 20 °C, flow rate ≈ 30 l/h)



If you measure over a small temperature range, the pressure change is correspondingly small. If you require accurate pressure data, we advise manual plotting of a pressure-temperature curve.

Pressure: controlled with a special controller

To control the pressure in dynamic measurements, you can attach a pressure controller to the outlet GAS OUT (see also section 4.3.5: *Overview*).

Note: We work with, e.g. a pressure controller from BROOKS INSTRUMENT (pressure controller: model 5866 as an upstream pressure controller, control and display unit: model 5876) and describe here the procedure for controlled pressure measurements.

(1) Connect the pressure controller input to the GAS OUT outlet.

(2) As appropriate, attach the tubing connection to the pressure controller outlet and connect tubing to lead off the outflowing gas.

(3) Connect the pressure controller to the control and display unit (cable).

(4) Build up the pressure to somewhat above the target value (inlet GAS IN).

(5) Close INLET valve.

(6) Set the target pressure at the control unit and switch on the instrument.

(7) Open OUTLET valve and wait until a constant pressure is shown.

(8) Start the measurement.

If you start your measurements at a relatively high start temperature, in other words the measuring cell is heated up rapidly, we advise waiting for a constant pressure display before starting the experiment (confirm `Insert Sample` after getting a constant pressure).

4.3.5 Purging the measuring cell

The DSC27HP offers the possibility of purging the measuring cell with the same gas that you use for pressure buildup or with another gas. A reactive gas, e.g. oxygen is used for the oxidation of the sample, an inert gas for the purging off gases that are evolved by the sample.

Never use a purge gas that can react with the pressurizing gas (see *Safety Notes*)!

Never build up the pressure of the measuring cell via the inlet AUX IN! This can raise the furnace lid.

The second gas source must also have a check valve to avoid contamination with the pressurizing gas (see *Safety Notes*).

Setting the flow with a flow meter in isothermal measurements

To set the flow rate (approx. 50 ml/min) of the purge gas and to keep the gas pressure constant in isothermal measurements, you can attach a flow meter (see section 4.8.: *Optional accessories*).

We recommend first performing a pseudo experiment at the desired pressure to determine the setting of the OUTLET valve. You thus waist no time during the actual measurement:

(1) Attach the tubing connection (see *Accessories*) at outlet GAS OUT and connect to the flow meter using plastic tubing.

(2) Open the needle valve of the flow meter fully.

(3) Set the pressure for both gas cylinders (pressure buildup/purging) at the reducing valve to the same value.

(4) Connect both gas cylinders (GAS IN for pressure buildup, AUX IN for purging) and open.

(5) Open INLET valve until pressure buildup is complete (if need be, empty and fill with gas to obtain a pure gas atmosphere).

(7) Open the experiment window and select the method you need. Also key in sample name and weight for the coming experiment. Send the experiment to the module and wait until the cell is heated to the insert temperature.

(8) Do **not** confirm INSERT SAMPLE with OK, but release the pressure (OUTLET valve) due to heating.

(9) Open AUX IN and AUX CONTROL valves fully.

Since the pressure from the purge gas cylinder (after the reducing valve) is exactly the same as that of the measuring cell, there is no additional pressure buildup. If it should be somewhat lower, the check valve prevents the ingress of the pressurizing gas.

(10) Set the flow with the OUTLET valve and check for a few minutes.

The gas that escapes is topped up by the purge gas cylinder, the set pressure remains constant.

To ensure the same OUTLET setting for the measurement, do not touch the valve again:

(1) Close AUX IN valve.

(2) Close the gas cylinder (pressure buildup) and disconnect the gas connection from GAS IN.

(3) Open INLET valve so that the gas is vented via GAS IN and reattach the gas connection (see *Note a*).

(4) Open pressure cell.

The furnace is still at the insert temperature! You could burn yourself!

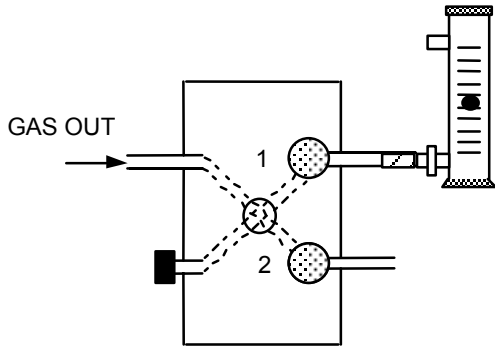
(5) Insert sample and close the cell.

(6) Build up pressure via GAS IN, then close INLET valve and open AUX IN valve fully.

The flow rate set with the OUTLET valve lowers the pressure, but it is compensated by inflowing purge gas.

(7) Confirm INSERT SAMPLE on the TA Controller: the measurement starts.

Notes: a) In order not to have to remove the gas connection from GAS IN, you can attach a gas distributor, e.g. at outlet GAS OUT (see section 4.8: *Optional accessories*).



(8) In this case, attach the flow meter to outlet "Valve 1".

(9) In the blank experiment, close valve 2.

(10) Open the OUTLET valve completely and set the flow rate with valve 1, then leave alone.

(11) To release the pressure, open valve 2 fully.

Notes: b) For measurements at ambient pressure, you can set a gas flow of 50 ml/min with the flow meter before the gas is led to the measuring cell.

– Connect the flow meter between gas source and AUX IN and open the AUX IN and OUTLET valves fully.

– Set the flow rate with the AUX CONTROL valve.

Controlling the flow and pressure with a special controller

To control the flow rate of the purge gas and the pressure in dynamic measurements, you can attach a flow meter and a pressure controller.

Note: We work with, e.g. a mass flow controller and a pressure controller from BROOKS INSTRUMENT (mass flow controller: model 5850E, pressure controller: model 5866 as an upstream pressure controller, control and display unit: model 5876) and describe here the procedure for controlled flow and pressure measurements.

(1) Connect the pressure controller input to the GAS OUT outlet.

(2) As appropriate, attach the tubing connection to the pressure controller outlet and connect tubing to lead off the outflowing gas.

(3) Connect the flow controller output to the AUX IN inlet.

(4) Connect the flow controller inlet to the purge gas line.

(5) Connect the flow controller and pressure controller to the control and display unit (cable).

(6) Set the target values of the pressure and flow rate at the control unit.

(7) Build up the pressure somewhat above the target value (GAS IN inlet).

(8) Close INLET valve.

(9) Set the pressure of the purge gas with the reducing valve somewhat above the measuring cell pressure and open the purge gas valve.

(10) Switch on control unit.

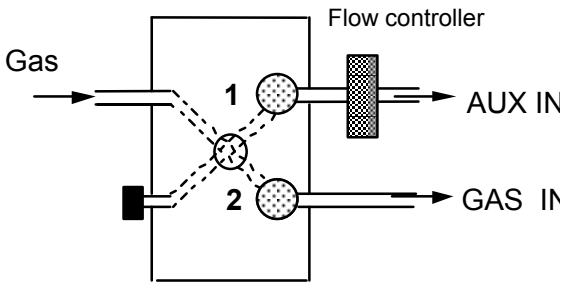
(11) Open first the AUX IN and AUX CONTROL valves then the OUTLET valve fully and wait until the pressure reading is constant.

(12) Start the measurement.

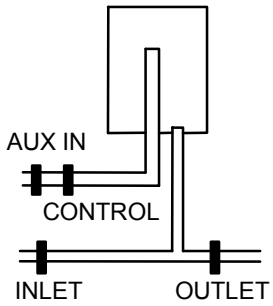
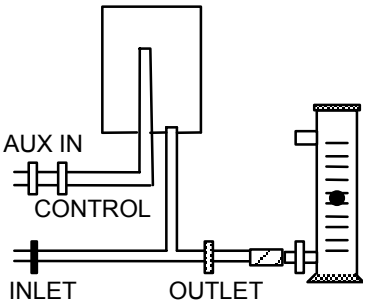
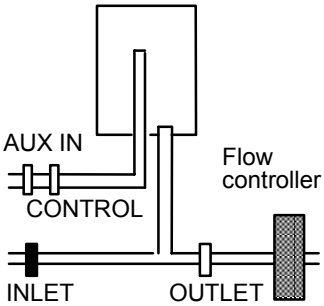
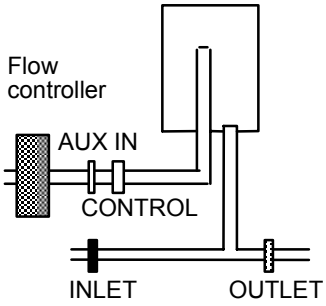
(13) At the end of the measurement, set the pressure on the control unit to 0 to relieve the pressure.

Notes: a) If you start your measurements at a relatively high start temperature, in other words the measuring cell is heated up rapidly, we advise waiting for a constant pressure display before confirming INSERT SAMPLE on the TC15.

b) If you use the same gas for pressure buildup and purging, you can, e.g. attach a gas distributor at the GAS IN inlet and connect to the flow controller inlet (see section 4.8: *Optional accessories*).

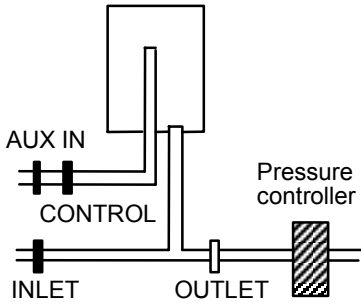
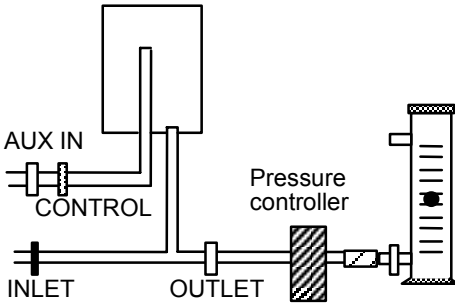
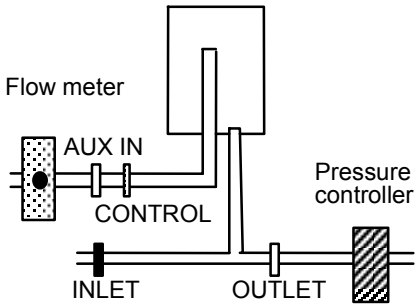
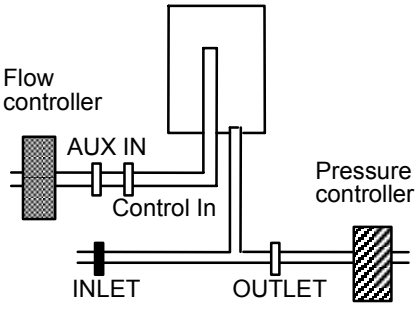


Overview: Pressure and purge gas

Purge gas	Without pressure control	
Without		AUX IN closed AUX CONTROL closed INLET closed OUTLET closed **isothermal**: pressure constant **dynamic**: pressure increase
With flow rate measurement in isothermal measurements * Flow rate e.g. 50 ml/min		AUX IN open AUX CONTROL open INLET closed OUTLET open: flow of e.g. 50 ml/min **isothermal**: pressure constant **dynamic**: pressure increase*
With flow rate control in isothermal measurements * Flow rate e.g. 50 ml/min (Reducing valve of purge gas source set to same pressure as measuring cell pressure)		AUX IN open AUX CONTROL open INLET closed OUTLET open **isothermal**: pressure constant **dynamic**: pressure increase*
With flow rate control in isothermal and dynamic measurements. Flow rate e.g. 50 ml/min (Reducing valve of purge gas source set somewhat higher than measuring cell pressure)		AUX IN open AUX CONTROL open INLET closed OUTLET open: flow of e.g. 50 ml/min **isothermal**: pressure constant ** **dynamic**: pressure increase

* In dynamic measurements, the flow supplied by the purge gas cylinder decreases in accordance with the volume expansion in the pressure cylinder. Depending on the heating rate and the temperature range, this can cause the pressure to remain practically constant.

** The volume of the pressure cylinder is approx. 0.9 l. With a flow rate of the purge gas of 50 ml/min, the pressure would increase only by around 0.1 MPa within 18 min with OUTLET closed.

Purge gas	With pressure control	
Without		AUX IN closed AUX CONTROL closed INLET closed OUTLET open **isothermal**: pressure constant **dynamic**: pressure constant
With flow rate setting in isothermal and dynamic measurements *** Flow rate e.g. 50 ml/min (Reducing valve of purge gas source set somewhat higher than measuring cell pressure)		AUX IN open AUX CONTROL: Set flow rate of e.g. 50 ml/min INLET closed OUTLET open **isothermal**: pressure and flow rate constant **dynamic:** pressure and flow rate constant
With flow rate measure-ment Flow meter with operating pressure of 10 MPa, e.g. from BROOKS, model 5860E (Reducing valve of purge gas source set somewhat higher than measuring cell pressure)		AUX IN open AUX CONTROL: Set flow rate of e.g. 50 ml/min INLET closed OUTLET open **isothermal**: pressure and flow rate constant **dynamic**: pressure and flow rate constant
With flow rate control (Reducing valve of purge gas source set somewhat higher than measuring cell pressure)		AUX IN open AUX CONTROL open INLET closed OUTLET open **isothermal**: pressure and flow rate constant **dynamic**: pressure and flow rate constant

*** In isothermal measurements, the display of the flow meter remains constant, in dynamic measurements not.

4.3.6 The calorimetric sensitivity E

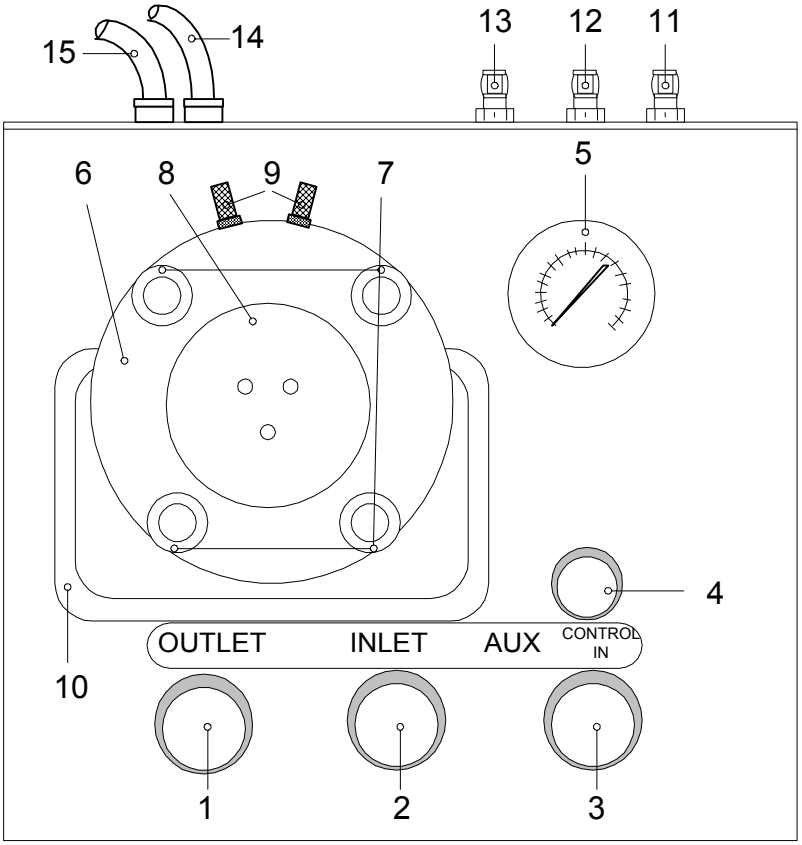
At elevated pressure, the value of the calorimetric constant E_{indium} is lowered compared with that at atmospheric pressure: The increasing gas density leads to a change in the thermal resistance between the measuring cell and the sample crucible.

The decrease amounts to approx. 0.6 %/MPa.

For pressure DSC experiments with maximum calorimetric accuracy, you do a heat flow calibration E_{In} under the pressure you need, e. g. 5 MPa nitrogen.

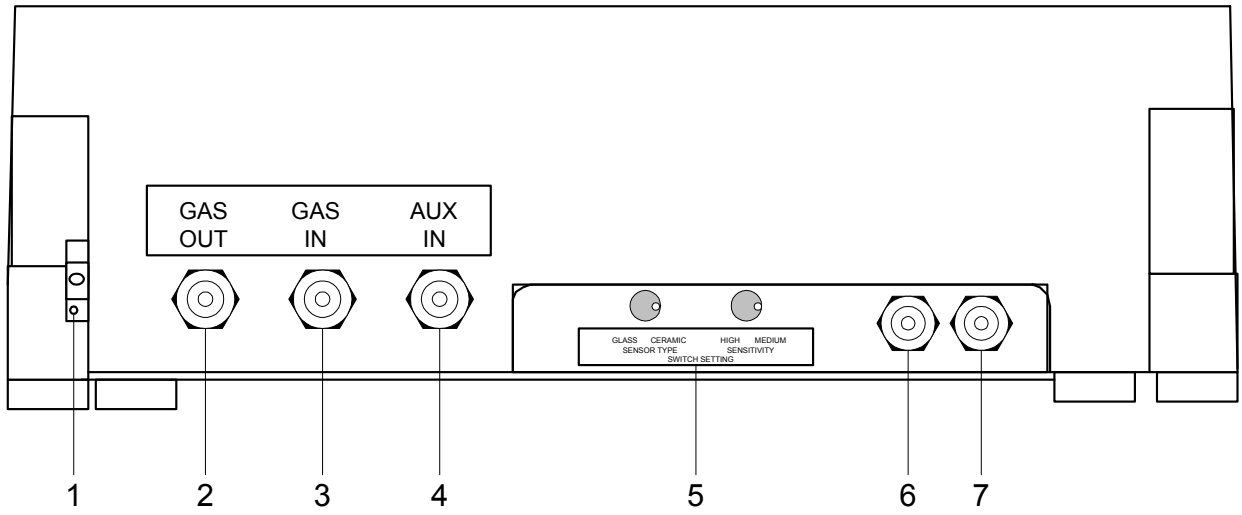
4.4 Description of the DSC27HP

4.4.1 Top view



1 Gas-Auslassventil (Druckentlastung)
2 Gas-Einlassventil (Druckaufbau)
3 Spülgas-Einlassventil (Spülgas)
4 Nadelventil für die Feindosierung des Spülgasflußes
5 Druckmanometer
6 Meßmoduldeckel (Druckdeckel)
7 Rändelmuttern
8 Wasserkühlhaube
9 Kühlwasserein- und auslaß
10 Bügel zum Lösen des Meßmoduldeckels
11 Gasanschluß GAS OUT (Meßgasauslaß)
12 Gasanschluß GAS IN (Druckaufbau)
13 Gasanschluß AUX IN (Spülgas)
14 Signalkabel
15 Leistungskabel

4.4.2 Rear view



1 Schraube der Sicherheitsberstscheibe

2 Gasanschluß GAS OUT (Gasauslaß)

3 Gasanschluß GAS IN (Druckaufbau)

4 Gasanschluß AUX IN (Spülgas)

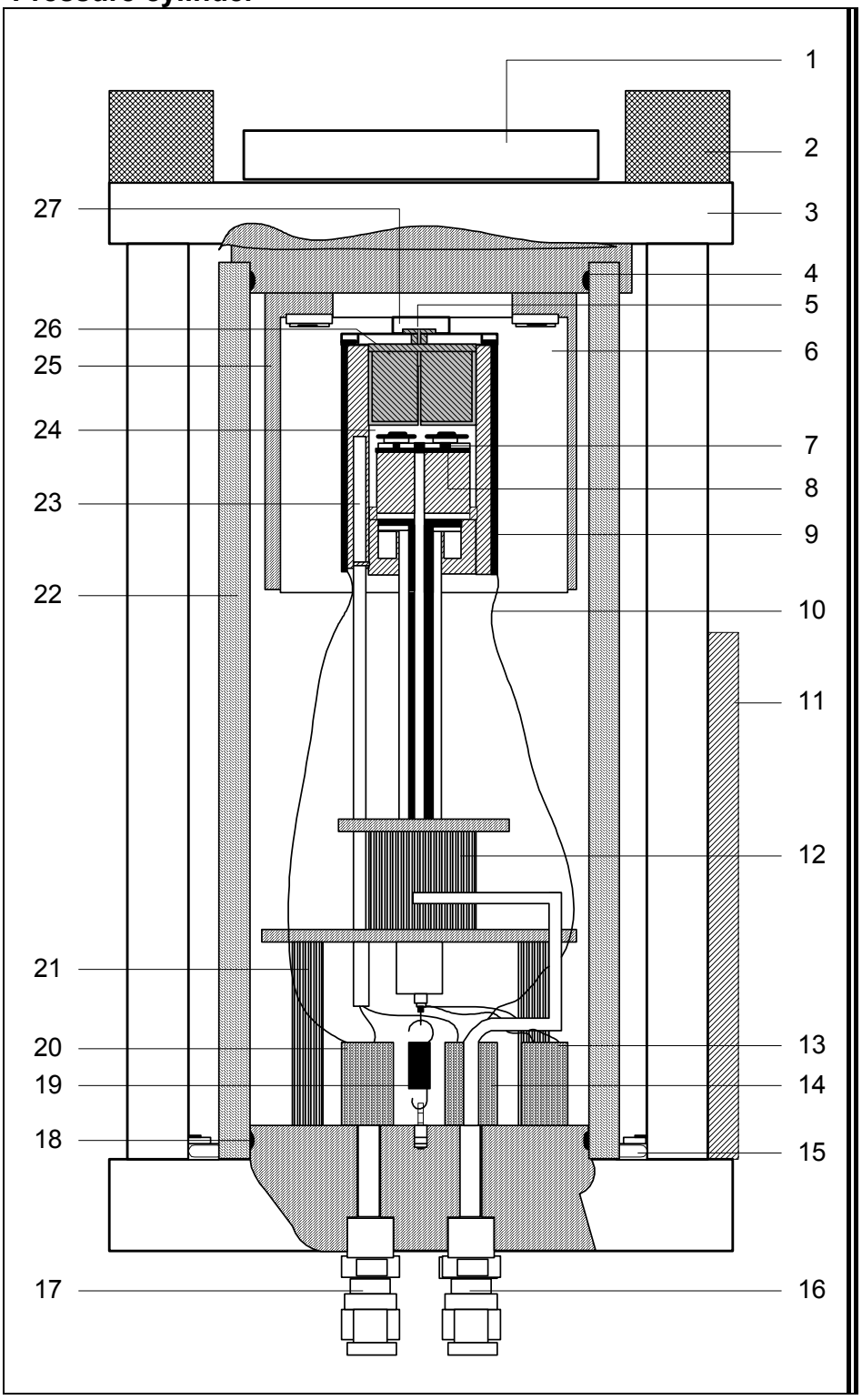
5 Wahlschalter für Meßsignalverstärkung (Empfindlichkeit) und Meßfühlertyp

6 Signalkabel

7 Leistungskabel

4.4.3 The internal layout

Pressure cylinder



Legende:

1 Kühlhaube
2 Kombimutter
3 Druckzylinderdeckel
4 O-Ring des Druckzylinderdeckels
5 Spülgasaustritt
6 Alox-Watte des Druckzylinders
7 Sensor
8 Sensorscheibe
9 Ofen
10 Heizdraht
11 Mantelrohr
12 Verteilersockel
13 Sensoranschluss
14 Heizungs- und Pt100 Anschluss
15 Niederhalter
16 Einlass für Spülgas
17 Gas- und Auslass (Druck)
18 O-Ring der Druck-zylinder-Grundplatte
19 Zugfeder für Sensor
20 Heizungs- und Pt100 Anschluss
21 Distanzsäule
22 Druckzylindermantel
23 Pt100 Temperaturfühler
24 Messzelle
25 Flanschrohr des Druckzylinderdeckels (Hitzeschild)
26 tiefer Ofendeckel
27 Schutzhaube

Gas connections

4.5 Maintenance

In this section, we describe the maintenance work that you yourself can perform (see also section 4.6: *Malfunctions*).

Faulty gas lines and valves or a faulty pressure gage may be changed only by trained service engineers!

4.5.1 Changing the rupture disc

Disassemble and reassemble the rupture disc following the enclosed instructions (HOKE: Rupture disc replacement kit, order No. 71733).

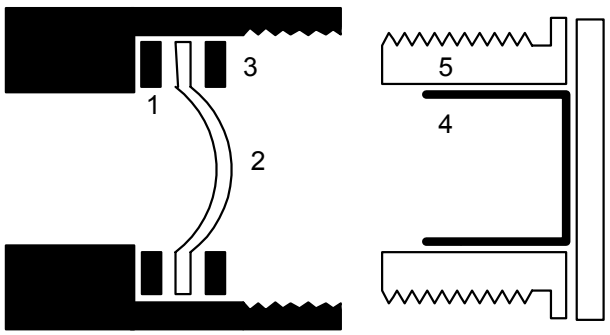
Disassembly

(1) Open rupture disc screw (5) and remove the rupture disk.

(2) Clean contaminated parts with acetone or ethanol.

(3) Grease thread with a little silicone grease.

Assembly



(1) Insert gasket (1).

(2) Insert rupture disc (2) with the curvature facing the screw.

(3) Insert slip ring (3)

(4) Lay safety screen (4) in the rupture disc screw (5).

(5) Screw in rupture disc screw.

Check

Before you start measurements, check the new rupture disc:

(1) Attach tubing connection to the safety rupture disc screw.

(2) Build up a pressure of 7 MPa with an inert gas and check for leaks (see section 4.3.1). 1 MPa ≈ 145 PSI.

4.5.2 Changing ceramic mat of the pressure cylinder cover

The ceramic mat serves to stabilize the pressurizing gas circulation. If you discover that the ceramic mat has become darker or small particles fall off, you should replace it (see section 4.8: *Accessories*).

4.5.3 Changing O-rings

Pressure cylinder

As soon as you notice a pressure drop in the measuring cell and have checked the gas inlets and outlets,

(1) Change the O-rings of the cylinder cover and base (see section 4.8: *Accessories*).

(2) Grease new O-rings with a little silicone grease, **before** inserting them.

Access to cylinder base (see also illustration of the pressure cylinder, section 4.4 3):

(3) Remove bracket and lift up jacket tube.

(4) Unscrew holding-down device of pressure cylinder and lift up pressure cylinder.

Cooling cover

If water flow out of the cooling cover,

(1) undo the screws of the cooling cover using an Allen key and change the inner and outer O-rings (see section 4.8: *Accessories*).

4.5.4 Cleaning Gas line OUT

Decomposition products of samples can condense in gas line OUT and block it.

To clean the entire gas line:

(1) Attach tubing to gas outlet OUT (lay end in a collecting vessel).

(2) Close INLET valve, open OUTLET valve.

(3) Lift up bracket and remove pressure cylinder cover.

(4) Remove bracket and lift up jacket tube.

(5) Unscrew holding-down screw of the pressure cylinder and lift up pressure cylinder.

(6) Inject solvent into the opening of the gas line (10) using a syringe (see section 4.5.7: *Illustration of the pressure cylinder base*).

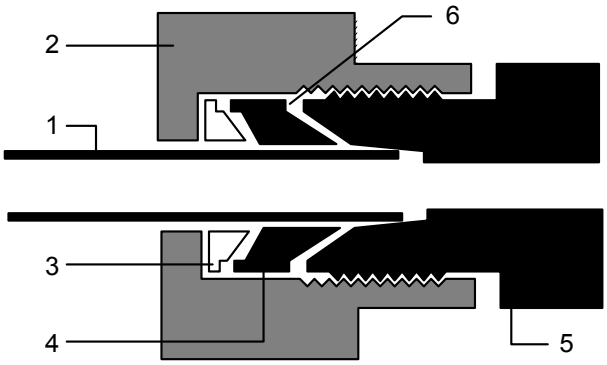
(7) Mount pressure cylinder and close.

(8) Build up pressure with inert gas via the AUX inlet so that the solvent is forced out of the gas line OUT. Depending on the solvent, flush the line and dry with gas.

Note: You can clean gas line IN in a similar manner: close tubing connection at gas inlet GAS IN, open INLET valve, close OUTLET valve.

4.5.5 Bulkhead union

The gas inlets and outlets IN, AUX and OUT have a two-ferrule tube fitting (Gyrolok) whose ferrules can be lost when unscrewing. You can order these as spare parts and replace them (see section 4.8):



(1) First lay the rear ferrule (3) in the unscrewed nut (2), then the front ferrule (4).

(1) is the tube, (5) the valve and (6) the shoulder of the front ferrule.

4.5.6 Cleaning sensor, sensor support and furnace lid

Sensor

You need clean the sensor only if the blank curve is not to your satisfaction:

(1) Clean the sensor surface with a cotton bud dipped in alcohol
or
heat the open measuring cell for 15 min at 600 °C.

Sensor support

With disassembled measuring sensor, you should check whether the support surface is clean (see next section). An absolute flat and clean support is a prerequisite for precise heat flow measurements.

(1) Clean the support surface with a cotton bud dipped in ethanol.

Furnace lid and lid support

If the furnace lid can not be removed,

(1) Heat up the furnace to, e.g. 400 °C and remove lid.

The furnace is still at hight temperatures! You could burn yourself!

(2) After cooling, clean lid and lid support with a cotton bud dipped in ethanol.

4.5.7 Changing the sensor

Removing the sensor

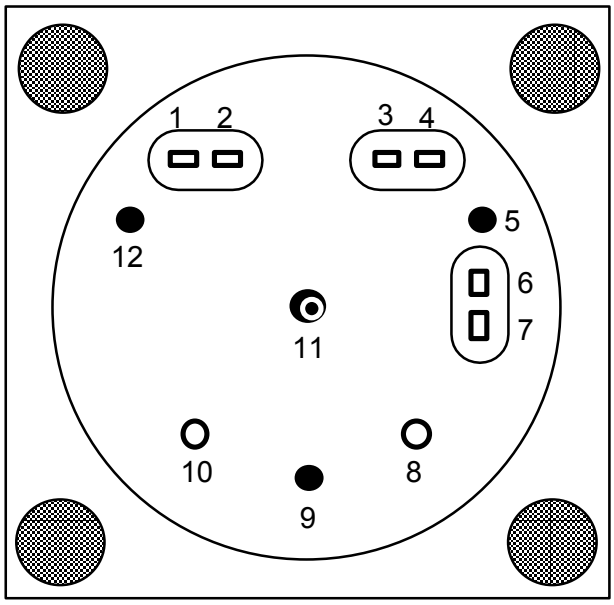
(1) Switch off TC15.

(2) Disconnect cable connections of the measuring cell at the processor.

(3) Lift up bracket and remove pressure cylinder cover.

(4) Remove bracket and lift up jacket tube.

– Unscrew holding-down screw of the pressure cylinder and lift up pressure cylinder.



2 Pt100 connection (left)
3 Pt100 connection (right)
4 Heating connection (right)
5 Spacer column
6 Connection for short sensor wire
7 Connection for long sensor wire
8 Feedthrough for purge gas
9 Spacer column
10 Feedthrough for gas inlet and outlet (pressure)
11 Spring support for tension spring
12 Spacer column

1 Heating connection (left)

(5) Undo screws for both sensor connections at the sensor block (6 and 7) with a screwdriver and take out the gold pins with tweezers.

(6) Unhook tension spring from wire eye using tweezers.

(7) Carefully straighten out the two sensor wires.

(8) Carefully lift up sensor and disk with the tweezers and grip by hand as soon as possible. If the wires stick, turn them carefully until the sensor can be withdrawn without resistance.

(9) If the disc adheres to the bottom of the sensor, pull it off carefully with the tweezers.

Installing the sensor

(1) Check whether the sensor support is clean.

(2) Lay ceramic disc on the sensor support.

(3) Carefully push the Teflon tubing that covers the two ends of the sensor wires of a new sensor through the hole.

If you reinstall the old sensor, since you only wished to clean the sensor support or insert a new disk, we advise sliding Teflon tubing (Ø 2 mm) over the sensor wires.

(4) Remove Teflon tubing.

(5) Plug the gold pins of the sensor wires into the block – the longer wire in connection 7 – and tighten the screws.

(6) Align sensor so that the letters can be read from the front.

(7) Hook the tension spring into the wire eyelet and clamp (11) so that the sensor is made fast.

(8) Bend the sensor wires to prevent any short circuiting.

(9) Check Pt100 and heating wires: no wire may be in contact with another!

(10) Center sensor and disk exactly on the support with tweezers.

(11) Before you remount the pressure cylinder, check the O-ring of the cylinder base and change if need be (grease with a little silicone grease).

(12) Screw on holding-down screw of the pressure cylinder, mount jacket tube and attach bracket.

(13) Set up the connections to the TC15 and at ambient pressure heat measuring cell at 600 °C for 15 min (otherwise the sensor will not show constant sensitivity).

(14) Perform an Indium check at ambient pressure.

If the indium melting point deviates from the true value of 156.6 °C by more than 0.5 °C, you should perform the temperature calibration.

4.6. Malfunctions

General error messages, warnings and malfunctions are displayed on the Personal Computer. The following Table shows malfunctions, their causes and measures pertaining to the pressure measuring cell.

Malfunctions	Causes	Measures
No pressure buildup	Inlet valve closed	Open valve
	Outlet valve open	Close outlet valve
Too little pressure buildup	Gas source with insufficient pressure	Check gas source
	Expansion of the gas: leads to internal ice formation	Always preflush lines with dry inert gas
	Pressure cylinder cover not screwed on tightly	Tighten nuts
	Line blocked	Clean line (see section 4.5.4)
	Lines leaking	Call METTLER TOLEDO service
	Valves faulty	Check bulkhead union (see section 4.5.5), otherwise call METTLER TOLEDO service
	Safety rupture disc faulty	Replace rupture disc (see section 4.5.1)
	Pressure gauge faulty	Call METTLER TOLEDO service
	O-rings of pressure cylinder faulty	Change O-rings (see section 4.5.3)
	Unknown leaks	Call METTLER TOLEDO service
Too much pressure buildup	Pressure regulator of gas source faulty or set too high	Check reducing valve, set pressure buildup with INLET valve
No pressure drop	Outlet valve closed	Check valve

Malfunctions	Causes	Measures
Pressure drop too small	GAS OUT line blocked	Clean line (see section 4.5.4)
Rapid pressure change	Abrupt opening or closing of gas source	Close INLET valve beforehand
Pressure cylinder too hot	No or insufficient cooling	Check water flow and temperature: 30 l/h and ≤20 °C
Water flows out of cooling cover	O-rings defective	Change O-rings (see section 4.5.3)

4.7 Specifications

Temperature

Range	Room temperature up to 600 °C
Reproducibility	±0.2 °C
Heating rate	0 ... 100 °C/min

Pressure

Range	0.1 ... 7 MPa

Cooling of the pressure cylinder

Water	Flow rate: approx. 30 l/h, temperature: 20…30 °C External diameter of cooling cover nipple: 1/8 inch

Pressure cell

Furnace	Silver
• Heater coil	88 V AC maximum
Cylinder material	Stainless steel 1.4435 (AISI 316)
Screw material	Stainless steel 1.4305 (AISI 303)
Cooling cover	Stainless steel 1.4435 (AISI 316)
Jacket tube	Aluminum 3.2315
Valves (connections)	Stainless steel 1.4435 (AISI 316)
Needle valve	Stainless steel 1.4435 (AISI 316)
Pressure gage	Stainless steel 1.4435 (AISI 316)
Pressure lines	Stainless steel 1.4435 (AISI 316)
Gas connections	Gyrolok, external diameter: 1/8 inch
• Tubing connection	External diameter: 1/8 inch
Safety rupture disc	Stainless steel 1.4435 (AISI 316)
• Tubing connection	External diameter: 15 mm
Pressure buildup	No corrosive gases No explosive gas mixtures
Purge gas	No corrosive gases No gases that can produce an explosive mixture with the gas for the pressure buildup
Dimensions	
• Width x depth x height	325 x 300 x 310 mm
Weight	17 kg
Volume	approx. 0.9 liters

DSC Signal

Amplifier setting	HIGH	MEDIUM
Range	±17 mW	±60 mW
E_{In}	1000 mW^{-1}	300 mW^{-1}
Digital resolution	18000 points	18000 points
S	21000 K^{-1}	6000 K^{-1}
Noise, RMS		
– (0.1 MPa at 150 °C for 1 min)	0.009 mW	0.024 mW
– (5 MPa at 150 °C for 1 min)	0.010 mW	0.025 mW
Enthalpy measurement (0.1 MPa):		
– Accuracy	2 %	
– Precision	0.5 %	

Note: Since the noise increases with increasing temperature, there is nothing to be gained by using high amplification above 300 °C.

Thermal resistance, R_{th}

Following values apply for the thermal resistance R_{th} as a function ot temperature (for standard aluminum crucibles):

T_r	–100	0	100	200	300	400	500	600	°C
R_{th}	0.03	0.036	0.04	0.054	0.063	0.067	0.069	0.072	K/mW

4.8 Accessories

Standard accessories

- Furnace lid (high) 26740
- Furnace lid (flat, for high crucibles) 29119
- Ceramic sensor (14p) 26614
- Ceramic disk 26741
- Tension spring for DSC sensor 11612
- Cover 26809
- Alox wool 26711
- O-Ring 71739
- O-Ring (∅ 68 mm) 71738
- O-Ring (∅ 32 mm) 71543
- Hose connection (Out), 1/8" 71749
- Hose connection (burst disk), ∅15 mm 26735
- Nut M14 26753
- Screw driver 73070
- Phillips screw driver 73072
- Hexagon wrench, 1.3 mm 70171
- Flat wrench 20/22 mm 72059
- Socket wrench 17 mm 71401
- Socket wrench SW 18 mm 71750

Optional accessories

- Crucible press 119410
- Operating instruction crucible press (e/g/f) 709301
- Crucible holder 28699
- Crucible set 119091
- High aluminum crucible, 150 µl (40 pcs) 27811
- Copper crucible, 40 µl (100 pcs) 29860
- Gold crucible, 40 µl (6 pcs) 27220
- Platinum crucible, 150 µl (4 pcs) 24126
- Calibration set (indium, lead, zinc) 29321
- Indium pills 29749
- Burst disk set 71733
- Gas distributor 26840
- Glass sensor 29553
- Sapphire disc 29684
- Cooling device 27342
- Flow meter for purge gas 40 - 360 ml/min air (max: 1 Mpa) 27243
- Cap nut 71752
- Locking ring (front) 71745
- Locking ring (rear) 71746
- Silicone grease 71300

5 The DSC30 Module in operation with the TC15 TA Controller

Content

Safety Notes

The instruments have been tested for the experiments and determinations documen-ted in the appropriate operating instructions. However, this does not absolve you from the responsibility of performing your own tests of the products supplied by us regard-ing their suitability for the methods and purposes you intend to use them for. You should therefore observe following safety measures.

Measures for Your Protection

- Ensure that you plug in the power cable supplied into a socket which is grounded! In absence of grounding, a technical default could have lethal consequences.
- Let the DSC30 furnace cool down and disconnect the module from the mains before you open the housing. Switch the instrument off and disconnect the power cable before you open the housing or change blown fuses! An electrical shock could be lethal!

- Never work in a hazardous area! Explosion hazard through hot surfaces!
- Never use combustible gases or explosive gas mixtures to purge the sample chamber! An explosion could occur!

- Make sure that the power and the signal cable of the same module are connected to the same TC15. The measuring cell could melt, if only the power cable is connected!!
- Never switch off the TC15 when the cell temperature is above 300 °C. The cooling fan would no longer work and the cell cover could be heated unduly!

- Never touch the furnace, the furnace lid or a sample just removed from the furnace! The temperature of the furnace can reach 600 °C.
- Open the furnace only when the temperature is lower than 100 °C! Always use tweezers to remove the lid or the crucible! Place hot items on the stainless steel area on the measuring module.
- Wear gloves and goggles when handling liquid nitrogen. Liquid nitrogen can cause severe skin burns!

– Switch off the TA processor immediately when the safety valve responds (humming noise), then :
    1. Wait until only a small amount of gas escapes through the safety valve.
    2. Pull out the aluminium cap of the safety valve. The excess pressure escapes from the nitrogen reservoir.
    3. Disconnect the measuring cell. Pull out the nitrogen heater

– Set up the instrument in a fume hood, if a sample may produce toxic gases during reaction.
– When working in closed rooms ensure good ventilation (danger of suffocation).
– Never push objects of any kind through ventilation openings around the furnace!

5 The DSC30 Module in operation with the TC15 TA Controller

5.1 Introduction to the DSC30 Module

The DSC30 allows DSC measurements from -170 to 600 °C. The measurement is based on the Boersma or heat flux principle.

The DSC30 cell is equipped with the glass sensor with a time constant of 7 s. The ceramic sensor can also be used but a prerequisite is a silver furnace with a flat and clean heater plate.

The experiment parameters are composed in the Personal Computer and sent to the TC15 where the segments of the temperature program are controlled.

Below ambient purging the cell with a dry gas is a must. The flow is adjusted by the needle valve of a flow meter.

During a measurement the data are transferred to the Personal Computer for the online curve in the module control window. At the same time they are available on the fluorescent display of the TC15. Scroll through the lines of the display by ROTATE.

At the TC15 display you also get messages such as INSERT SAMPLE. On the keypad of the TC15 you confirm the message by the OK key or you may abort the running experiment by the RESET key.

5.2 Installing the DSC30

Location

The DSC30 is a sensitive calorimeter. Today there is a certain electromagnetic noise field everywhere. It can disturb the sensitive measuring signal causing artefacts.

Please note the requirements concerning EMC (electro magnetic compatibility):

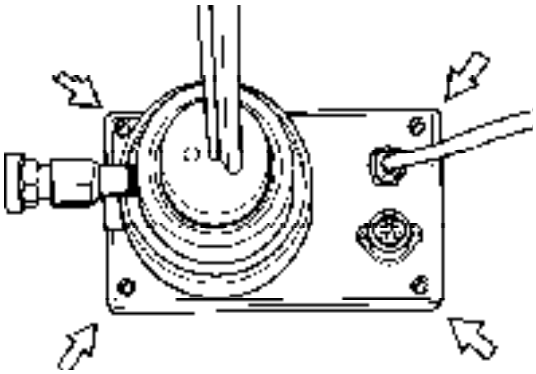
- There should be no rising mains, motors, or the like in proximity of the DSC820. Mind the neighbouring rooms, too!
- There are the minimum distances between the DSC30 with its TC15 and, e.g.:
  - the Personal Computer or a personal computer with CRT screen: 0.5 m
  - a printer or a plotter with a power transformer: 0.5 m
  - a cryostat: 0.5 m
  - any lamp with fluorescent tube: 0.5 m
  - a refrigerator or a deep freezer [1]) : 2.0 m
- All other electric equipment are noise sources and should therefore kept away from the DSC30.
- During measurements do not use a wireless phone or walkie-talkie.

Also protect the DSC30 from even small mechanical shocks. The DSC30 operates trouble-free at room temperatures of +10 [1]) ... +32 °C and at relative humidity of 20 … 80%.

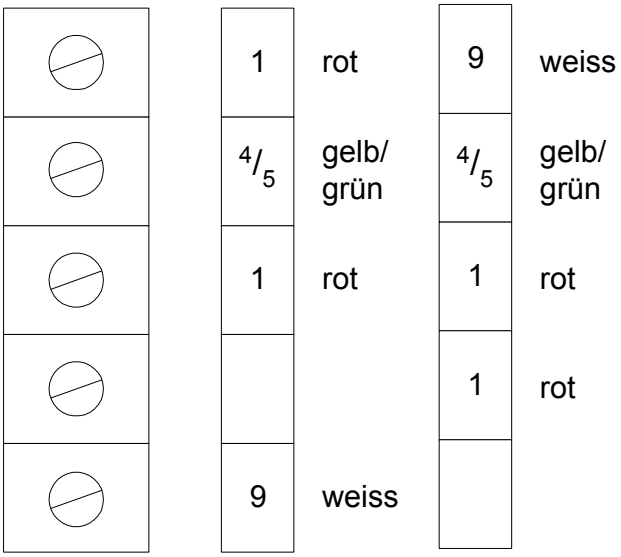
[1]) Accept reduced specifications when running the DSC30 in a deep freezer.

Setting up the DSC30

Check of the mains voltage of the DSC30 nitrogen heater:



The DSC30 nitrogen heater is set to either 110 V (110 - 120 V) or 220 V (220 - 240 V) at works. A check should be made that the setting corresponds to the mains voltage. For this purpose, the housing is opened by loosening the 4 screws on the underside of the heating. The colour of the connection cables must agree with the diagram below for the two supply voltages:

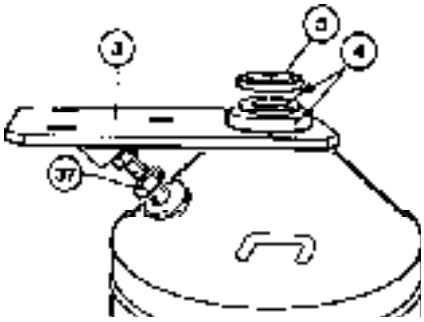


Terminal

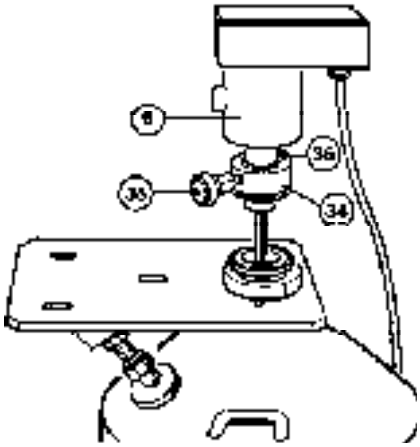
block

Installation of the Equipment with DSC30 Measuring Cell

The DSC30 measuring cell is packed in dismantled form and is made ready for use as follows:



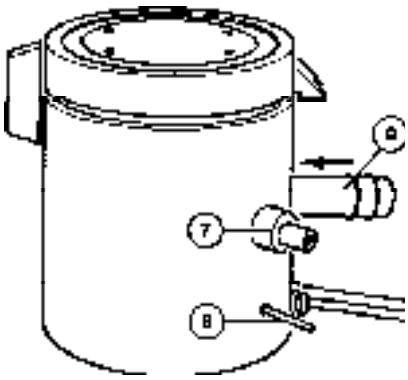
– Fill the nitrogen reservoir.
– Attach base plate support (37). The support is used to take any load off the small flange.
– Place the base plate (3) on the nitrogen reservoir and screw in the two screws (4).
– Place the centering ring (5) on the neck of the flask.
– If you are using a three-legged roller support, make sure one of the wheels is located underneath base plate (3) so that the instrument does not tip over when the nitrogen container is empty



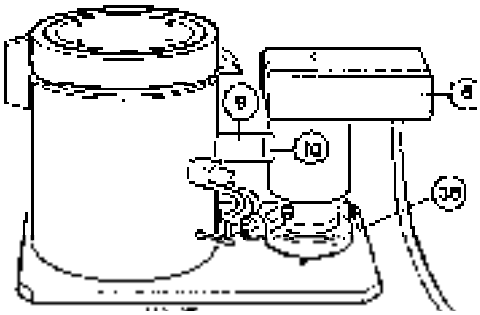
– Place the nitrogen heater (6) in the nitrogen reservoir. Turn flange (34) in such a manner that safety valve (35) is on the same side as cooling gas outlet (7) of the measuring cell.

Function of the safety valve

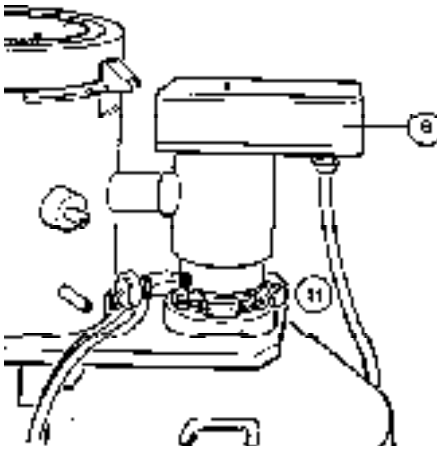
- The safety valve responds at an excess pressure of 50 kPa (0.5 atm). At 70 kPa (0.7 atm), it lets the maximum amount of cooling gas escape with a loud humming noise (see page 313).



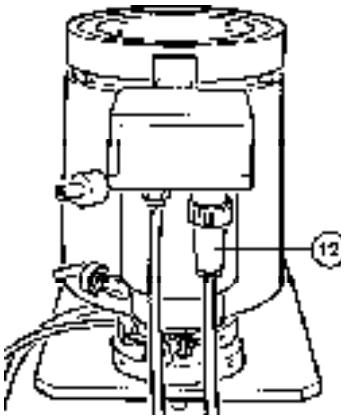
– Insert the gas escape tube (7) in the DSC furnace above the purge gas connection (8).
– Insert the connecting tube (9) in the DSC furnace on the right of the gas escape tube (7). Care should be taken not to damage the furnace insulation.



– Place the furnace on the base plate so that the connecting tube (9) points in the direction of the nitrogen heater (6) and engage the foot of the furnace in the grooves in the base plate.
– Align the nitrogen heater (6) so that the opening (10) points towards the connecting tube (9).
– Adjust knurled screw (36) located on the front side of flange (34) in such a manner that opening (10) comes to rest at the same level as connecting tube (9).



- Secure the nitrogen heater (6) to the neck of the flask with the chain clamp (11).



– Push the DSC furnace towards the nitrogen heater until the connecting tube is at the stop.
– Plug the power cable (12) for the DSC furnace in the bush on the nitrogen heater and screw on.

– After opening the measuring cell cover, remove the foam packing.

When the safety valve responds (humming noise), the TA processor must be switched off immediately and be absolutely sure to follow the following instructions:

The TC15 must be switched off immediately. Then wait until only a small amount of gas escapes through the safety valve. The excess pressure can now be completely eliminated from the nitrogen reservoir by pulling out the aluminum cap of the safety valve. The measuring cell may now be disconnected and the nitrogen heater can be pulled out. If the nitrogen heater were to be removed right away after the safety valve responds, a lot of nitrogen could escape. And if the nitrogen container is full, some liquid nitrogen could even have spilled over.

If it is not possible to remove the obstruction from the normal path of the cooling gas, it is necessary to inform your METTLER TOLEDO Service Department.

Connecting the DSC30 to the TC15

Connect the power cable with its round 7 pin plug to the appropriate socket at rear of the TC15. Connect the signal cable with its flat 15 pin plug to the flat socket.

Make sure that the power and the signal cable of the same module are connected to the same TC15, if you have several modules or several TC15s!

Note: When using the TC110 Module Switch box check that the signal and the power cables of the DSC30 are plugged into sockets with the same number.

Connect your purge gas to the purge gas inlet at rear of the DSC30. The gas connector opens when the appropriate nipple is engaged. Adjust the flow rate to approx. 50 ml/min.

Check the color of the code plug Through the small round window at the bottom of the DSC30:

Green	when using the yellowish glass sensor
Blue	when using the blue ceramic sensor.

The amplification is defined by the orientation of the code plug. Through the small round window the following word is visible:

Medium	normal amplifier setting for DSC signals of ± 60 mW
High	high amplification (3.5 times higher than medium) for small signals (± 20 mW) and reduced signal noise.

Filling the Liquid Nitrogen Container

When the level of liquid nitrogen falls so low that the heater is only just immersed, a level sensor stops the heater and thus the cooling gas flow. The red lamp on the housing indicates that the nitrogen must be topped up. To do this, only the furnace and the heater need be removed.

If there is enough space on the laboratory bench for the furnace and nitrogen heater, the tubing and cables do not need to be disconnected. Remove the furnace together with the tubing and place it on the laboratory bench. Then loosen the tension chain and withdraw the heater from the nitrogen container.
On mounting after filling, ensure that the center ring is properly located on the flange. Insert the nitrogen heater in the container. Place the furnace, with the connection tubing towards the heater, on the base plate so that the feet engage with the notches.

Then the heater is aligned with the furnace and secured with the tension chain. The furnace is pushed against the nitrogen heater up to the stop.

Icing and condensation in the equipment:

Icing during intensive cooling is limited to the nitrogen outlet where there is no risk of blockage. Condensation of water in the aluminium housing of the nitrogen heater and in the connection tubing is normal.

Purge gas

It is essential to use a dry purge gas with a flow of 50 ml/min, because otherwise icing of the furnace can occur. The purge gas is fed into the furnace through the tube connector under the outlet for the cooling nitrogen. It flows out through the gap in the sealing ring on which the glass plate of the cell cover rests.

Preparing the Personal Computer for the DSC30

Follow instructions in the Operating Instructions STARe Software File for the install procedure.

Preparing the DSC30 for Experiments

Prior to the first measurement, a temperature calibration has to be performed once. This is not needed if another module connected to the same TC15 was calibrated in the temperature range of interest.

To avoid artefacts on DSC curves, check the following points:

(1) Check the DSC sensor position. Is it in the center of the furnace? If not, move it towards the center by tweezers (or with the centring gauge of the DSC820) and heat the furnace 20 minutes at 600 °C without crucibles. Create a method from 25 to 600 °C with 50 °C/min and 20 min isotherm at 600 °C, use pan type `No Pan` .

(2) Check initial deflection and blank curve :

- A clean DSC measuring cell with a correctly inserted glass DSC sensor should give an initial deflection of not more than 1 mW with 2 empty standard aluminium pans. (Difference between starting point and stabilized signal at 10 K/min). A larger deflection can often be corrected by slight horizontal movement or rotation of the DSC sensor.
- The blank curve of the DSC cell with the glass sensor (DSC curve with 2 empty pans) should be constant within a range of 2 mW for a heating rate of 10 K/min up to 500 °C. It must be free from peaks and discontinuities greater than 0.1 mW. Otherwise, the DSC cell should be cleaned by heating for 30 minutes at 500 °C, if possible with oxygen or air (50 ml/min) as purge gas. Subsequently a new blank curve is measured. If necessary, the measuring cell should be cleaned as described under maintenance.
- With the ceramic sensor the tolerances are wider: Initial deflection ± 3 mW, drift 50...500 °C within a range of 3 mW.

(3) Run the `Check DSC ^exo In` when using the sign rule exothermal to the top or `Check DSC^endo In` with endothermal to the top. You find details in section 7.

Remark: For measurements below ambient the deep silver lid (see accessories) has to be used to obtain undisturbed DSC curves. Above ambient the flat lid can be applied.

5.3 Operating the DSC30

Switching On

There are no switches at the DSC30, please refer to chapter 1.4 (TC15 TA Controller).

Performing an Experiment

(1) Consult section 6 regarding sample preparation, choice of crucibles and furnace atmosphere (purge gas).

(2) If a purge gas is needed ensure the appropriate gas is connected to the cell and check the flow. The usual flow rate is 50 ml/min.

(3) When an experiment has been sent to the TC15 the display INSERT SAMPLE reminds you to place the sample pan:

- Open the furnace cover by disengaging the handle and tilting the cover backwards.
- With tweezers remove the silver lid and place it on the stainless steel area behind the furnace.
- Place the pan carefully on the left pan position of the DSC sensor and ensure there is a (empty) reference pan on the right. When using pans without center pin check position visually.
- Carefully place the silver lid on the furnace.
- Put the cover back. Ensure proper engaging.
- Start the measurement with OK.

Remark: For measurements below ambient the deep silver lid (see Accessories) has to be used to obtain undisturbed DSC curves.. Above ambient the flat lid can be applied.

(4) At the end of the experiment REMOVE SAMPLE indicates to open the cell and remove the sample. Confirm with OK and the cell goes to the insert temperature.

Switching Off

Never switch off the TC15 when the cell temperature is above 300 °C. The cooling fan would no longer work and the cell cover could be heated unduly.

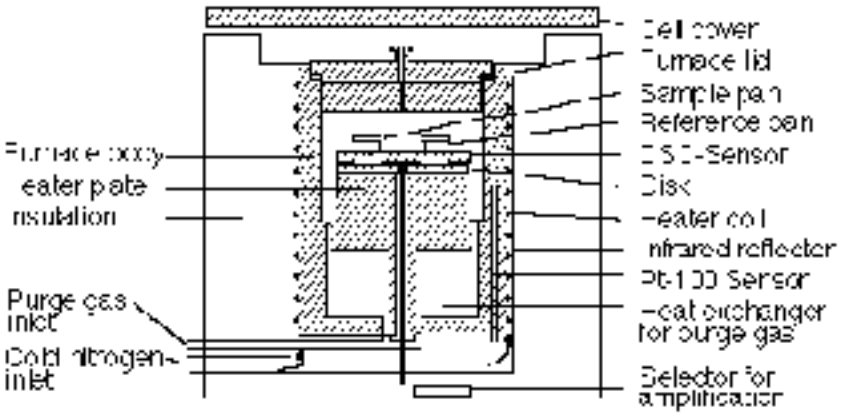
(1) Always remove the last sample pan before switching off. The order of switching off the Personal Computer and the TC15 is not of importance.

5.4 Description of the DSC30

The DSC furnace made of pure silver is heated by means of a coaxial heater coil. A temperature sensor, Pt100, generates the temperature signal. The DSC sensor with the 5 fold Au/Ni thermopile on a glass substrate is placed on a sapphire disk that is in direct thermal contact with the heater plate of the silver furnace. To cool the DSC furnace a suitable amount of nitrogen is evaporated in the liquid nitrogen container and the cold gas flows through the heat exchanger around the furnace.

The purge gas inlet guides the gas - usually 50 ml/min - to the bottom of the furnace body Here it is heated to the cell temperature and enters into the sample chamber. It finally escapes through the center hole of the lid. Cooling is provided by cold nitrogen gas flowing through the gap between the silver furnace and the infrared reflector.

Note: The optional ceramic sensor (14 Au/Au-Pd thermopile on a ceramic substrate) needs a ceramic disc instead of the sapphire disk. The ceramic sensor has a long life time even when exposed to corrosive decomposition products that would attack the glass censor



Schematic cross section through the DSC30 cell. The heat flows from the heater plate via disk and DSC Sensor to sample and reference pan. The obtained DSC signal is amplified and converted to digital in the TC15.

When required cold nitrogen gas is evaporated in the liquid nitrogen container and flows through the gap between the furnace and the infrared reflector.

A code plug appropriate to the installed DSC sensor is used to select the amplification (medium or high). The code plug with the actual setting is visible through a small window in the base plate of the DSC module.

5.5 Accessories

6 DSC Sample Preparation

Content

6 DSC Sample Preparation

6.1 Introduction

In the following introduction, the preparations for a DSC measurement are described. The instrumental possibilities as well as the correct use of the accessories are discussed. There are two main goals in sample preparation:

- Good thermal contact of the sample with the pan to obtain reproducible curves and sharp peaks (good resolution).
- Defined type of exposure to the furnace atmosphere (open: constant pressure; sealed: constant volume).

6.2 Weighing the Sample

It is recommended that the pan and the lid are tared, the sample is then placed in the pan, which is closed and the net weight read on the balance (with a glass pan, the sealed off section beyond the seal is also weighed). This procedure reduces errors arising from spillage or evaporation of the sample.
When investigating unknown samples you should always weigh the total mass of crucible, lid and sample before the experiment. Compare the initial mass with the mass after the measurement. Possible weight changes during the course of the ex-periment are thus detected. This is helpful for correct interpretation of DSC curves. So-me hints regarding sample size are given in the next section.

In a blank experiment, the blank pan weight is keyed in under `Options/Pan weight` in the experiment window. Very similarly, the sample pan weight must be keyed in for specific heat evaluations.

With a balance connected to a serial port of the Personal Computer: During a current measure-ment, the next weighing can be made and the result transferred to the Personal Computer by pressing the print button at the balance. The values are stored in a buffer.

6.3 Choosing the Appropriate pan for a Measurement

The table shows the available crucibles with their most important properties:

Pan type	Volume [µl]	Maximum Pressure [MPa] [bar]	Maximum Temperature [°C]	Order number	Number of pieces
Aluminium Standard	40	0.2 (2)	600	ME-27331	100
Tall Aluminium	160	0.2 (2)	600	ME-27811	40
Medium Pressure (stainless steel)	120	2 (20)	300	ME-29990	25
Gold	40	0.2 (2)	1000	ME-27220	6
High pressure (nimonic 80A)	270	10 (100)	750	ME-29889	1
High pressure (steel gold plated)	50	15 (150)	750	ME-26732	25
High pressure (glass)	100	5 (50)	500	ME-27812	50
Platinum	150	-	1500	ME-24126	4
Alumina (Al_2O_3)	70	-	2000	ME-24123	20
Copper (without lid)	40	-	1000	ME-29860	100

(1) Avoid interactions with pan. In other words the pan normally should be inert. Aluminum, e.g. reacts with:

- alkaline (NaOH, Na_2CO_3, cement water mixtures),

  metals (Hg, Ga forming a low melting alloy which leads to a hole in the pan.

  Remedial action: spray a small amount of , e.g. blue paint from a commercial paint spray can onto the pan)

- acids (HCl, H_2SO_4)

- water at elevated temperature

Glass reacts with

- strong alkaline (NaOH)

- hydrofluoric acid

Copper and platinum catalyze redox reactions

(2) Define type of exposure to the furnace atmosphere:

open, self generated atmosphere, hermetically sealed see paragraph *Closing the pan*. A sealed pan allows measurements at constant volume. The limitation is given by the maximum pressure of a pan. In safety investigations high pressure crucibles are used. They should withstand the sum of the vapor pressure of all components. In such a case each exothermal reaction can be detected that otherwise could be masked by endothermal volume work.

(3) Size of sample:

For safety reasons samples with strong effects, e.g. explosive, peroxides, nitro compounds, are applied in quantities of fractions of a mg up to 1 mg maximum.

Samples with small effects such as most inorganic compounds are used in the range 10 through 30 mg.

Diluted samples such as aqueous solutions often give very small effects. Therefore high volume pans are used to obtain good results.

(4) Mind the maximum temperature of each pan. The Personal Computer would anyhow refuse a method having a segment surpassing the maximum temperature of the used pan.

6.4 Closing the Pan

The type of closing depends on how much contact is required with the atmosphere:

A cover with many holes allows free access for the measuring cell atmosphere. At the same time the lid hinders liquid products creeping out of the pan and spoiling the DSC sensor, which can be important in the study of oxidation stability under dynamic conditions. Isothermal measurements of the oxidation stability can be carried out in a pan without a lid. In general, the lid is perforated before sealing the pan in order to avoid distortion of the pan (procedure: the inverted lid is placed on a soft support, such as India-rubber, and about 5 holes are pierced with a thick pin).

A restricted exchange of gas is important in the determination of the boiling behaviour of liquids, for example, where the lid is placed on a hard surface (e.g. the pan box), and a single hole is pierced with a sharp pin. If the perforated lid is inspected under a microscope, the hole should ideally be about 50 µm in diameter.

A sample is hermetically sealed off so that no components can evaporate (e.g. during chemical reactions), in order to suppress unwanted degradation reactions at elevated temperatures (e.g. in purity determinations) and to avoid oxidation reactions.

The following pans can be hermetically sealed by cold welding with the crucible sealing press:

- Standard aluminum pan
- Tall aluminum pan
- Gold pan

In a sealed pan the internal pressure increases according to the sum of the partial pressures of the components. The pressure may exceed the maximum pressure of the Al pans. To avoid artefacts caused by the sudden blow up high pressure crucibles are applied.

The glass pan is sealed by melting the neck with a micro burner, the nimonic high pressure pan by screwing down, and the medium pressure pan by pressing down the lid containing the O-ring (see Accessories). The gold plated high pressure pan is sealed by pressing an insert onto a burst disc placed in the pan.

It is good laboratory practice to compare the total mass of a high pressure crucible after the scan with its initial mass. A loss below 20 µg can be due to splitting off surface moisture and thus indicates a tight crucible.

Using the sealing press with the round base plate is explained in the Operating Instructions of the *Crucible Sealing Press*.

Using the sealing press with the Trapezoidal base plate:

(1) Use tweezers to locate the pan on the base.

Warning: The rim of the pan must be kept clean, if a hermetic seal is to be made. (The pans must likewise be protected from dust during storage.)

(2) To allow inserting a tall aluminium crucible, remove the base from the press.

(3) Place the lid on the crucible.

(4) Slowly rotate the hand wheel once in a clockwise direction.

(5) Remove the pan from the base with tweezers.

6.5 Reference Pan

In general, the sample pan is measured against a reference pan in all DSC measurements. Apart from the sample, the reference pan should be as similar as possible in weight and shape to the sample pan. Normally an empty pan with perforated lid is used as a reference to avoid distortion at temperatures above 250 °C (blow up due to increasing pressure). As the pan can be used repeatedly it is recommended that two holes are pierced in the lid in order to identify it.

6.6 Inserting the Pan in the DSC Cell

After opening the DSC cell, the sample pan is placed in the left hand measurement position so that the centre pin of the pan is located in the hole surrounded by the thermocouples. The reference pan is inserted in the right hand measurement position (mnemonic: Reference = Right). As soon as the pan has been inserted, the furnace lid is placed over the furnace opening.

6.7 Using Purge Gas

Purge gas may be used for several reasons:

- To purge gas and vapour products formed during analysis from the cell. The cell is thus protected from corrosive gases (e.g., containing halogens) and cleaning is seldom required.
- Displacement of atmospheric oxygen in order to avoid unwanted oxidation of the sample.
- Introduction of a reactive gas in order to investigate its chemical reaction with the sample. Reactive gases are, e.g. air, oxygen or carbon dioxide.

During the experiment a flow of 50 ml/min is normally used. There is among the accessories a flow meter with needle valve for adjustment of the gas flow. An aquarium air pump is suitable as a source when purging with air above room temperature. Some purge gases alter the calorimetric sensitivity of the DSC cell. Such a change is automatically compensated by the respective gas factor stored in the database of the Personal Computer.

7 Calibration of DSC Cells

Content

7 Calibration of DSC Cells

7.1 Introduction

Calibrations that are performed wrongly lead to a wrong temperature or heat flow scale. Hence this work should be carried out only by especially qualified personnel !

Contrary to the calibrations, the Indium Check is a normal method with automatic evaluation and validation of the result. It doesn't change any instrument parameters.

Performing Calibration Experiments

A step by step description of a calibration proce-dure is given in section 7.7.

In the TA Station there are some calibration methods ready for use. There names begin with `Calib`.

You may also compose your own calibration methods in the method window. Don't forget to select the type of calibration under `Miscellaneous/Calibration/Type`.

7.2 The Indium Check

It is good laboratory practice to check the temperature and the heat flow accuracy ones every month. The check is based on measuring the onset temperature of fusion and the heat of fusion of Indium.

ΔH_f: 28.45 J/g ±0.3 J/g

T_f: 156.6 °C ±0.3 °C

You perform the suitable check in the version `^exo` when using the DSC sign exothermal to the top. The respective methods are named:

```
Check DSC ^endo In
Check DSC ^exo In
```

If you are interested in high temperatures as well - you can compose a similar Zinc Check.

A calibration of temperature or heat flow only has to be performed when the check has given results with deviations no longer tolerable: As long as the measured melting point remains within the tolerances, your measuring cell does not need a temperature calibration.

As long as the ΔH value remains within the tolerances, your measuring cell does not need a heat flow calibration. If you are in doubt, run a second Indium sample for comparison.

With an indium check after calibration experiments you make sure that the calibrations have been done properly.

7.3 Sample Preparation for the Indium Check and the Calibrations

Cut a piece (only one) of your substance with a weight of approx. 3…7 mg. For the Indium check and the heat flow calibration use a micro balance to get an accurate weighing in. For best heat transfer press your sample to a flat disk . When the maximum temperature exceeds 250 °C, pierce a small hole in the lid before cold welding in the crucible sealing press.

Check a second measurement with the same pan. After the first fusion often the heat transfer is improved thus giving a slightly lower onset temperature.

The so called multi sample pan (Indium and Zinc) has to be prepared in such a manner as to prevent the sample disks getting in touch with each other (they would form a low melting eutectic with "wrong" temperatures). Place the disks in the crucible as far away from each other as possible. Press some aluminum foil (e.g. an aluminum lid with cut off rim) over the disks using the teflon rod. This foil should keep a distance between the different metals. Experience shows that such a pan with Indium and Zinc can be used several times without interactions.

7.4 Calibrating Tau Lag

The tau lag calibration is based on onset temperature determinations with different heating rates. As a first calibration after exchanging the DSC sensor or after changing the cooling option, tau lag should be calibrated. When running more than one calibration substance (e.g. not only Indium, but also Zinc) the temperature function of tau lag is measured, too:

$$\text{Tau lag} = A + B \cdot T + C \cdot T^2$$

The default values are: A = 3.5 s, B = C = 0

Remark: In the current version the term C is zero all the time (linear regression).

Create a method `Calib Tau Lag: In` so that the method premelts the sample to ensure a good heat contact and then melts the sample using 2, 5 and 10 °C/min. Determine the onset temperatures and calculate the slope of their function of the applied heating rate. This slope is added to the previous value of tau lag at this temperature to obtain the new value of tau lag. Each sample gives an entry in the Tau Lag Calibration box (Fig. 1). An additional experiment with e.g. Zinc (method `Calib Tau Lag: Zn`) would give an entry at the second position. If there is no additional measurement just the A value is changed by the calibration. Only the rows up to the actual position are considered. `Clear` clears all entries.

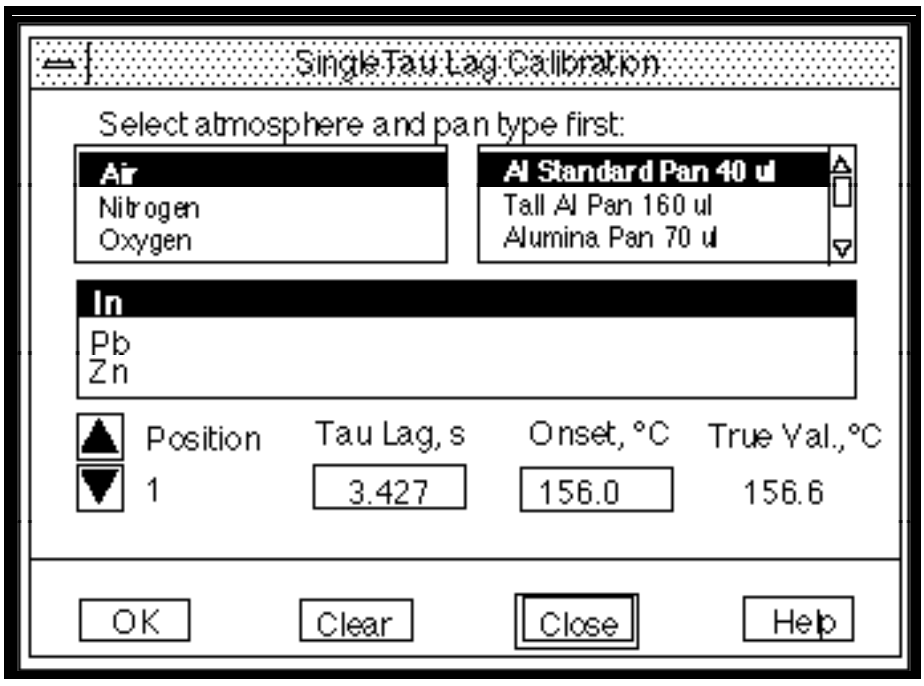


Fig. 1: In the first row or position tau lag and the onset temperature (extrapolated to rate zero) has been entered automatically by the method `Calib Tau Lag: In`.

You may also compose your own calibration methods in the method window. Don't forget to select `Tau Lag Single` as type of calibration under `Miscellaneous/ Calibration/Type`. Create a heating and a cooling segment prior to the segments you design for the measurements. The minimum number of measurement segments is two. The ratio of the heating rates should be at least 2, e.g. 2 and 5 °C/min. Heating segments are considered only.

The `Single Tau Lag Calibration` box can be used for manual entries, as it has been done with the factory calibrations (see section "Manual Entry" in the Operating Instructions of the STARe Software).

After `OK` you get the `Tau Lag Calibration` box displaying the new A, B and C values. On the right in brackets you see the previous values that would remain active when quitting the box with `Cancel`. For your information the deviations caused by the new tau lag function from the old one are calculated at two temperatures: 25 and 500 °C.

With `OK` you accept the new tau lag values. `OK` also clears all previous entries.

7.5 The Automatic Multiple Temperature Calibration

The TA4000 calibration crucible with its three imbedded metals In, Pb and Zn (melting points 156.6; 327.5 and 419.6 °C) can be used to perform the so called TA4000 temperature calibration (`Method/Miscellaneous/Calibration/Type/Temp.TA4000`). This special calibration is performed with a heating rate of 10 °C/min in the whole temperature range of the DSC module. At the same time the onsets of the three fusion peaks are compared with the true values to calculate the new ordinate intercept, A, the slope, B, and the non linearity of the temperature function, C.

The temperature function of the electrical resistance is modelled as follows:

$R = A + B \cdot T + C \cdot T^2$

The default values are: $A = 100\ \Omega$, $B = 0.3908\ \Omega \cdot °C^{-1}$, $C = -58.02 \cdot 10^{-6}\ \Omega \cdot °C^{-2}$

The **multiple temperature** calibration results in a higher temperature accuracy.

The automatic **multiple** sample temperature calibration is based on one experiment using a crucible with at least two calibration standards such as Indium and Zinc. The different substances have to be kept separately to avoid formation of a low melting alloy. As a result of this calibration the temperature function of the Pt100 is corrected (the ordinate intercept, A, and - with more than one measurement - the slope, B, are corrected, i.e. the non linearity of the temperature function, C, is not deformed. The analog/digital converter of the Pt100 temperature measurement is calibrated, too.).

Select method `Calib DSC Temp. In/Zn`. You may also compose your own calibration method in the method window. Don't forget to select `Temp.Multiple` as type of calibration under `Miscellaneous/Calibration/Type`. After the experiment you get the Temperature Calibration box displaying the new A, B, C values. On the right in brackets you see the previous values that would remain active when quitting the box with `Cancel`. For your information the deviation of the new temperature scale from the one based on the default Pt100 values is calculated at two temperatures: 25 and 500 °C.

With `OK` you accept the new calibration.

7.6 The Single Temperature Calibration

In this temperature calibration one or several **single** sample crucibles are measured in individual experiments. There are two procedures of single temperature calibrations:

- **Performing single temperature calibrations** with automatic entry into the single temperature calibration box of the module control window. You get an example method in the experiment window by `Select Method/Calib Temp: In.`
- **Manual entry** of onset temperature(s) into the single temperature calibration box of the module control window. Such onset temperatures can be based on an indium check for example.

Perform an experiment with the method `Calib DSC Temp Single In` . When finished call `Calibration/Single Temp. Calib.` in the module control window:

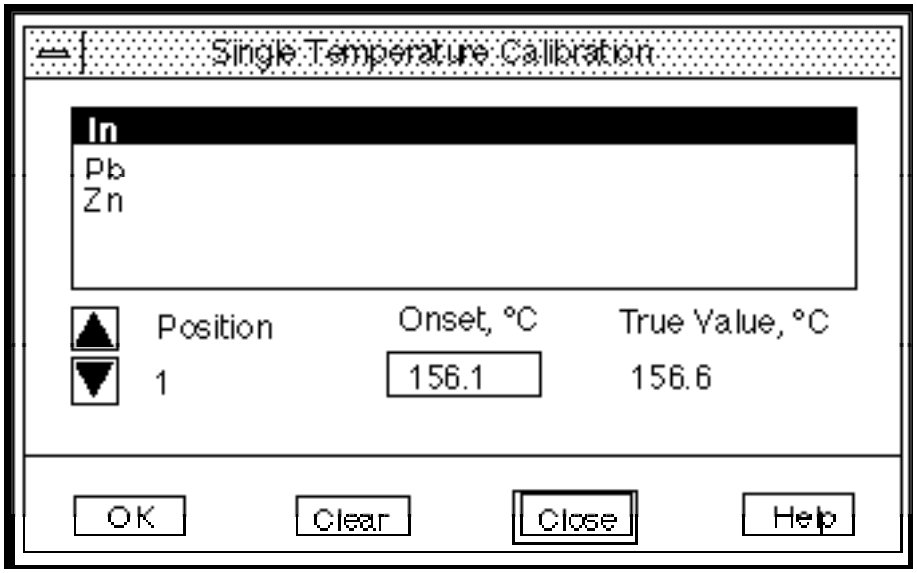


Fig. 2: In the first row or position the onset temperature has been entered automatically. OK at position 1 would only recalculate the A value of the Pt100. After `Close` an additional single temperature calibration performed with e.g. Zinc, enables recalculation of B as well (check position 2 and click OK).

After `OK` you get the Temperature Calibration box displaying the new A, B and C values. On the right in brackets you see the previous values that would remain active when quitting the box with `Cancel`. For your information the deviation of the new temperature scale from the one with the default Pt100 values is calculated at two temperatures: 25 and 500 °C.

With `OK` you accept the new calibration.

Note: When running more than one single temperature calibration, open the `Single Temperature Calibration` box after having finished the last standard. Press `OK` to activate the calculation of the Pt100 parameters based on several experiments. Make sure that you are at the last row (position) of the table produced. Only the values down to the actual position are considered.

The **procedure with manual entry** of the onset temperature(s), e.g. obtained by the indium check, is described as follows:

(1) Call `Calibration/Single Temp. Calib.` in the module control window and select the first calibration substance. Enter the measured onset temperature. The true value is already printed for comparison.

(2) Click the arrow down to come to the next position.

(3) Select the next calibration substance and enter the measured onset temperature. Go on until all measurements are entered and click the `OK` button. Only the rows up to the actual position are considered. `Clear` clears all entries.

(4) After `OK` you get the Temperature Calibration box displaying the new A, B and C values. On the right in brackets you see the previous values that would remain active when quitting the box with `Cancel`. For your information the deviation of the new temperature scale from the one with the standard Pt100 values is calculated at two temperatures: 25 and 500 °C.

(5) With `OK` you accept the new calibration. As a result of this calibration the temperature function of the Pt100 is corrected (the ordinate intercept, A, and - with more than 1 calibration standard - the slope, B, are recalculated, i.e. the natural non linearity of the temperature function is not deformed).

If you prefer interactive evaluation of onset temperatures, develop methods with start temperatures approx. five times the value of the heating rate below the expected temperature of fusion of the substance[1]) and approx. twice the heating rate above the expected temperature of fusion. Usual heating rates are 1…10 °C/min depending on the rates you apply for your later work.

With `None` under `Miscellaneous/Calibration/Type` you suppress the automatic determination of the onset temperatures as well as the automatic entry into the `Single Temperature Calibration box.`

Examples:

Gallium	(29.8 °C):	25 °C through 32 °C with 1 °C/min
Benzoic acid[2])	(122.4 °C)	100 °C through 135 °C with 5 °C/min.

Perform the experiments. In the evaluate window determine the onset temperatures of all fusion peaks. Enter them as above mentioned.

Remark: Several determinations with equal calibration substances give a mean value.

[1]) Only use first order transitions - preferably melting peaks - of high purity calibration substances. The common substances are already available but you may add some new ones under `Install/ Calibration Substance`.

[2]) Seal the pan hermetically to avoid sublimation and evaporation of substances with high vapour pressure.

7.7 The Heat Flow Calibration

This calibration compares the measured heat of fusion of indium with the true value of 28.45 J/g. The result of the heat flow calibration is a new value of the calorimetric sensitivity, E_{In}, expressed in digital steps per milliwatt.

Select the method `Calib DSC Heat Flow` and perform the experiment. At the end a `Heat Flow Calibration` box opens in the module control window , where you see the measured heat of fusion (its true value in brackets) and the new value of E_{In} (the previous in brackets). Accept by `OK`.

Remark: You can run more than one calibration pan, e.g. three Indium pans to get a **mean value:** To do this, compose your own calibration method of the type `Cal. Heatflow Single:.` Open the Method `Calib Heat Flow` in your method window and change the type (under `Miscellaneous/ Calibration`) to `Heat Flow Single`. Save your calibration method, e.g. as `E In Mean`.

Perform some calibration runs using this method. After the last experiment you open the `Single Heat Flow Calibration` box in the module control window. It shows the measured heats of fusion in as many rows (positions) as experiments involved. Go to the last row (position) of the table and press `OK` to activate the calculation of the mean value of E_{In}. Only the values down to the actual position are considered. Now the new E_{In} is displayed. Accept it with `OK`.

7.8 Performing the Calibrations

There is a basic procedure for all necessary calibrations given:

A. Tau Lag Calibration (approx. 1 hour)

(1) Prepare an Indium sample pan according to chapter 7.3.

(2) Open the experiment window and select your method `Calib Tau Lag:In.`

Note for DSC 27HP: Please change the cooling rates (in the segments 2, 4, 6) to 3°C per minute. Save the method as `Calib Tau Lag:In DSC27HP.`

(3) Enter the sample weight `Size` and start the experiment by clicking the respective module button.

(4) At `Insert Sample` open the cell cover and place the In pan on the left pan position of the DSC sensor. Check that there is an empty reference pan on the right-hand side. Close the cell cover and start the measurement by OK.

(5) When finished open the `Single Tau Lag Calibration` box by pressing L in the module control window. You find the determined tau lag value in seconds. Accept it with `OK` when it is between -3…+12 s, else do a second determination. In the `Tau Lag Calibration` box you see the A, B and C values of tau lag. This single sample calibration only changes the A value. Leave the box with `OK`.

(6) Remove the In pan from the cell and place it in the sample box for later use.

B. First Temperature Calibration of a TA4000 DSC Module (approx. 50 min)

The first temperature calibration is performed with a calibration pan included in the standard accessories. This pan contains an indium, lead, and zinc disk in separate compartments. This special calibration is performed with a heating rate of 10 °C/min in the whole temperature range of the DSC module since the analog/digital converter of the Pt100 temperature measurement is calibrated, too.

(1) DSC20, 25, 27HP: Open the experiment window and select the method `Calib Temp:TA4000DSC.`

DSC30: change the start temperature of method `Calib Temp:TA4000DSC` to -100 °C in the method window and save it under, e.g. `Calib Temp:TA4000 DSC30. Now` open the experiment window and select this method

(2) Enter the sample weight `Size` of the indium only and start the experiment by clicking the respective module button.

(3) At `Insert Sample` open the cell cover and place the TA4000 calibration crucible with its three imbedded metals In, Pb and Zn on the left pan position of the DSC sensor. Check that there is an empty reference pan on the right-hand side. Close the cell cover and start the measurement by OK.

(4) When finished a box appears in the module control window viewing the A, B and C values of Pt 100. This triple sample calibration can change the A, B and C values. At the bottom the deviations from the default scale (A=100, B=0.3098) are indicated. Leave the box with OK.

(5) Remove the sample pan from the cell and place it in the calibration pan box for later use.

C. Further Temperature Calibrations (approx. 35 min)

(1) Prepare a dual sample pan (In and Zn) according to chapter 7.3.

(2) Open the experiment window and select the method `Calib DSC Temp In/Zn.`

(3) Enter the sample weight of indium only and start the experiment by clicking the respective module button.

(4) At `Insert Sample` open the cell cover and place the In&Zn pan on the left pan position of the DSC sensor. Check that there is an empty reference pan on the right-hand side. Close the cell cover and start the measurement by OK.

(5) When finished a box appears in the module control window viewing the A, B and C values of Pt 100. This dual sample calibration can change the A and B values. At the bottom the deviations from the default scale (A=100, B=0.3098) are indicated. Leave the box with `OK`.

D. Heat Flow Calibration (approx. 8 min)

(1) Open the experiment window and select the method `Calib DSC Heat Flow.`

(2) Enter the sample weight `Size` of the indium of the pan used for the tau lag calibration and start the experiment by clicking the module button.

(3) At `Insert Sample` open the cell cover and place the sample pan on the left pan position of the DSC sensor. Check that there is an empty reference pan on the right-hand side. Close the cell cover and start the measurement by OK.

(4) When finished the `Heat Flow Calibration` box appears. The measured heat of fusion is indicated. If it is in the acceptable range of approx. 23 … 32 J/g click the `OK` button. Else prepare a new sample and go back to D.1.

(5) Remove the sample pan from the cell and place it in the sample box for later use.

8 The TMA40 Module in operation with the TC15 TA Controller

Content

Safety Notes

The instruments have been tested for the experiments and determinations documen-ted in the appropriate operating instructions. However, this does not absolve you from the responsibility of performing your own tests of the products supplied by us regard-ing their suitability for the methods and purposes you intend to use them for. You should therefore observe following safety measures.

Measures for Your Protection

- Ensure that you plug in the power cable supplied into a socket which is grounded! In absence of grounding, a technical default could have lethal consequences.
- Switch the instrument off, let the TMA40 furnace cool down and disconnect the power cable before you open the housing or change blown fuses! An electrical shock could be lethal!

- Never work in a hazardous area! Explosion hazard through hot surfaces!
- Never use combustible gases or explosive gas mixtures! An explosion could occur!

- Make sure that the power and the signal cable of the same module are connected to the same TC15. The measuring cell could melt, if only the power cable is connected!
- Never switch off the TC15 when the cell temperature is above 300 °C. The cooling fan would no longer work and the cell cover could be heated unduly!

- Never touch the top of the furnace, the probe, the sample support, or a sample just removed from the furnace! The temperature of the furnace can reach 1000 °C.
- Open the furnace only when the temperature is lower than 100 °C! Always use tweezers to remove the lid or the crucible! Place hot items on the stainless steel area on the measuring module.

- Set up the instrument in a fume hood or **ensure a local ventilation**, if a sample may produce toxic gases during reaction.
- Never push objects of any kind through ventilation openings around the furnace!

Measures for operational reliability

- Always keep all air vents clear for proper cooling!
- Always keep the hardware away from any source of liquid!
- When you measure samples with corrosive decomposition products (e.g. HCl split off from PVC), always use a purge gas (50…80 ml). If possible, stop the measurement after the start up of the reaction. With the option *Conditional Experiment Termination* you may create a method with automatic termination!
- Never use corrosive or combustible gases to purge the sample chamber!
- Avoid pushing the probe. Fused silica is brittle !
- Always keep all air vents clear for proper cooling.
- The TMA should not be operated above 300 °C with the low temperature accessory. The dewar vessel could break!
- Avoid the contact of the sample support or the measuring probe (made of fused silica) with alkaline containing substances. Alkaline containing substances corrode the fused silica at higher temperatures.

8 The TMA40 Module in operation with the TC15 TA Controller

8.1 Introduction to the TMA40 Module

In thermomechanical analysis, the length change of a sample subjected to a temperature program is measured. Length changes are monitored by means of a displacement sensor, LVDT.

The temperature range is ambient to 1000 °C, with the low temperature accessory -100…+300 °C.

8.2 Installing the TMA40

8.2.1 Transport of the TMA40

Remove the probe and fix the moving parts with a cylindrical piece of foam before transporting the TMA40.

8.2.2 Location

The TMA40 is a sensitive instrument. Today there is a certain electromagnetic noise field everywhere. It can disturb the sensitive measuring signal causing artefacts.

There should be no rising mains, motors or the like in proximity of the TMA40.

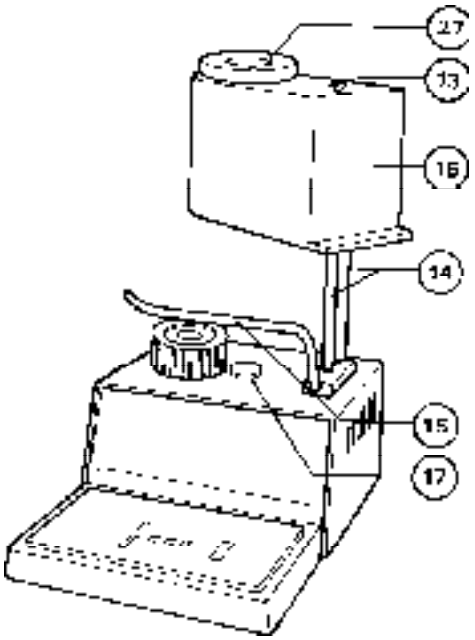
Mind the neighbouring rooms, too!

The measuring cell must stand on a vibration free sturdy table in order to obtain a sufficiently stable TMA signal. A printer working on the same table can create a noisy signal !

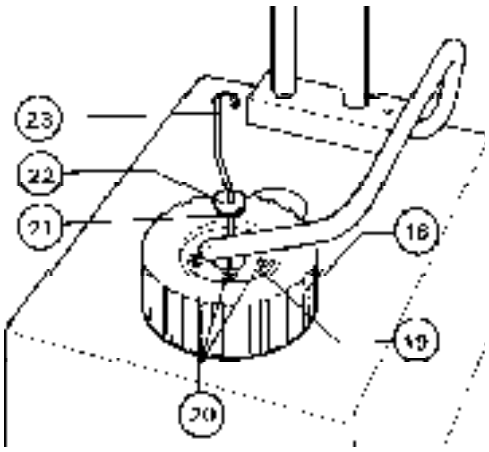
The TMA40 operates trouble-free at room temperature of +10...+32°C and at relative humidity of 25...80%.

8.2.3 Installation of the TMA40 Measuring Cell.

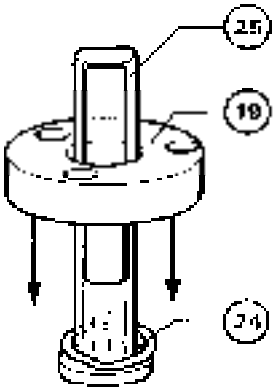
Installation of the Equipment with the TMA40 Measuring Cell: The TMA40 is packed in dismantled form and is made ready for use as follows:



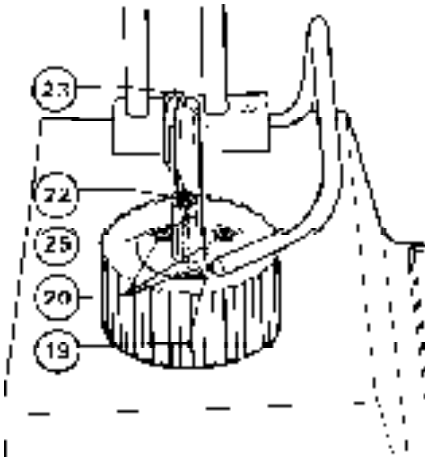
- Remove the knurled screw (13) from the furnace stand rod (14).
- Put the hand rest (15) on the furnace stand rod and push down.
- Put the furnace (16) on its stand rod (14), replace the knurled screw (13) and screw down.
- Take the furnace lid from the attachments and place it on top of the heater body. To do this the standard lead tube for cooling air (27) is taken out.
- Take off the pad placed under the plastic cover (17) which immobilizes the calibration weight during transport.



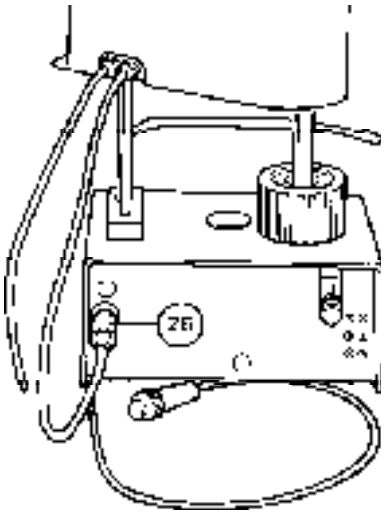
- Rotate the height adjustment ring (18) clockwise to screw it down to the lower stop. The flange (19) of the sample support is also lowered by this.
- Loosen the three screws (20) in the flange (19) of the height adjustment ring and remove the flange.
- Slide the O-ring (21) and reflective washer (22) on the measuring probe (23) upwards to the 1st bend.
- Insert the measuring probe (23) in the central lead through in the height adjustment ring and, holding the probe at the lower vertical part, carefully screw it in to the stop. Then, the measuring probe is released again by at least the measuring system would be to susceptible for vibrations. Note: The measuring probe is made of quartz glass and accordingly fragile.



- Put the spring washer (24), and then the flange (19) on the sample support (25).



- Pass the sample support (25) with flange (19) carefully over the measuring probe, loosely secure with the three screws (23), align and screw down firmly. The reflective washer (22) and the measuring probe should nowhere touch the sample support (25).
- Raise the sample support by rotating the height adjustment ring anti-clockwise until the tip of the measuring probe (23) is in contact with the sample support (25). Now make two more turns.
- Push the reflective washer (22) down with tweezers until it is about 1 cm above the upper rim of the height adjustment ring.



- Insert the power cable (26) for the furnace in the socket at the back of the TMA40 and screw in.

Function Test

Run an isothermal measurement with no sample and a load of 0.10 N at 25 °C or 30 °C during 5 min. Before the start of measurement, go to the sensitive ±0.2 mm range by rotating the right adjustment ring (see chapter 8.4). The resulting measurement curve may drift if the instrument is cold, the noise (peak-peak) should not exceed 0.030 µg, if so, the TMA40 should be placed on a better table without oscillations.

8.2.4 Connecting the TMA40 to the TC15

Connect the power cable with its round 7 pin plug to the appropriate socket at rear of the TC15. Connect the signal cable with its flat 15 pin plug to the flat socket. Connect the 5 pin data cable to the appropriate plugs of the TMA40 and TC15.

Make sure that the power and the signal cable of the same module are connected to the same TC15. The measuring cell could melt, if only the power cable is connected!

Note: When using the TC110 Module Switchbox check that the signal and the power cables of the TMA40 are plugged into sockets with the same number.

8.3 Sample Preparation

The maximum dimensions of the sample under investigation has a height of 20 mm displacement and a diameter of 10 mm.

The sample height (or thickness) to be measured should be adjusted to the analytical problem. The measurement of coefficients of expansion generally requires a tall sample as the expansion is small. On the other hand, determinations of the softening temperature and penetration measurements of e.g. coatings can be carried out even on very thin samples (a few micrometers).

Care should be taken when preparing a sample that the two surfaces that come into contact with the sample support and measuring probe are as nearly parallel as possible. Otherwise false results may be obtained in some situations: Crooked samples or those with ridges on the cut surfaces can for example simulate a large penetration on slight softening.

The sample support and measuring probe are made of fused silica (quartz glass) with a very low coefficient of expansion and a high temperature stability. When preparing the sample, consider that certain substances can harm fused silica. Alkaline containing substances corrode fused silica at higher temperatures so that the measuring attachment should be protected from direct contact with such samples. For this purpose, small inconel trays are included in the standard accessories as support protection which detain metal drops from the calibration sample for example. (drops of tin can adhere so firmly to the sample support that mechanical loosening causes some of the fused silica to be broken off. Fused silica disks or small pieces of aluminum foil can also be used as liners for adherent samples. Other substances cause crystallization of fused silica (e.g. NaCl).

For checking purposes, a blank curve can be recorded without sample. The blank should be reproducible, and show a drift not greater than 1 µm between 50 and 600 °C, or 3 µm over the whole temperature range.

Accurate expansivity measurements require a blank curve. You tell the TA Station that you run a blank by clicking `Run Blank Curve` in the experiment window.

Set the TMA signal to zero by rotating the height adjustment ring until the two center lamps are lit (0.2 mm range, see chapter 8.4) before starting a blank experiment. Otherwise the blank subtraction would shift the TMA curve.

The gas atmosphere around the sample is air flowing from bottom to the top of the furnace ("chimney effect"). Since the system is not tight, measurements in absence of oxygen are impossible (except when using the low temperature accessory).

8.4 Operating the TMA40

8.4.1 Switching On

When you switch on the TC15, the weight of the moving parts of the TMA40 is detected. This takes about 20 s and during this period, the range display on the TMA40 flashes.

The measurement can only be carried out properly if the probe rests freely on a hard base, normally directly on the sample support (the probe may not stick at the support). The position display should not be blinking beacause the position of the probe would be out of range in this case. In addition, the probe must not be manipulated during the measurement.

If the compensation force cannot be determined," ERROR " is displayed on the TC15. After correction of the cause (release of the sticking probe, level adjustment of the sample support, damping of a too fast moving up of the probe), measurement of the compensation force is re-started by operating the key to raise the measuring probe or by switching off and on again the TC15.

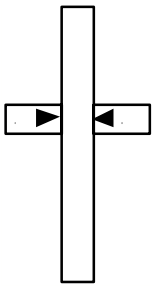
The TMA40 should by switched on (warm up) for at least 2 hours prior to accurate measurements. Consult section 8.3 regarding sample preparation and atmosphere.

Access to the sample chamber is obtained when the furnace body is raised to the upper stop and then swung out to the back.

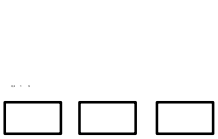
To put on the furnace, the body is swung out to the front in the course of which it is slightly raised to draw it out over the safety barrier and then lowered over the measurement attachment. Move and swing the furnace carefully to avoid shocks to the sample support. It could change the position of the sample.

The small furnace lid, accessible from above, allows visual checking of the sample even after the furnace has been lowered. However, once measurements have begun, the furnace lid should not be opened.

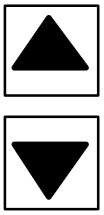
Keyboard:



LED display of the position of the measuring probe in the actual range.



Display of the automatically selected measurement range in positive and negative direction.



Keys for raising and lowering the measuring probe.

To combine a large measurement range with maximum resolution, the range is divided in three sub-ranges with different resolutions. If the probe is displaced from the zero position, it first passes through the most sensitive range of ±0.2 mm. With larger shifts, automatic switching occurs to the ±1 mm and then the ±5 mm range, whereupon the position display jumps back accordingly. If the measuring probe reaches a displacement outside the largest range, the display flashes at the upper or the lower margin.

The exact zero position is indicated by the illumination of both diodes at the zero mark. The measuring probe can be displaced over a range of ±5 mm from the zero position.

The keys for the probe lift are always active even during the measurement. Care should therefore be taken not to press them during measuring. If the measuring probe cannot be raised, although the position display indicates an in-range positionn, the measuring probe has become stuck to the sample. It must be carefully released with tweezers or a razor blade or the sample is softened by heating to e.g. 300 °C.

Height adjustment

The level of the sample support can be moved through about 20 mm with the height adjustment ring in order to adjust the measuring attachment to the size of the sample. Thus it is possible to make measurements within the 0.2 mm range with samples up to a thickness of 5 mm. One complete turn of the height adjustment ring displaces the sample support by 2 mm. If the measuring probe is in contact with the sample support or with a sample, the height adjustment can be followed on the display.

The height adjustment ring can also be rotated when the furnace is lowered.

The sample support should not be raised above the upper range limit (flashing position display) as the measuring probe can be break.

Probe Force

The probe force defined by the method in the TA Station is applied to the sample as compression stress when the probe is lowered. In the standby state, the probe force as specified in the last method used always remains active. When starting a new method, the probe force is altered to the new value. (The message "NEW LOAD" is quickly shown on the display of the TC15.)

Note: Make sure the two entries (min/max load) are identical (method window) to achieve a constant load.

Instead of a constant probe force, an alternating force between a minimum and a maximum value given in the method can be used. This square wave has a fixed frequency of 1/12 Hz. Thus it is possible to monitor viscoelastic changes. In this mode, the range is always ±5 mm to suppress problems with frequent range changes.

The constant probe force attainable without additional weights is limited internally to 0.5 N, corresponding to 50 g. However, it is always possible to increase the force by adding weights to the calibration weight. This weight adds to the force given in the method. For this purpose, the plastic cover beside the height adjustment ring is removed to give access to the calibration weight. Each additional gram increases the probe force by 0.01 N ($9.81 \cdot 10^{-3}$ N). Maximum weigth is 200 g —> +2 N.

With very small probe forces, an increase in signal noise is to be expected especially for hard samples because of the greater sensitivity to vibration. Therefore, for hard samples a load of 0.1 N is recommended which will normally not deform a rigid sample. For soft samples such as plastics, the compression stress has to be lowered by distributing the force with a fused silica disk.

During a measurement, automatic range switching can occur. When this switching from one range to another occurs during a fast length change, it can happen that a discontinuity appears on the plot.

Before sending an experiment to the module control window, the sample size (initial length, thickness) can be measured. The initial length is important, e.g. for expansiti-vity measurements.

(1) Lift the furnace.

(2) Remove any sample and press Probe Lift down.

(3) Press OK at the TC15 to get the display SET ZERO. Here you may adjust the probe position by the height adjustment ring. (For samples larger than 5 mm, go to a negative position, e.g. -3.125 mm, to extend the measurement range.)

(4) Press OK to zero the display.

(5) Press probe lift up. Insert your sample and press probe lift down to get the initial length.

(6) Confirm the initial length with OK. The display changes to CHECK RANGE. Here you may adjust the probe position to the ±0.2 mm range for high resolution. Remain in the negative part when expecting expansion and vice versa.

(7) Lower the furnace, check proper position of furnace lid, and confirm with OK.

(8) To start the experiment, send it to the module control window by clicking on the `TMA` button in the experiment window. Select the probe in the module control window [1]) and press OK.

Notes

- The length display in the module control window only is correct during measurement.
- The length display on the TC15 is set to zero for higher resolution after measuring the initial length.
- Instead of measuring the initial length by the TMA40, you may enter a value determined elsewhere into the field `Size` of the experiment window. Then just click the `TMA` button.

8.4.2 Switching Off

Remove the sample. Ensure the probe is down and the position display in the 0.2 mm range before switching off. If the probe is up, it could break when falling down, If the position display has not been in the 0.2 mm range, at the next power up, the weight detection can fail.

1) **Correcting the expansion of the measuring device**: As a matter of fact, the fused silica probe expands on heating, too. Most of the expansion is automatically compensated by design: the sample support gives an upward contribution on heating, the probe an equal downward contribution as long as there is no sample. But the downward contribution of the probe length that corresponds to the sample thickness is not compensated by an upward contribution of the sample support. This missing upward contribution is corrected mathematically when choosing in the module control window either :

`Ballpoint probe 3mm`, or

`Probe, 1.1 mm diameter`, or

`Probe, 3mm diameter`.

With `Probe with no correction`, the correction is suppressed.

Even more important corrections are made for the expansions of the inconel clamps of the Film Attachments and the Three Point Bending Device.

8.5 Calibrations

The TMA40 needs the following calibrations:

- Length calibration where the actual digital resolution of the three ranges (0.2 mm, 1 mm, 5 mm) of the displacement sensor, LVDT, is determined with suitable gauge blocks.

  The length calibration is carried out with the standard accessory for expansion and penetration measurements, and is valid for the film and fiber attachments, too.

- Force calibration where the two terms of the linear relation between coil current and probe force are determined with the built in calibration weight.

  The force calibration should be done whenever the probe has been exchanged, and especially to obtain accurate loads around zero force. It can be done with the expansion and penetration attachment as well as with the film and fiber attachments.

- Temperature calibration where the three terms of the polynomial $R_{Pt100} = f(T)$ are determined with three melting point standards.

  The temperature calibration with melting point standards is carried out with the attachment for expansion and penetration measurements only. It has to be performed when the `Indium Check TMA` has given a deviation no longer tolerable.

8.5.1 The Length Calibration

The calibration of the displacement sensor is performed with three gauge blocks. These are precision components, and they must be used only when in a clean condition. Before use, the gauge blocks must be cleaned with the deerskin leather supplied.

This calibration is based on difference measurements by interchanging the gauge blocks. Since the TMA40 has three different measuring ranges, they all need calibration.

For the ±0.2 mm range: gauge blocks 1.7 and 2 mm, Δ = 0.3 mm

For the ±1 mm range: gauge blocks 1.0 and 1.7 mm, Δ = 0.7 mm

For the ±5 mm range: gauge blocks 1.0 and 1.7 + 1.0 and 1.7 + 2 mm, Δ = 3.7 mm

The tolerances of the gauge blocks are ±0.0004 mm. Now do the following:

In the module control window, select `Calibration/Length Calibration`. Click `Start` if the displayed gauge thickness values are correct. Follow the TC15 display:

TC15 commands:		**Things to do on the TMA40:**
TC15:	SET ZERO	Place the 1.7 gauge block on the sample support. Press Probe Lift down. By turning the height adjustment ring, bring the the probe into the range of ±0.2 mm: turn the ring until the fourth lamp below zero is lit.
TC15:	OK	
TC15:	***CALCULATING***	The zero position in the range ±0.2 mm is measured.
TC15:	INSERT SAMPLE 0.30	Press Probe Lift up and remove the 1.7 mm gauge block. Place the 2.0 mm gauge block and lower the probe.
TC15:	OK	
TC15:	***CALCULATING***	The difference in thickness is measured in the range of ±0.2 mm and compared with the value of 0.3 mm..
TC15:	REMOVE SAMPLE	Lift the probe and remove the 2.0 mm gauge block. Place the 1.0 mm gauge block and lower the probe. By turning the height adjustment ring, bring the probe to the zero position (one or both lamps in the middle of the position display are lit).
TC15:	OK	
TC15:	***CALCULATING***	The zero position is measured.
TC15:	INSERT SAMPLE 0.70	Lift the probe and replace the 1.0 mm gauge block by the 1.7 mm gauge block. Press Probe Lift down.
TC15:	OK	
TC15:	***CALCULATING***	The difference in thickness is measured in the range of ±1 mm and compared with the value of 0.7 mm.
TC15:	REMOVE SAMPLE	Replace the 1.7 mm gauge block by the 1.0 mm gauge block and lower the probe. By turning the height adjustment ring, bring the probe to the zero position, if need be (one or both lamps in the middle of the position display are lit).
TC15:	OK	
TC15:	***CALCULATING***	The zero position is measured.
TC15:	INSERT SAMPLE 3.7	Remove the 1 mm gauge block. Lay the gauge blocks one on top of the other at an angle of 90 ° and squeeze out the air by turning them together. Place all three gauge blocks and lower the probe.
TC15:	OK	
TC15:	***CALCULATING***	The difference in thickness is measured in the range of ±5 mm and compared with the value of 3.7 mm.
TC15:	REMOVE SAMPLE	Remove the gauge blocks and lower the probe.
TC15:	OK	The length calibration box appears. If the calculated values are correct confirm with `OK` in the module control window. Otherwise click `CANCEL` and repeat the calibration procedure.

8.5.2 The Probe Force Calibration

This calibration should be performed whenever the measuring probe is changed, but at least four times a year. To do this, the compensating force is measured with and without the calibration weight that is normally inserted.

Calibration is carried out with the measuring probe in use but without any sample. Care should be taken to ensure that the probe can freely move. It should not stick nor touch the sample support. The measuring probe is adjusted to the center of the ±0.2 mm range with the height adjustment ring.

In the module control window, select `Calibration/Force Calibration`. Confirm with `OK` on the TA Station. Follow the TC15 display, and press OK on the TC15 when done, wait during CALCULATING. The force calibration box appears in the module control window with the offset value and the slope (default value for offset is 219 Bit, for slope -414 Bit/N). Confirm your calibration with `OK`. `Cancel` will not save the new data.

Note: If the probe touches the upper limitation - especially during `Remove Calibration` - the calibration stops with ERROR2. Solution: Limit the upward movement during calibration with your left forefinger (approx. 5 mm above the probe).

8.5.3 The Temperature Calibration

Temperature calibrations that are performed wrongly lead to a wrong temperature scale. Hence this work should be carried out only by especially qualified personnel !

Contrary to the temperature calibrations, the Indium Check is a normal method with automatic evaluation and validation of the result. It doesn't change any instrument parameters.

In the TA Station there are some calibration methods ready for use. There names begin with `Calib`.

You may also compose your own calibration methods in the method window. Don't forget to select the type of calibration under `Miscellaneous/Calibration/Type`.

The Temperature Check

It is good laboratory practice to check the temperature accuracy once every month. The Indium check is based on measuring the melting point of an indium sample. For this pupose, a very small flat piec of indium is placed between fused silica disks. When molten, the sample is squeezed out causing a TMA step.

The Indium check is passed when the inflection point is found within a tolerance of ±2 °C compared with the true value of 156.6 °C.

The respective method is named : `Indium Check TMA`. Use a very small piece of indium, approx. 0.2 mg (1/30 of an indium pill, see Accessories). Place it between fused silica disks on the sample support. A bigger sample would be squeezed out too late since the whole sample has to be in the liquid state.

Press Probe lift down, lower the furnace, and turn the weight adjustment ring to a probe position in the center of the 0.2 mm range. A size entry is not required.

If you are interested in other temperatures as well - you can compose a similar lead (Pb) or aluminum check.

A calibration of temperature has to be performed when the check has given results with deviations no longer tolerable: As long as the measured melting point remains within the tolerances, your measuring cell does not need a temperature calibration.

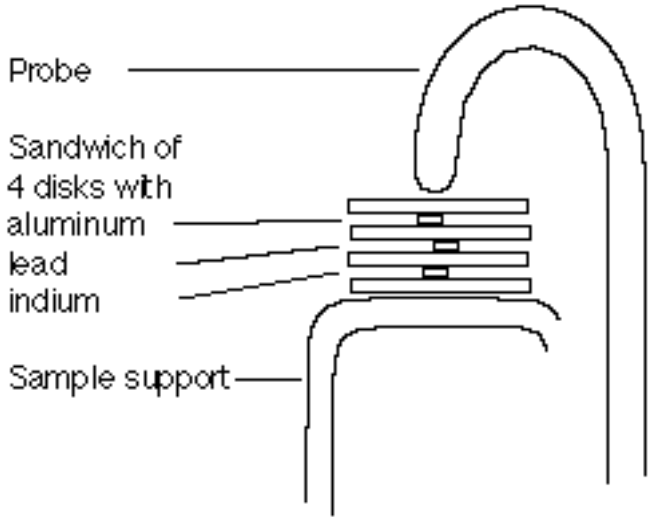
With an indium check after calibration experiments you make sure that the calibrations have been done properly.

8.5.4 Performing Temperature Calibrations

There is a basic procedure for all necessary calibrations given:

First Temperature Calibration of a TMA40 Module (approx. 85 min)

The first temperature calibration is performed with a sandwich of 4 fused silica ("quartz") disks, containing a very small disk of indium, a very small disk of lead, and a very small disk of aluminum. Cut off small pieces from the delivered disk. The maximum weight is 0.5 mg each. This special calibration is performed with a heating rate of 10 °C/min in the whole temperature range of the TMA module since the analog/digital converter of the Pt100 temperature measurement is calibrated, too.



(1) Check the default values for tau lag on the module printout (`Install/ Module/ Open/ Calibration Overview`): A= 116, B= -0.2299 T, C= 0.000121 T^2.

(2) Open the experiment window and select the method `Calib Temp: TA4000 TMA`. The sample thickness `Size` is not entered.

(3) Place the sandwich in the center of the sample support. Lower the probe and the furnace.

(4) Move the probe position to the top of the 0.2 mm range.

(5) Start the experiment by clicking the TMA module button.

(6) At `Insert Sample` check the 0.2 mm range and the proper position of the lid on top of the furnace. Start the measurement by OK.

(7) When finished a box appears in the module control window viewing the A, B and C values of Pt 100. This triple sample calibration can change the A, B and C values. At the bottom the deviations from the default scale are indicated (A = 100, B = 0.3908 and C = $-58.02 \cdot 10^{-6}$) are indicated. Leave the box with OK.

(8) Remove the sample sandwich from the cell below 50 °C.

Note: Since the melting point standards are squeezed out after the run, the sandwich can only be used once.

Further Temperature Calibrations (approx. 85 min)

(1) Prepare a triple sample sandwich as described in 5.3.1.

(2) Open the experiment window and select the method `Calib Temp: TMA`.

(3) Place the sandwich in the center of the sample support. Lower the probe and the furnace.

(4) Move the probe position to the top of the 0.2 mm range.

(5) Start the experiment by clicking the TMA module button.

(6) At `Insert Sample` check the 0.2 mm range and the proper position of the lid on top of the furnace. Start the measurement by OK.

(7) When finished a box appears in the module control window viewing the A, B and C values of Pt 100. This triple sample calibration can change the A and B values. At the bottom the deviations from the default scale (A=100, B=0.3908) are indicated. Leave the box with OK.

(8) Remove the sample sandwich from the cell below 50 °C.

(9) Perform an `In Check TMA`.

8.5.5 Background Information Concerning Calibrations

The Automatic Multiple Temperature Calibration

A sandwich of 4 fused silica disks with the enclosed melting point is used at least once to perform the so called TA4000 temperature calibration (`Method/ Miscellaneous/ Calibration/ Type/ Temp.TA4000`). This special calibration is performed with a heating rate of 10 °C/min in the whole temperature range of the TMA module since the analog/digital converter of the Pt100 temperature measurement is calibrated, too. At the same time the inflection points of the TMA steps caused by the squeezed out melting point standards are compared with the true values to calculate the new temperature function, C.

The temperature function of the electrical resistance of the Pt100 is modelled as follows:

$R = A + B \cdot T + C \cdot T^2$

The default values are:

$A = 100\ \Omega$

$B = 0.3908\ \Omega \cdot °C^{-1}$

$C = -58.02 \cdot 10^{-6}\ \Omega \cdot °C^{-2}$

After having performed a TA4000 temperature calibration a further temperature calibration can result in a higher temperature accuracy:

The automatic multiple sample temperature calibration is based on one experiment using a sandwich with at least two calibration standards such as In and Pb. As a result of this calibration the temperature function of the Pt100 is corrected (the ordinate intercept, A, the slope, B, are corrected, i.e. the non linearity of the temperature function, C, is not changed).

Select method `Calib Temp.: TMA`. You may also compose your own calibration method in the method window. Don't forget to select `Temp.Multiple` as type of calibration under `Miscellaneous/Calibration/Type`. After the experiment you get the Temperature Calibration box displaying the new A, B, C values. On the right in brackets you see the previous values that would remain active when quitting the box with `Cancel`. For your information the deviation of the new temperature scale from the one based on the default Pt100 values is calculated at two temperatures: 25 and 500 °C.

With `OK` you accept the new calibration.

The Single Temperature Calibration

In this temperature calibration one or several single sample crucibles are measured in individual experiments. There are two procedures of single temperature calibrations:

- **Performing single temperature calibrations** with automatic entry into the single temperature calibration box of the module control window. Compose your own methods with each time the same experimental condition (tempreature range, heating rate) in the method window. Don't forget to select `Single Temperature Calibration` as type of calibration under `Miscellaneous/Calibration/Type`.
- **Manual entry** of measured melting temperature(s) into the single temperature calibration box of the module control window. One measured melting temperature can be based on an indium check for example.

Perform the experiment with the single temperature calibration. When finished call `Calibration/Single Temp. Calib.` in the module control window:

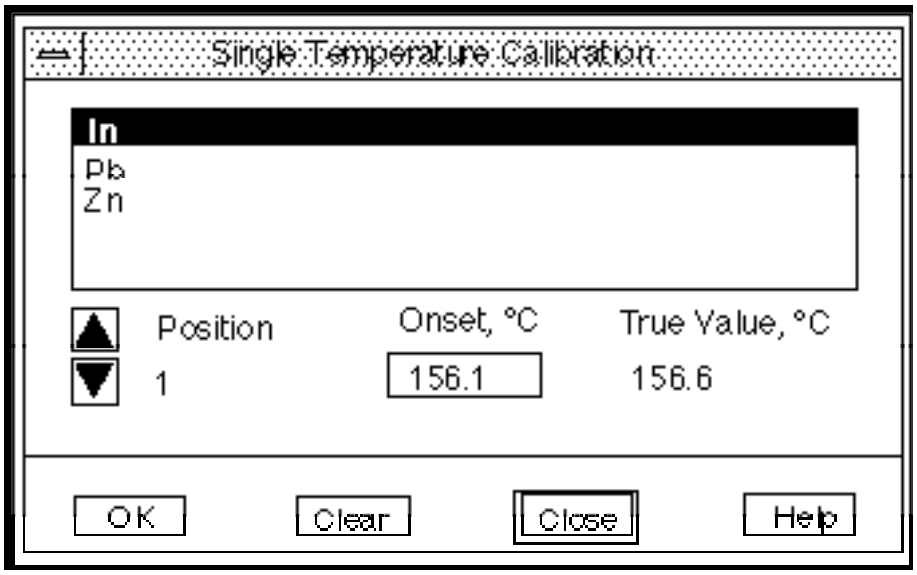


Fig. x: In the first row or position the measured melting temperature has been entered automatically. OK at position 1 would only recalculate the A value of the Pt100. After `Close` an additional single temperature calibration performed with e.g. isatherm, enables recalculation of B as well (check position 2 and click OK).

After `OK` you get the `Temperature Calibration` box displaying the new A, B and C values. On the right in brackets you see the previous values that would remain active when quitting the box with `Cancel`. For your information the deviation of the new temperature scale from the one with the default Pt100 values is calculated at two temperatures: 25 and 500 °C.

With `OK` you accept the new calibration.

Note: When running more than one single temperature calibration, open the `Single Temperature Calibration` box after having finished the last standard. Press `OK` to activate the calculation of the Pt100 parameters based on several experiments. Make sure that you are at the last row (position) of the table produced. Only the values down to the actual position are considered.

The **procedure with manual entry** of the measured melting temperature(s), e.g. obtained by the indium check, is described as follows:

(1) Call `Calibration/Single Temp. Calib.` in the module control window and select the first calibration substance. Enter the measured melting temperature. The true value is already shown for comparison.

(2) Click the arrow down to come to the next position.

(3) Select the next calibration substance and enter the measured melting temperature. Go on until all measurements are entered and click the `OK` button. Only the rows up to the actual position are considered. `Clear` clears all entries.

(4) After `OK` you get the `Temperature Calibration` box displaying the new A, B and C values. On the right in brackets you see the previous values that would remain active when quitting the box with `Cancel`. For your information the deviation of the new temperature scale from the one with the standard Pt100 values is calculated at two temperatures: 25 and 500 °C.

(5) With `OK` you accept the new calibration. As a result of this calibration the temperature function of the Pt100 is corrected (the ordinate intercept, A, and - with more than 1 calibration standard - the slope, B, are recalculated, i.e. the non linearity of the temperature function is not changed).

If you prefer an interactive evaluation of Curie temperatures, develop methods with start temperatures approx. five times the value of the heating rate below the expected measured melting temperature of the substance and approx. five times the heating rate above the expected melting point temperature. Usual heating rates are 1…10 °C/min (select the rate you apply for your later work).

With `None` under `Miscellaneous/Calibration/Type` you suppress the automatic determination of the temperatures at the inflection point as well as the automatic entry into the `Single Temperature Calibration box.`

Examples:

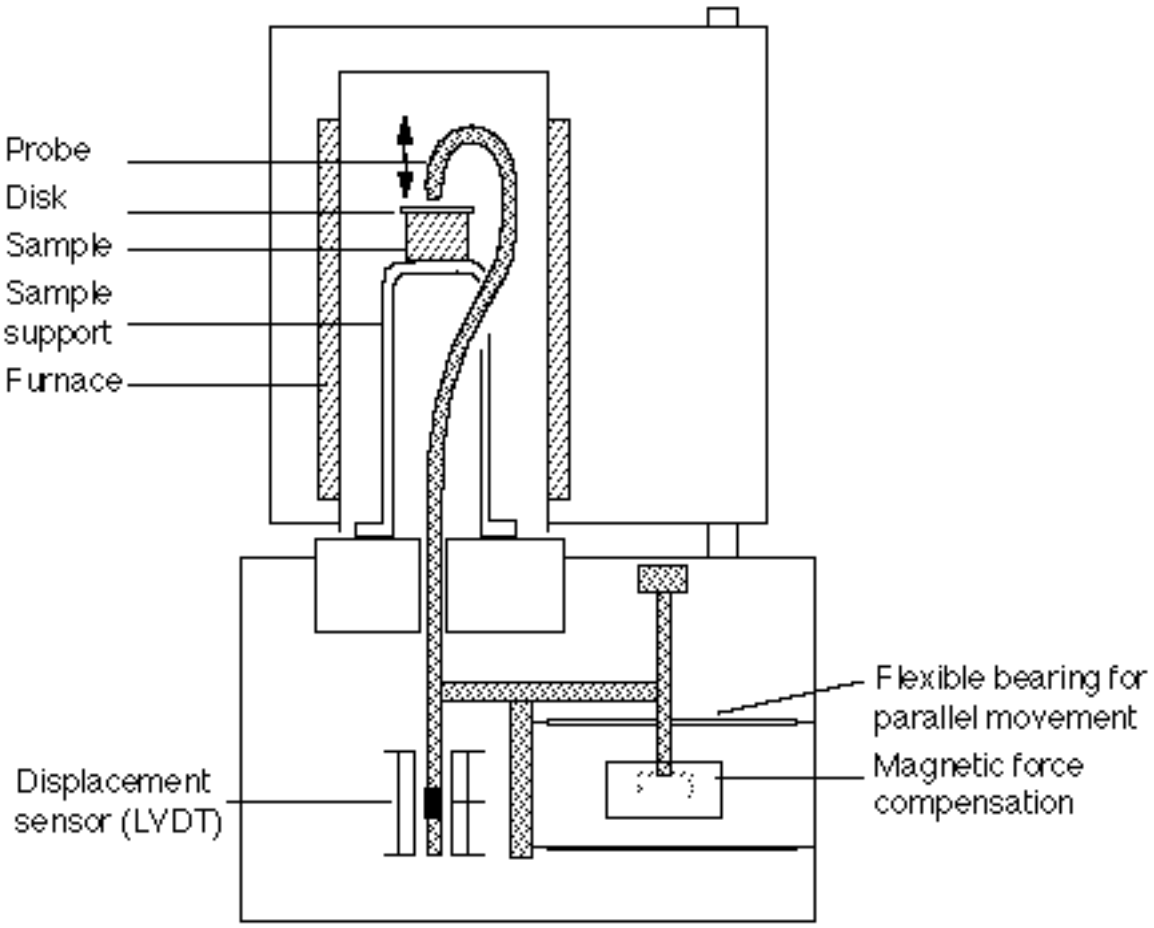
indium In	(156.6 °C):	140 °C through 170 °C with 2 °C/min
lead Pb	(327.5 °C)	300 °C through 350 °C with 5 °C/min.

Perform the experiments. In the evaluate window determine the inflection point of the TMA step (`Evaluate/TA/Step Tang.`). Enter them as above mentioned.

Remark: Several determinations with equal calibration substance give a mean value.

8.6 Description of the TMA40

8.6.1 Construction of the TMA40 Module



The sample is placed on the sample support made of fused silica ("quartz glass"). Any dimensional changes are monitored by the displacement sensor, LVDT. The ferromagnetic core of the LVDT moves up and down with the probe that is in contact with the sample surface. The probe is also made of fused silica. Fused silica has an extremely small expansivity. The probe force is controlled by the magnetic force compensation device and ranges from 0…0.5 N. The actual stress on the sample depends on the geometry of the probe tip (ball point, 1.1 mm Ø, 3 mm Ø) and is much influenced by topping the sample with a fused silica disk to distribute the force evenly. In addition to the constant load mode, square waves of a period of 12 s are also possible (Dynamic Load TMA, DLTMA).

In addition to the standard expansion and compression setup, there are attachements for:

- tensile strain measurements of films and foils
- tensile strain measurements of fibers
- 3 point bending measurements

When the furnace housing with the built in cooling fan is lowered, the furnace body covers the whole sample support and the probe. The actual temperature of the furnace is measured by a Pt100 sensor.

8.6.2 Temperature Equilibration

The temperature should follow a program predefined in the method. To ensure this the sample is first brought to the insert temperature, and subsequently the furnace temperature is controlled in a suitable manner by the TC15. The tau lag parameters A, B and C define the temperature function of the time constant, tau lag, between furnace and sample.

The settling period

During the settling period before the start of the first segment, (display: SETTLING), the sample is brought to the start temperature. The settling period depends on the initial temperature as is shown in the table settling time. The values given assume that the sample has the ambient temperature of approx. 25 °C at the moment of insertion, thus the settling time is zero when starting at 25 °C.

The following equation estimates the time necessary to bring the sample from ambient 25 °C to the isothermal furnace start temperature T:

$$t_{SETTLING} = \text{tau lag (T)} \bullet \ln (T - 25\ °C)$$

The equation only is valid for T ≥ 26 °C. With 25 < T < 26 °C the settling time is zero.

This settling time automatically precedes the measurement in order to ensure that the sample has reached the initial temperature to within one degree. The settling times for selected insert temperatures are tabulated below.

During heating to the insert temperature, the fast furnace control can appreciably overshoot the insert temperature. The sample itself is not heated above the insert temperature, however, owing to the slow temperature equilibration.

If the settling period is skipped (FORCED START by pressing OK during settling,) the sample does not necessarily reach the preset temperature at the start.

START TEMPERATURE	When ever possible use 25 °C. In this case the settling period is zero.
HEATING RATE	The heating rate depends on the application: - Rough screening 50 K/min - Screening 20 K/min - For good temperature homogeneity in the sample: 5 K/min
END TEMPERATURE	Use a method with a high enough end temperature. The measurement can be stopped early simply by pressing RESET.The maximum

value of the TMA40 is 1000 °C.

8.6.3 The Temperature Control

The furnace temperature is controlled in such a way that the theoretical sample temperature follows the desired profile. The theoretical sample temperature is the temperature of an inert sample with the same heat capacity as the real sample. A real sample undergoes endo- or exothermal reactions causing temperature differences compared with the theoretical sample.

The time constant of the heat transfer from furnace to the sample is called tau lag and depends on temperature. The time constant is calculated as follows:

$$\text{tau lag} = A + BT + CT^2$$

where the default values of A, B and C are:

$A = 116$
$B = -0.23\ T$
$C = 0.000121\ T^2$

To ensure that the sample temperature follows the temperature program in a dynamic measurement, the furnace temperature must be higher by a certain amount. This temperature difference depends on tau lag and on the heating rate. The same applies to controlled cooling in an analogous manner. The furnace advance is calculated with the following equation:

$$\Delta T = T_{furnace} - T_{sample} = \text{tau lag} \bullet \beta$$

where β is the heating rate. Furnace and sample temperature during a dynamic measurement of 1 segment are shown graphically in the illustration.

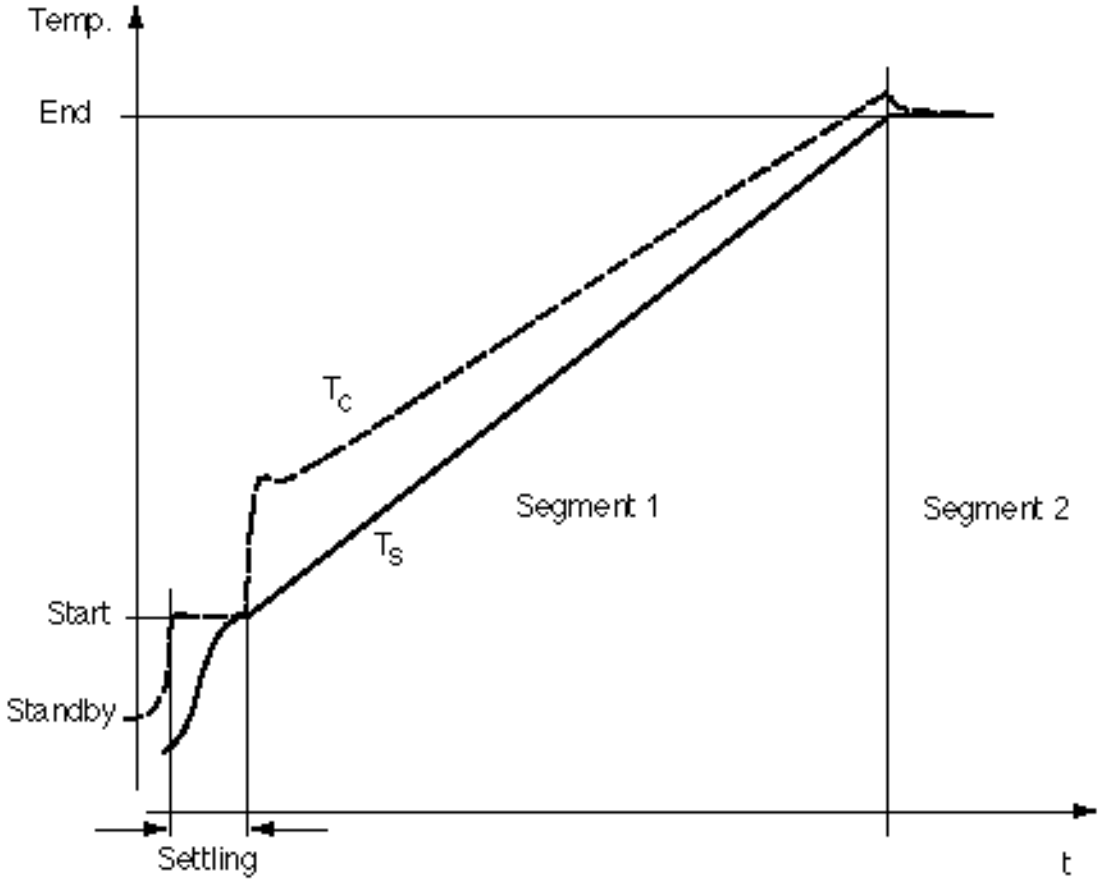


Table for estimating the settling time and the advance of the furnace temperature with the default tau lag parameters:

Temperature	**τ lag**	**SETTLING time**	**Advance °C**		
°C	min	min	10 K/min	20 K/min	50 K/min
20	1.86	2.99	19	37	93
25	1.84	0	18	37	92
30	1.82	2.93	18	36	91
50	1.75	5.62	18	35	87
100	1.57	6.78	16	31	79
200	1.25	6.44	12	25	62
500	0.52	3.21	5	10	26
900	0.12	0.74	1	2	6

8.7 The Low Temperature Accessory

Measurements can be carried out in the range -100 °C up to a maximum of 300 °C with the low temperature accessory and liquid nitrogen as refrigerant. Controlled cooling is possible, too. Purging with dry purge gas (helium or possibly nitrogen) is indispensable for cooling as well as to prevent moisture condensation and icing up. The necessary time to cool from ambient to -100°C is approx. 5 minutes with helium but 15 minutes with nitrogen.

– It is essential to wear gloves and protective goggles when handling liquid nitrogen! Liquid gases can cause severe skin burns!

– When working in closed rooms, ensure good ventilation (danger of suffocation).

– The containers may be handled only by people trained for such a purpose and who pay attention to the accident prevention regulations of the manufacurer of the liquid nitrogen container.

– The TMA40 should not be operated above 300 °C with the low temperature accessory. The dewar vessel could break!

8.7.1 Installing

(1) Remove metal insert from the furnace housing.

(2) Remove standard furnace lid and insert special aluminum lid.

(3) Strip the ceramic fiber disk with the large hole over the furnace. Strip the ceramic fiber disk with the small hole over the sample support and cover it with the guard disk.

(4) Connect purge gas tubing carefully to the purge gas inlet of the low temperature accessory using the screw fitting.

(5) Insert low temperature accessory in the furnace housing. This automatically disconnects the fan. Turn the accessory in order to get vacuum outlet always to the same side , e.g. at rear.

8.7.2 Preparing the TA Station

(1) Go to Install/Topic/Module and select TMA40 from the New Module box.

(2) Enter the identification number of your TC15.

(3) Don't select any gas under Gas Control in version 2 and save the module as , e.g. TMA LT/He.

(4) Connect the module to a free port and double click the module icon.

(5) Enter the tau lag constants under Calibrations/Single Tau Lag Calibration.

(6) Select Air and In.

(7) Click the OK button to get the Tau Lag Calibration box

(8) Enter A, B and C as follows:

- with helium purge A= 64 B=0.02 C=-0.00075
- with nitrogen purge A=180 B=-0.174 C=-0.00097

(9) Leave the box with OK

Now the low temperature TMA is ready for temperature calibration.

8.7.3 Temperature Calibration

(1) Prepare a TMA method of the calibration type `Temp TA4000` using `n-coctane, gallium` and `indium` as calibration substances. Starttemperature, endtemperature and heating rate are -100 °C,+200 °C and 10K/min. Enter an `Insert Temperature/User` of -100 °C to allow the octane freezing at the insert temperature. The force is 0.4/0.4 Newton. Don't change the gas air to helium. Save your method as, e.g. `Calib Temp TMA/ LN2`

(2) Call the method, place 4 fused silica disks on the sample support, lower probe lift and rotate the height adjustment ring until you reach the ± 0.2 mm range.

(3) Press `OK` and after SET ZERO, 3 times `OK` again

(4) In the experiment window choose your calibration method and enter a size of 1 mm. Send it to the TMA module.

(5) Start the experiment by clicking the respective module button.

(6) Set the helium purge to 150 ml/min. Fill the dewar with liquid nitrogen and keep the furnace swung out (the furnace temperature goes to the insert temperature of -100 °C).

(7) Meanwhile prepare your sandwich consisting of (from botton to top):

- fused silica disk
- ≤ 0.5 mg In
- fused silica disk
- ≤ 0.5 mg Ga
- fused silica disk
- dropplet of n-octane
- now place the last fused silica disk swimming on the n-octane

(8) Lower the furnace carefully over the sample

(9) Add liquid nitrogen, if need be and allow the n-octane crystallizing during approx. 5 minutes (the TC15 display shows INSERT SAMPLE).

(10) Then lower the probe lift on the frozen sample (if stuck touch the calibration weight with tweezers) until the display of the probe position moves towards center.

(11) To start the measurement, confirm INSERT SAMPLE by `OK`.

(12) Check the 3 steps caused by squeezing out the molten samples.

(13) Finally you get the `Temperature Calibration` box and confirm it by `OK`

8.8 Attachment for Film Measurements

The attachment for film measurements is used for the investigation of foils and films with the TMA40. The sample is stretched between the sample support and the lower lying measuring probe. The probe force thus here acts as a tensile stress to the sample.

8.8.1 Installation of the Film Attachment

(1) Switch on TMA40 with the standard penetration attachment

(2) When the range display no longer flashes, remove the 3 screws in the flange of the sample support

(3) Remove the flange carefully

(4) Press PROBELIFT UP, carefully remove the sample support without breaking the probe

(5) Unscrew the probe carefully and switch off the TMA

(6) Insert the film probe and carefully screw it into the stop. Release the probe by at least half a turn. Make sure the reflective washer is mounted approx. 20 mm below hooks.

(7) Insert the sample support and the spring washer

(8) Insert the flange and fix the 3 screws. Align the sample support in order it doesn't touch the reflective washer nor the probe

(9) Lower the height adjustment ring until you can insert the probe holder (fig.1)

(10) Switch on the TMA and bring the range display into the 0.2 mm range and perform the force calibration

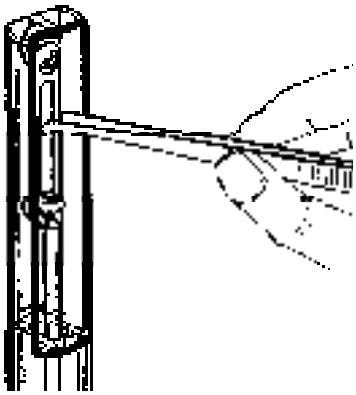


Fig. 1: **Important** : Before switching on, check whether the probe holder is placed between the sample support and the measuring probe, so that the probe is held at about the middle of the ±0.2 mm range. The weight of the moving parts can only be determined when this is done.

Before switching off, place the probe holder and bring the probe position to the ±0.2 mm range

(11) Select the probe `film attachment with inconel clamps` in the module control window. A lowering of the measuring probe is now interpreted as an extension of the sample and the expansion of the clamps is compensated by calculation..

(12) Whenever you change the measuring attachment , the probe force must be re-calibrated as the measuring probes have different weights.

8.8.2 Temperature Calibration

When the film attachment is employed, it is not posssible to use the melting point method. The calibration carried out with the penetration system is inexact as different supports and measuring probes are used. The actual sample temperature for a fixed parameter set A, B, C differs by approx. 10....20 K for the film attachment and the penetration system. The best is to insert a thermocouple consisting of thin glass fiber insulated wires using the respective clamps. With the parameters A_{Pt100}= 100, B_{Pt100} =0.3908, C_{Pt100}= -5.802x10^{-5}, perform a heating curve in the temperature range of interest using 10 °C/min or your own heating rate.

(1) Choose three temperatures evenly distributed over the range of interest, e.g. 50 °C, 150 °C and 250 °C (true values).

(2) Enter these values under `Install/Calibration Substance`

(3) Save as, e.g. `Elect 50, Elect 150` and `Elect 250`.

When a digital thermometer connected to the thermocouple shows one of the choosen temperatures, read the TC15 display simultaneously. These values are later on entered as "Onset".

When all value pairs are collected call `calibration/Single Temperature Calibration` in your module window. Choose `Air` and your 3 "Elect" Calibration substances.

(4) Enter the TC15 value as an Onset in the respective three positions. Press `OK` and accept the obtained A, B, C parameters by `OK`.

The film measuring attachment includes a glass fiber insulated thermocouple of type K(NiCr-Ni) that can be used up to +500 °C. A pocket thermometer can be used, e.g. Keithley 871.

Note: If you often switch between the penetration and the film attachment, you best define an appropriate module for each configuration. This procedure is time saving since all calibrations are kept in memory.

8.8.3 Sample Preparation

When films are being investigated, samples of 15 times 6 mm are stamped out with the sample punch contained in the standard accessories. For this purpose, place the film on a relatively soft material (e.g. cardboard). A sample is obtained with cleanly cut edges with a sharp blow on the vertical punch.

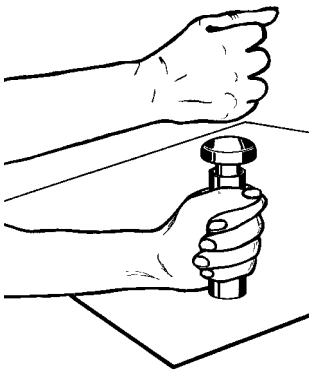
Note: Vibrations near the TMA40 should be avoided during the measurement.

(1) After cutting out, fix the sample in the clamps with the help of the assembly jig. The screws should not be tightened too much as the elastic behavior is affected by deformation of the film, furthermore the clamps would deform.

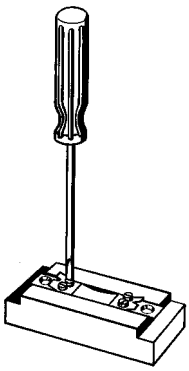
(2) After fixing, the sample should have a free length of exactly 10 mm in the absence of stress.

(3) Enter the effective film length of 10 mm in the entry field `Size` in the experiment window.

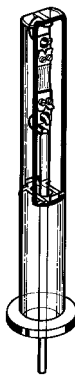
(4) Attach the sample first to the sample support and then to the measuring probe. Mind the brittle fused silica hooks. In order to prevent the lower clamp from falling into the sample support tube in case the sample melts, place the collecting plates.



Stamping our the sample



Assembly jig
with sample in place



Film
attachment

Correctly mounted samples should be neither crooked nor twisted. The edges of the sample should be straight and parallel in the long dimension.

When relatively large changes in length are to be measured, move the measuring probe with the sample support to the upper or lower limit of the measuring range before starting the measurement by rotating the height adjustment ring.

Notes:

- Never move the probe above the range limit (flashing position display) as it can then break.
- The inconel clamps allow measurements up to approx. 600 °C.
- The slight extension of the inconel clamps is compensated by the software (provided the `probe with attachment with inconel clamps` is selected.

8.9 Attachment for Fiber Measurements

The fiber attachment comprises a probe with twin traction hooks and mounted infrared reflector as well as a sample carrier with two hooks.

The TMA fiber attachment may be installed only in an instrument calibrated with the penetration accessory (see TC15 TMA Operating instructions, temperature and length calibration). The calibration of the length measurement is used for the fiber attachment, too.

8.9.1 Installation of the Fiber Attachment

(1) Switch on TMA40 with the standard penetration attachment

(2) When the range display no longer flashes, remove the 3 screws in the flange of the sample support

(3) Remove the flange carefully

(4) Press PROBELIFT UP, carefully remove the sample support without breaking the probe

(5) Unscrew the probe carefully and switch off the TMA

(6) Insert the fiber probe and carefully screw it into the stop. Release the probe by at least half a turn. Make sure the washer (IR reflector) is mounted approx. 20 mm below hooks.

(7) Insert the sample support and the spring washer

(8) Insert the flange and fix the 3 screws. Align the sample support in order it doesn't touch the IR reflector nor the probe

(9) Lower the height adjustment ring until you can insert the probe holder (fig.1)

(10) Switch on the TMA and bring the range display into the 0.2 mm range and perform the force calibration

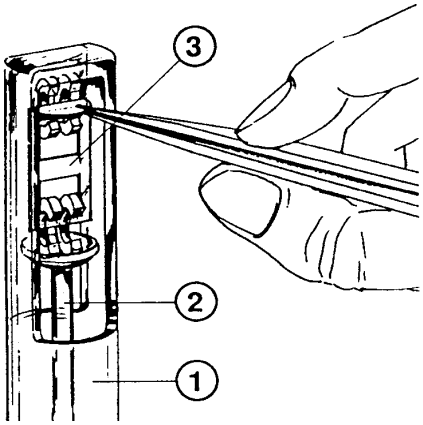


Fig. 1: **Important** : Each time the instrument is switched on, the probe holder (3) must be between sample support (1) and measuring probe (2), and the measuring probe should be approximately in the middle of the measurement range. Only with this arrangement the compensation force for the measuring probe weight can be determined.

Note: Recalibrate the probe force each time you change the measuring attachment, since each measuring probe has a different weight.

(11) Select the probe fiber attachment in the module control window

A lowering of the measuring probe is now interpreted as an extension of the sample

(12) Enter the tau lag parameters under `Calibration/Single Tau Lag` as follows:

C1 120

C2 -0.451

C3 0.000493

8.9.2 Temperature Calibration

When the fiber attachment is employed, it is not posssible to use the melting point method. The calibration carried out with the penetration system is inexact as different supports and measuring probes are used. The actual sample temperature for a fixed parameter set A, B, C differs by approx. 10....20 K for the fiber attachment and the penetration system. The best is to insert a thermocouple consisting of thin glass fiber insulated wires using the respective clamps. With the parameters A_{Pt100}= 100, B_{Pt100} =+0.3908, C_{Pt100}= -5.802x10^{-5}, perform a heating curve in the temperature range of interest using 10 °C/min or your own heating rate.

- Choose three temperatures evenly distributed over the range of interest, e.g. 50 °C, 150 °C and 250 °C (true values).
- Enter these values under `Install/Calibration Substance`
- Save as, e.g. `Elect 50, Elect 150` and `Elect 250`.

When a digital thermometer connected to the thermocouple shows one of the choosen temperatures, read the TC15 display simultaneously. These values are later on entered as "Onset".

When all value pairs are collected call `calibration/Single Temperature Calibration` in your module window. Choose `Air` and your 3 "Elect" Calibration substances.

- Enter the TC15 value as an Onset in the respective three positions. Press `OK` and accept the obtained A, B, C parameters by `OK`.

A glass fiber insulated thermocouple of type K(NiCr-Ni) can be used up to +500 °C. (Order number 29964). Pocket thermometers can be used, e.g. type Keithley 871.

Note: If you often switch between the penetration and the fiber attachment, you best define an appropriate module for each configuration. This procedure is time saving since all calibrations are kept in memory.

8.9.3 Sample preparation

(1) Place the fiber (optimum length 80 mm, minimum 45 mm) between the copper clamps fitted in the fiber mounting device (distance 13 mm for fibers with small length changes. The smaller distances are good for fibers with strong changes).

(2) Clamp the fiber by turning the hand wheel.

Very brittle fibers require careful turning.

(3) Shorten the projecting fibers to a length of approx. 2mm.

(4) Enter the effective fiber length of 13 mm in the entry field `Size` in the experiment window.

Notes:

- The copper clamps allow measurements up to approx. 600 °C.
- The slight extension of the 1 mm copper clamps, is compensated by the software (provided the probe `fiber attachment with copper clamps` are selected).
- If the adhesion is inadequate, the grip of the copper clamps can be improved, e.g. by heating to redness at around 800 °C and quenching in cold water. Oxide layers can be removed with dilute hydrochloric acid (approx. 5 % HCl) to prevent any disturbing effect on the measurements.

8.10 The Three Point Bending Device

8.10.1 Compression vs. Bending

Rigid samples give very small length changes in the compression mode. When the length change comes close to the one without sample the bending device often is advantageous.

The length change without sample is given by the TMA's spring constant of approx. 10 µm per Newton, i.e. a force change of 0.1 N causes a "blank" deflection of approx. 1 µm. With the bending device the measured flexure depends mainly on the thickness of the sample specimen and can amount to several 100 µm.

8.10.2 Using the Bending Device

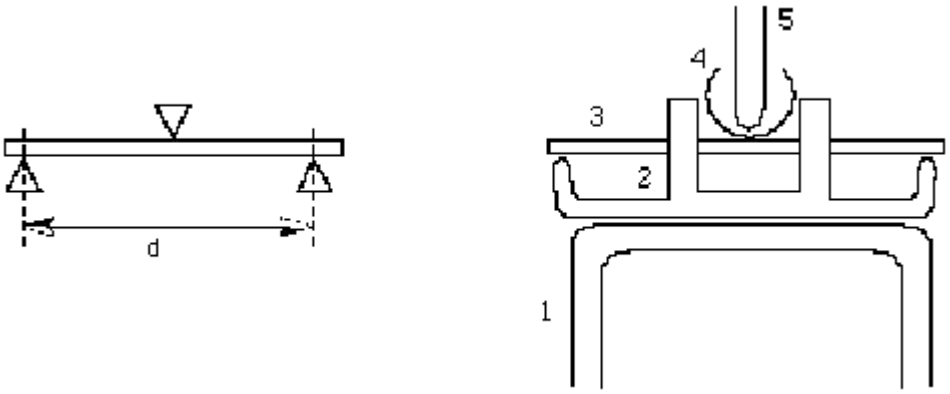


Fig.2: Left: Schematic view with the distance "d", between the knives. Right: Using the 3 point bending device: 1 Fused silica sample support, 2 bending device with the centring guides, 3 specimen, 4 centring tube, 5 ballpoint probe

The deflection, ΔL, caused by changing load, F_1 and F_2 is:

$$\Delta L = \frac{(F_2 - F_1) * d^3}{4 * E * a^3 * b}$$

ΔL	deflection, flexure	E	Young's Modulus
$F_2 - F_1$	force amplitude	a	thickness of the specimen
d	distance between knives	b	width of the specimen

In the TA-station there are 2 possibilities to program a changing load (method window, `Segment/Load`):

1. DLTMA (Dynamic load TMA):

Enter different values for minimum and maximum load and you get an automatic change every 6 s (6 s F_1, 6 s F_2, period 12 s).

2. Segments with different load

First segment, e.g. $F_1 = F_2 = 0.02$ N

Duration, e.g. 1 min

Second segment, e.g. $F_1 = F_2 = 0.40$ N

Duration, e.g. 5 min.

Third segment, e.g. $F_1 = F_2 = 0.02$ N duration, e.g. 10 min.

Such a method gives the deflection, ΔL, and the elastic recovery (100% $\Delta L_2/\Delta L$)

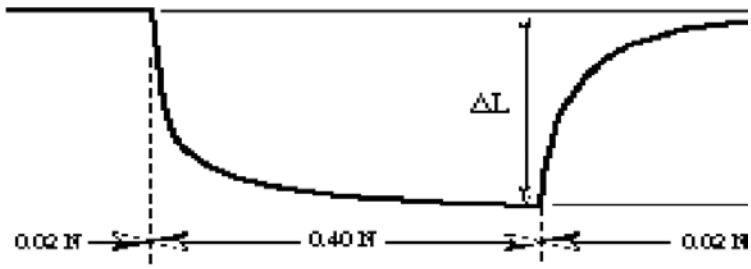


Fig.1: Isothermal deflection, ΔL, caused by the load 0.40 N, an elastic sample recovers to a certain extent when the load is switched off (to sense the specimen a minimum load of, e.g. 0.02 N is applied). Polymers usually show a plastic deformation ΔL - ΔL_2.

The Young's modulus is calculated:

$$E = \frac{(F_2 - F_1) * d^3}{4 * \Delta L * a^3 * b}$$

E	Young's Modulus	ΔL	deflection, flexure
$F_2 - F_1$	force amplitude	a	thickness of the specimen
d	distance between knives	b	width of the specimen

For good accuracy ΔL should be within 20 and 200 µm. Adjust the force change and the thickness of the specimen accordingly. For Young's modulus determination always use the centring tube (make sure it doesn't touch the centring guides). Select "3 point bending" in the module window to automatically compensate the expansion of the 3 point bending device. For qualitative bending tests you may directly place the ball point probe onto the center of the specimen. Before lowering the furnace, remove the furnace lid and check if the specimen is centered.

Example : **PET film, 0.41 mm thick**

F_1 = 0.05 N, F_2 = 0.15 N, l = 17 mm, ΔL = 111 µm, ΔL_{Blank} = 10 µm/N ∗0.1 N = 1 µm

a = 0.41 mm, b = 7.1 mm

$$E = \frac{0.1\mathrm{N}(17\mathrm{mm})^3}{4*0.11\mathrm{mm}*(0.41\mathrm{mm})^3*7.1\mathrm{mm}} = 2280\ \mathrm{N/mm^2}$$

The bending device is also used to measure softening temperatures of highly filled polymers that would probably give straight expansion or penetration curves. For this application a constant force can be used. Small object that do not allow cutting a 20 mm long specimen often can be exposed to bending stress by placing the specimen on an U-shaped wire. The distance between the shanks shall be 5 to 10 mm.

8.11 Maintenance

8.11.1 Cleaning the Measuring Attachment

Note: Measuring probe and sample support are made from quartz and are thus brittle.

Remains of samples should be removed as well as possible without using force. Solidified drops of metal may stick so well to the glass surface that some quartz is brocken off during removal. The metal residues should therefore be wiped off when hot and molten. It is however better to use an inconel disc as tray as with the calibration sample.

Organic sample residues can be decomposed by heating for 10 minutes to 950 °C (measuring probe raised up). The ashes can be wiped away after cooling.

Note: With alkali containing samples do not heat as the alkali will react with the quartz.

After dismantling the quartz components can of course be cleaned with the usual solvents and cleaning agents.

Caked inorganic materials can be removed with the grindstone (see optional accessories). The sample support is moved right down with the height adjustment ring and the measuring probe is raised up. The grindstone should be moved without great pressure parallel to the sample holder surface, until the resistance with the polished surface becomes very small. The rubbing causes the original mirror surface to become matt but this has no effect on the measurement.

8.11.2 Changing a Damaged Measuring Probe

If the measuring probe breaks, the lower part can be removed as follows:

– If the equipment was in use, do *not* switch off the current.

– Move the sample support right down by rotating the height adjustment ring clockwise.

– Remove the sample support by loosening the 3 three screws.

– Raise the measuring probe by pressing the key. If the equipment was not in operation at the time of the mishap, the calibration weight under the plastic cover is removed. The mechanism can be drawn upwards with tweezers, until the base of the measuring probe can be grasped.

– The remaining part of the measuring probe is carefully screwed out.

– **Note**: The moving parts of the mechanism must never be strained by sideways pressure.

– Mount the new probe following the instructions on page 4 (section 8.2.3)..

8.11.3 Changing Rubber Components

The O-ring on the measuring probe which carries the reflective washer can become embrittled with use. After unscrewing the measuring probe, the O-ring can be slid over the tip of the latter and replaced by a new O-ring. After mounting the probe, the O-ring and reflective washer are pushed down with tweezers to about 1 cm above the edge of the height adjustment ring (see chapter 8.2.3).

The gasket sealing the connection between the furnace housing and the TMA unit may readily be pushed on the adapter.

8.11.4 Cleaning the Reflective Washer and Flange

The polished surface get dirty by condensation products so that they deflect heat less effectively. It is therefore recommended that the measuring probe is removed from time to time and that the reflective washer as well as the flange are cleaned with a solvent (alcohol, petrol).

8.12 Malfunctions, Errors Messages, Warnings

TMA40 Thermobalance

Fan doesn't run:	Power cable not plugged in.
Strong signal noise	The suspension is touching the sides of the passage hole or the furnace or the furnace wall. Depending on how the strong the oscillation is, the hanger can sometimes stick to the opening if the opening is contaminated with decomposition products (even if the hanger chain is well centered at the top). Or the support for the measuring cell is not free from vibrations. Or there are too strong air turbulences in the room (draught!). Or the plug at the lower end of the furnace is missing. Or the tube (approx. 1 m long) at the purge gas outlet is missing. Or the purge gas flow fluctuates too much Or the vibration and weighing process adapters of the microbalance do not have the optimum settings. Reset using MT5 RESET. Or the weighing chamber is not completely closed, or the weighing chamber cover is missing. Or the foam rubber seal is missing.
ERR.2 CL-CHANNEL:	The "current loop channel" (data line) to the TMA does not work. Possible reason: • the cable to the TC15 is not properly plugged in

8.13 Specifications

TMA40 Thermobalance

Temperature

Range	Room temperature to 1000 °C
Precision	± 2 °C
Heating and cooling rates	0…100 °C/min
Cooling time	
from 1000 to 100 °C	18 min
Cooling means	Air (fan)

Weight data

Weighing range, electrical	0…5100 mg
Resolution	1 µg to 99.999 mg, 10 µg to 999.999 mg, 100 µg above 1 g
Noise (50 °C isothermal)	4 µg peak/peak during 5 min.
Data output	Bidirectional data interface (RS-232C)

Sample chamber

Purge gas connector for inert and reactive gases. No corrosive gases may be used. Flammable gases may be used only with inert gas in a non-explosive mix.

Dimensions

TMA40-MT5	
width x depth x height	250 x 450 x 450 mm
Weight	25 kg

8.14 Accessories

9 The TG50 Module in operation with the TC15 TA Controller

Content

Safety Notes

The instruments have been tested for the experiments and determinations documen-ted in the appropriate operating instructions. However, this does not absolve you from the responsibility of performing your own tests of the products supplied by us regard-ing their suitability for the methods and purposes you intend to use them for. You should therefore observe following safety measures.

Measures for Your Protection

- Ensure that you plug in the power cable supplied into a socket which is grounded! In absence of grounding, a technical default could have lethal consequences.
- Let the TG50 furnace cool down and disconnect the module from the mains before you open the housing. Switch the instrument off and disconnect the power cable before you open the housing or change blown fuses! An electrical shock could be lethal!

- Never work in a hazardous area! Explosion hazard through hot surfaces!
- Never use combustible gases or explosive gas mixtures! An explosion could occur!

- Make sure that the power and the signal cable of the same module are connected to the same TC15. The measuring cell could melt, if only the power cable is connected!
- Never switch off the TC15 when the cell temperature is above 300 °C. The cooling fan would no longer work and the cell cover could be heated unduly!

- Never touch the furnace, the furnace lid or a sample just removed from the furnace! The temperature of the furnace can reach 1000 °C.
- Open the furnace only when the temperature is lower than 100 °C! Always use tweezers to remove the lid or the crucible! Place hot items on the stainless steel area on the measuring module.

– Set up the instrument in a fume hood, if a sample may produce toxic gases during reaction.

  In such cases, ensure a local ventilation, absorb the volatiles in an appropriate filter or the evolving gases can be led to the fume cupboard with a wide tube from the purge gas outlet. Care should be taken that the TG signal is not disturbed by pressure fluctuations in the fume cupboard.

– Never push objects of any kind through ventilation openings around the furnace!

Measures for operational reliability

– Always keep all air vents clear for proper cooling!
– Always keep the hardware away from any source of liquid!
  – An inert purge gas absolutely must be used with corrosive decomposition products.
– If a change from inert to oxidizing purge gas is programmed at high temperature, do not take large sample quantities! An occasional small explosion may damage the furnace.

9 The TG50 Module in operation with the TC15 TA Controller

9.1 Introduction to the TG50 Module

In thermogravimetry, the mass change of a sample subjected to a temperature program in a preselected atmosphere is measured. Recording of the mass or weight changes is carried out with a highly sensitive balance. The TG50 thermobalance consists of a microbalance and the base with the furnace and the gas purge system controlled by the TC15. The temperature range is ambient to 1000 °C. For the operation of the microbalance, consult the separate instruction manual concerning it.

9.2 Installing the TGA50

9.2.1 Transport of the TG50

The counterweight for the furnace in the rear column has to be locked with the yellow screw. For this, the furnace is slightly lowered from the upper position until the internal thread in the weight can be seen through the hole. The furnace is locked in the upper position. For the balance consult the separate manual.

9.2.2 Location

The TG50 is a sensitive thermobalance. Today there is a certain electromagnetic noise field everywhere. It can disturb the sensitive measuring signal causing artefacts.

There should be no rising mains, motors or the like in proximity of the TG50.

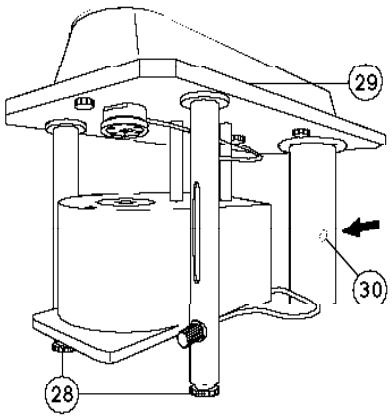
Mind the neighbouring rooms, too!

The measuring cell must stand on a vibration free support in order to obtain a sufficiently stable TG signal. In addition it is important that the cell is protected from draughts and other air turbulence.

The TG50 operates trouble-free at room temperature of +10...+32°C and at relative humidity of 25...80%.

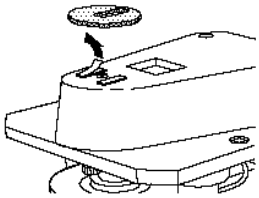
9.2.3 Installation of the equipment with TG50 Measuring Cell.

The installation of the microbalance is described in the instruction manual for it. The TG50 measuring cell is prepared for use as follows:

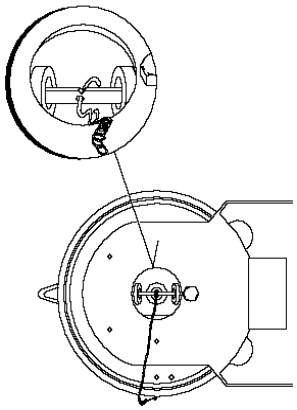


(1) Install the platform and align with the two levelling screws (28) so that the air bubble in the level (29) is at the centre of the cross.

(2) Remove the yellow screw (30) from the rear column. It is used to lock the counterweight for the furnace during transport.



(3) Detach protective film of the adhesive strips on the platform and stick on foam rubber seal.

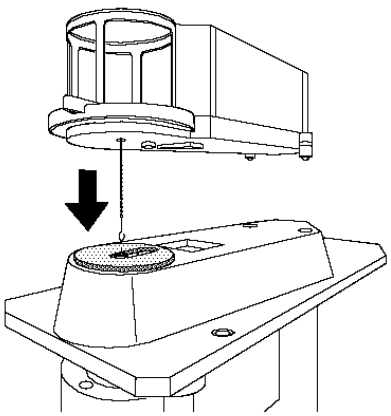


(4) Remove weighing pan and weighing chamber cover (glass!) of the microbalance.

(5) Place balance sideways on a soft support.

(6) Remove covers below the weighing chamber. Covers and spring washers are not needed and can be stored. Reinsert screw and tighten.

(7) Suspend hook of the hanger in weighing beam hole (visible in the opening between the two calibration weights).

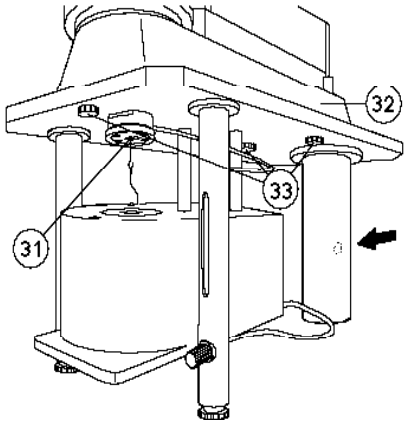


(8) Place balance on TG50 platform so that the hanger glides in the feedthrough without knotting.

(9) Level microbalance. Mount the lighter MT5-TG weighing pan (no edges) and the weighing chamber cover.

(10) Plug connection cable into balance and fix with clip at TG50.

(11) With the furnace lowered, suspend lower weighing pan on chain.



(12) The balance base (32) is installed in the factory so that the hanger is centered in the middle of the feedthrough hole (31) after mounting of the microbalance. If readjustment is necessary, the three knurled screws (33) at the bottom of the platform should be loosened by hand.

(13) Mounting a tube of approx. 1 m length at the purge gas outlet reduces the influence of air turbulence in the cell and therefore the signal noise. The free end of the tube is fixed below the TG50 platform (on right) with a clip.

Function Test

Run an isothermal measurement with an empty alumina crucible at 25 °C or 30 °C during 5 min. Before the start of measurement the microbalance is tared (Re-Zero). The resulting measurement curve may drift if the instrument is cold, the noise (peak-peak) should not exceed 4 µg, if so see the remedy text of the TG50 error messages in chapter 8.

9.2.4 Connecting the TG50 to the TC15

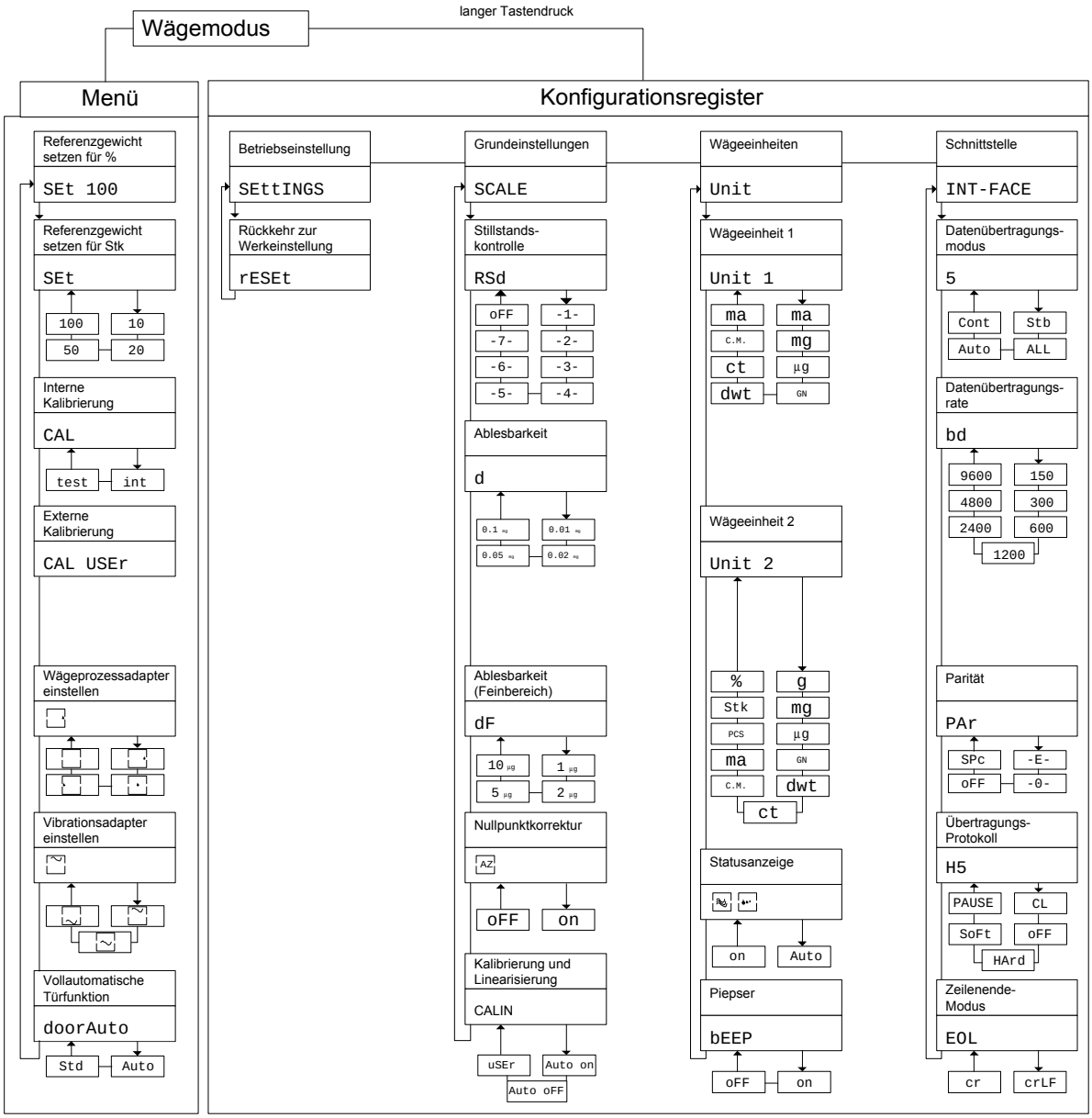
Connect the power cable with its round 7 pin plug to the appropriate socket at rear of the TC15. Connect the signal cable with its flat 15 pin plug to the flat socket.

Make sure that the power and the signal cable of the same module are connected to the same TC15. The measuring cell could melt, if only the power cable is connected!

Note: When using the TC110 Module Switchbox check that the signal and the power cables of the TG50 are plugged into sockets with the same number.

9.2.5 Configuring the MT5-TG Microbalance

The MT5-TG is configured in the factory as follows. The configuration can be changed as described in the MT5 Operating Instructions.



9.3 Sample Preparation

Chemical reactions usually occur during thermogravimetric measurements which are associated with an exchange of material with the surroundings. On the other hand physical processes, such as adsorption, desorption or evaporation of volatile components in the sample, can also be studied. In each of these cases, the rate of exchange of material and hence the shape of the TG signal depends on the sample preparation to a certain extent.

9.3.1 Quantity of Sample:

As the amount of sample increases, the temperature gradient in the sample increases on heating. Also the exchange of gas with the surroundings is more impeded. This results in a slower and less reproducible reaction. The quantity of sample should therefore be as small as possible as long as the size of the expected TG effect is sufficiently large. However, if the sample material is inhomogeneous, for example if it is a poorly mixed powder, a larger sample can become necessary. In this case, it is however often better to analyse several smaller samples whereby information is also obtained about the homogeneity. In general, samples of about 10 mg are used in a measurement.

Do not take large sample quantities, if an explosion or deflagration is to be expected.It may harm the furnace.

9.3.2 Particle Size

In order to obtain good exchange of matter, the sample should be powdered where possible, in order to increase the surface area. The powder is loosely poured into the pan and dispersed as well as possible in order to counteract the poor thermal conductivity.

9.3.3 Crucible Type

Samples are normally measured in alumina crucibles of a volume of 70 µl. Alumina crucibles with a volume of 150 µl are also available for larger samples. Alumina is completely inert towards most materials.

For a higher temperature homogeneity in the sample, platinum crucibles, available in the optional accessories, are used. A further reason, can be the catalytic effect of the platinum crucible on the reaction under investigation. Platinum crucibles are likewise used for ceramic materials as there is a risk here of an exchange reaction with alumina. Finally, with many inorganic samples the residue is easily removed from the platinum crucible while the alumina crucible must be replaced. When platinum crucibles are used in the higher temperature range, there is however danger of platinum poisoning especially with alloying metals and semi-metals which can damage the crucible.

Crucibles with lids are used when the sample is to decompose in the atmosphere of the products evolded (self-generated atmosphere). With an open crucible, the atmosphere is largely determined by the purge gas.

For an especially good contact with the atmosphere, the sample can be placed directly on the sample carrier. The sample carrier must however not be corroded by this. The sample carrier is made of inconel but is also available in platinum. When changing the sample carrier, check that the entire suspension, i.e., chain and sample carrier, does not touch either the furnace or the feedthrough in the base of the microbalance. Levelling and centering of the balance should be carried out again if necessary in accordance with the installation instructions.

9.3.4 Blank Curve

For checking purposes a blank curve can be recorded without sample but usually with an empty crucible and purge gas. The blank should be reproducible, and show a drift not greater than 300 µg over the whole temperature range.

In order to obtain good accuracy, especially of low ash contents, the measured curve needs blank subtraction. In this way the drag force (convection of furnace atmosphere) and the buoyancy (change in density of the furnace atmosphere) can be compensated. For this purpose an inert substance with a volume corresponding to that of the sample is inserted. In general with small samples, the blank experiment is however carried out with an empty crucible, i.e. with no sample. The experimental conditions have to be the same as in the analysis itself. That's why the method is used. You tell the Personal Computer that you run a blank by clicking `Run Blank Curve` in the experiment window.

To avoid blank residues tare the balance before starting a blank experiment. Otherwise the blank subtraction would shift the TG curve which would not affect a step evaluation but of course the residue (ash).

9.3.5 Gas Atmosphere

The gas atmosphere around the sample has an important influence on the TG curve as a potential reaction partner. In the absence of purge gas the sample can also be influenced by a self-generated atmosphere. Purge gas is be introduced for various reasons:

- Purging of evolved gases or vapours from the furnace. This prevents evolving gases from entering the balance.
- Displacement of atmospheric oxygen with an inert gas to avoid unwanted oxidation of the sample.
- Introduction of a reactive gas to act on the sample.

The purge gas is connected to the upper quick-action connector at the back of furnace. A corrosive purge gas (i.e. chlorine, sulphur dioxide) must never be used. In order to obtain a low noise TG signal, it is very important that the gas flow is constant. For this reason a constant inlet pressure of about 0.5 to 1 bar is necessary. In general a gas flow of 200 ml/min is set on the flow meter so that evolved gases are rapidly purged but the weighing is not disturbed.

A purge gas absolutely **must** be used with corrosive decomposition products. Evolving gases can be led to the fume cupboard with a wide tube from the purge gas outlet. Care should be taken that the TG signal is not disturbed by pressure fluctuations in the fume cupboard.

With the gas switching valve one purge gas can be changed to another during a measurement. For example, a temperature program can be carried out in nitrogen. Due to the open construction of the TG50 the nitrogen will contain approx. 0.1% of oxygen. After pyrolysis the atmosphere is switched to oxygen or air in order to measure the oxidation of the sample. Valve switching is only possible between two segments of the method.

If a change from inert to oxidizing purge gas is programmed at high temperature, do not take large sample quantities! An occasional small explosion may damage the furnace.

In order to connect the two purge gases, two quick-action connectors are mounted on the back side of the furnace body. The hose nipple is removed by pulling back the retaining ring. It re-engages automatically with light pressure on the insert. The first purge gas to be used during the first segment of the measurement and in the standby state (usually nitrogen) is connected to the upper inlet. The second purge gas is accordingly connected to the lower inlet.

The two purge gases should have flow rates as similar as possible in order to avoid disturbance of the TG signal at the change. This can be attained as follows:

Adjust the flow of the first gas by means of the valve below the built-in flowmeter to 200 ml/min. Adjust flow of the second gas by switching the gas valve to the second gas (GAS key on TC15). A small roman II on the TC15 display shows that gas 2 is active. Press GAS again and adjust the flow of gas I if need be (see chapter 1.3). To obtain identical flow rates also the pressure controller(s) have to be adjusted.

Check the adjustment in a dummy experiment. The dynamic or isothermal segments used in the region of the gas change are the same as used subsequently in the analyses. After the gas change, the TG signal should return to the same value as before (within a drift tolerance of approx. 30 µg). It is important here that the end of the purge gas exhaust tubing is at the same height as the weighing chamber of the microbalance.

A two step pressure reduction device is recommended for the second gas (e.g. 100 bar 10 bar 0.5 bar) to avoid any pressure build-up during the use of the first gas. Air instead of oxygen taken as a second gas offers the advantage of having physical properties close to those of nitrogen used as first gas. Compared with compressed air cylinders cheap air pumps available as aquarium accessories are advantageous due to their low pressure build up during the purge with the first gas.

The gas switching valve can also be used to reduce the consumption of purge gas: The purge gas is connected to the lower inlet and the valve switching is generally carried out at the beginning of the measurement. After the experiment the lower inlet will be closed.

Remark: The gas(es) connected to the TG50 must correspond to the ones in `Install/Module`.

The time required to purge the first gas completely after switching is about 1 minute at 200 ml/min. When switching to air, oxidation can however begin after about 20 seconds.

9.4 Operating the TG50

9.4.1 Switching On:

The microbalance should by switched on (or in stand by) for at least 2 hours.

9.4.2 Performing an Experiment

Consult section 11.3 regarding sample preparation, choice of crucible and atmosphere and experimental condition.

Before weighing the sample select the appropriate method in the experiment window of the Personal Computer and enter the sample name. Without keying in a sample weight in the size box[1)], send the experiment to the modul control window. This causes the TG50 to go to the start temperature (usually 25 °C).

In order to introduce the empty crucible on the sample carrier, the furnace must be lowered. To do this, the locking arm under the furnace is swung out by rotating the lower part of the left hand column. Then the balance is tared with the furnace raised.The current weight is displayed in the module control window.

Remark: When intending to use a lid on the pan don't forget to tare it together with the pan.

After adding the sample, the weight of the sample is displayed. Check whether it is in the range given in the experiment window.

Note: A business card placed on the furnace opening protects the furnace against spilled samples.

Before starting a measurement, the furnace is raised by hand until the locking arm can be swung under the furnace. A rubber gasket seals the contact line between furnace and balance base with the feedthrough. Press OK on the keypad of the TC15 to start the measurement immediately. This is mainly important when you are interested to get the moisture content of your sample.The sample could dry in the TG50 if you forget to start the measurement.

The TC15 accepts the weight of the sample as the first weight value transmitted after the settling period at the beginning of the experiment.

To weigh in a sample you can use the upper weighing pan if you prefer it[1)]. Don't forget to place the sample below before starting the measurement.

[1)]You should not enter the weight into the experiment window as it would shift the whole curve by the difference (upper weigh entered - first weight value transmitted). This would lead to a wrong residue. Make sure the method has a `sample range` 0...1000, otherwise in version 2 an error would occur.

9.4.3 Switching Off

Never switch off the TC15 when the cell temperature is above 300 °C. The cooling fan would no longer work and the ceiling ring could be heated unduly.

(1) Always remove the last sample pan before switching off. The order of switching off the Personal Computer and the TC15 is of no importance.

9.5 Calibrations

Temperature calibrations that are performed wrongly lead to a wrong temperature scale. Hence this work should be carried out only by especially qualified personnel !

Contrary to the calibrations, the Nickel-Check is a normal method with automatic evaluation and validation of the result. It doesn't change any instrument parameters.

The microbalance is calibrated as described in its separate instruction manual.

Use is made of the discontinuous change in the magnetic properties of certain metals on heating. The sample is pulled downwards by the calibration magnet hanging on the furnace which causes the balance to record an increase in weight. As the temperature program progresses, the metal sample now loses its ferromagnetic property at well defined temperature and thus is no longer influenced by the magnet. At the so-called Curie point, the weight of the sample is therefore suddenly reduced a little. The Curie temperature corresponds to the inflection point of the step or peak temperature of the DTG.

In the Personal Computer there are some calibration methods ready for use. There names begin with `Calib`.

You may also compose your own calibration methods in the method window. Don't forget to select the type of calibration under `Miscellaneous/Calibration/Type`.

9.5.1 The Nickel Temperature Check

It is good laboratory practice to check the temperature accuracy once every month. The check is based on measuring the Curie temperature of a Nickel sample.

The Ni check is passed when the inflection point is found within a tolerance of ±3.5 °C compared with the true value of 357 °C.

The respective method is named : NiCheck. Use two pieces of nickel in the alumina crucible. Use the same purge gas as the later experiment.

If you are interested in other temperatures as well - you can compose a similar isatherm or trafoperm Check.

A calibration of temperature has to be performed when the check has given results with deviations no longer tolerable: As long as the measured Curie point remains within the tolerances, your measuring cell does not need a temperature calibration.

With a nickel check after calibration experiments you make sure that the calibrations have been done properly.

9.5.2 Performing the Calibrations

There is a basic procedure for all necessary calibrations given:

First Temperature Calibration of a TA4000 TG50 Module (approx. 80 min)

The first temperature calibration is performed with an alumina crucible, 70 µl, containing 1 disk of trafoperm , 2 disks of nickel and 3 spikes of isatherm. This special calibration is performed with the same purge gas with identical flow as used for later analyse (200 ml/min) and with a heating rate of 10 °C/min in the whole temperature range of the TG module since the analog/digital converter of the Pt100 temperature measurement is calibrated, too.

(1) Check the default values for tau lag on the module printout (`Install/ Module/ Open/ Print`): A= 109, B= -0.1799 T, C= 9.17 e^{-5} T^2.

(2) Introduce the Curie point value read on the bottle for each metals in the Personal Computer (`Install/Calibration Substances`), leave the box for the enthalpy empty. Isatherm and trafoperm are alloys and the curie point can slightly change from batch to batch.

(3) Open the experiment window and select the method `Calib Temp:TA4000 TG N2.`

(4) The sample weight `Size` is not entered.

The calibration sample is placed in the center of the sample carrier and the furnace is raised . The balance is set to zero when the signal is stable. Then the calibration magnet is hung in front of the cell so that the ends of the mounting are seated in the holes of the furnace body. The additional weight due to the magnetic force should be 2.5 to 5 mg. If the magnetic force is too low, remove the damping disks from the magnet bracket.

(5) Start the experiment by clicking the respective module button.

(6) At `Insert Sample` check the gas flow and start the measurement by OK.

(7) When finished a box appears in the module control window viewing the A, B and C values of Pt 100. This triple sample calibration can change the A, B and C values. At the bottom the deviations from the default scale are indicated (A = 100, B = 0.3908 and C = $-58.02 \cdot 10^{-6}$) are indicated. Leave the box with `OK`.

(8) Remove the sample from the cell below 50 °C.

Further Temperature Calibrations (approx. 95 min)

(1) Prepare a dual sample crucible (3 spikes of isatherm, and 2 disks of nickel and 1 disk of trafoperm).

(2) Open the experiment window and select the method `Calib Temp: TG.`

(3) No sample weight, The calibration sample is placed in the center of the sample carrier and the furnace is raised . The balance is set to zero when the signal is stable. Then the calibration magnet is hung in front of the cell so that the ends of the mounting are seated in the holes of the furnace body. The additional weight due to the magnetic force should be 2.5 to 5 mg. If the magnetic force is too low, remove the damping disks from the magnet bracket. Start the experiment by clicking the respective module button.

(4) At `Insert Sample`, check the gas flow and start the measurement by OK.

(5) When finished a box appears in the module control window viewing the A, B and C values of Pt 100. This tripple sample calibration can change the A and B values. At the bottom the deviations from the default scale (A=100, B=0.3908) are indicated. Leave the box with OK.

9.5.3 Background Information Concerning Calibrations

Calibrating Tau Lag

The tau lag calibration has not the same importance as the temperature calibration. Tau lag slightly depends on the heat capacity of the sample and is a strong function of temperature. The defaults values can be used for all sample since the temperature accuracy anyhow is limited to approx. +/- 3 °C.

The tau lag calibration is based on the inflection point of the step of the Curie transition with different heating rates. When running more than one calibration substance (e.g. not only isatherm, but also nickel) the temperature function of tau lag is measured, too:

Tau lag = $A + B \cdot T + C \cdot T^2$ The default values are: A= 109
B= -0.1799
C= 9.17 e^{-5}

Remark: The term C is a constant all the time (linear regression when using more than 2 calibrations standards).

Compose your own calibration methods in the method window. Don't forget to select `Tau Lag Single` as type of calibration under `Miscellaneous/ Calibration/ Type`. Create a heating and a cooling segment prior to the segments you design for the measurements. The minimum number of measurement segments is two. The ratio of the heating rates should be at least 2, e.g. 2 and 5 °C/min. Heating segments are considered only.

The `Single Tau Lag Calibration` box can be used for manual entries, as it has been done with the factory calibrations (see chapter "Manual Entry" in the Operating Instructions STARe Software).

After `OK` you get the `Tau Lag Calibration` box displaying the new A, B and C values. On the right in brackets you see the previous values that would remain active when quitting the box with `Cancel`. For your information the deviations caused by the new tau lag function from the old one are calculated at two temperatures: 25 and 500 °C.

With `OK` you accept the new tau lag values. `OK` also clears all entries in the single Tau Lag calibration box.

The Automatic Multiple Temperature Calibration

Isatherm and trafoperm are alloys. Their Curie temperature can change slightly from batch to batch. It is important to refer to the true Curie temperature. The value written on the respective bottle is introduced under `Install/Calibration Substances`, e.g. isatherm 142 with the Curie point of 142 °C.

A 70 µl alumina crucible with the three metals isatherm, nickel and trafoperm (Curie points 142.5*, 357 and 745* °C) is used at least once to perform the so called TA4000 temperature calibration (`Method/ Miscellaneous/ Calibration/ Type/ Temp.TA4000`). This special calibration is performed with a heating rate of 10 °C/min in the whole temperature range of the TG module. At the same time the inflection points of the TG steps are compared with the true values to calculate the new ordinate intercept, A, the slope, B, and the non linearity of the temperature function, C.

The temperature function of the electrical resistance is modelled as follows:

$$R = A + B \cdot T + C \cdot T^2$$

The default values are:

$A = 100\ \Omega$

$B = 0.3908\ \Omega \cdot °C^{-1}$

$C = -58.02 \cdot 10^{-6}\ \Omega \cdot °C^{-2}$

After having performed a TA4000 temperature calibration a further temperature calibration can result in a higher temperature accuracy:

The automatic multiple sample temperature calibration is based on one experiment using a crucible with at least two calibration standards such as isatherm and nickel. As a result of this calibration the temperature function of the Pt100 is corrected (the ordinate intercept, A, the slope, B, are corrected, i.e. the non linearity of the temperature function, C, is not changed).

Select method `Calib Temp.: TG`. You may also compose your own calibration method in the method window. Don't forget to select `Temp.Multiple` as type of calibration under `Miscellaneous/Calibration/Type`. After the experiment you get the Temperature Calibration box displaying the new A, B, C values. On the right in brackets you see the previous values that would remain active when quitting the box with `Cancel`. For your information the deviation of the new temperature scale from the one based on the default Pt100 values is calculated at two temperatures: 25 and 500 °C.

With `OK` you accept the new calibration.

The Single Temperature Calibration

In this temperature calibration one or several single sample crucibles are measured in individual experiments. There are two procedures of single temperature calibrations:

- **Performing single temperature calibrations** with automatic entry into the single temperature calibration box of the module control window. Compose your own methods with each time the same experimental condition (atmosphere, heating rate) in the method window. Don't forget to select `Single Temperature Calibration` as type of calibration under `Miscellaneous/Calibration/Type.`
- **Manual entry** of Curie temperature(s) into the single temperature calibration box of the module control window. One Curie temperature can be based on an nickel check for example.

Perform the experiment with the single temperature calibration. When finished call `Calibration/Single Temp. Calib.` in the module control window:

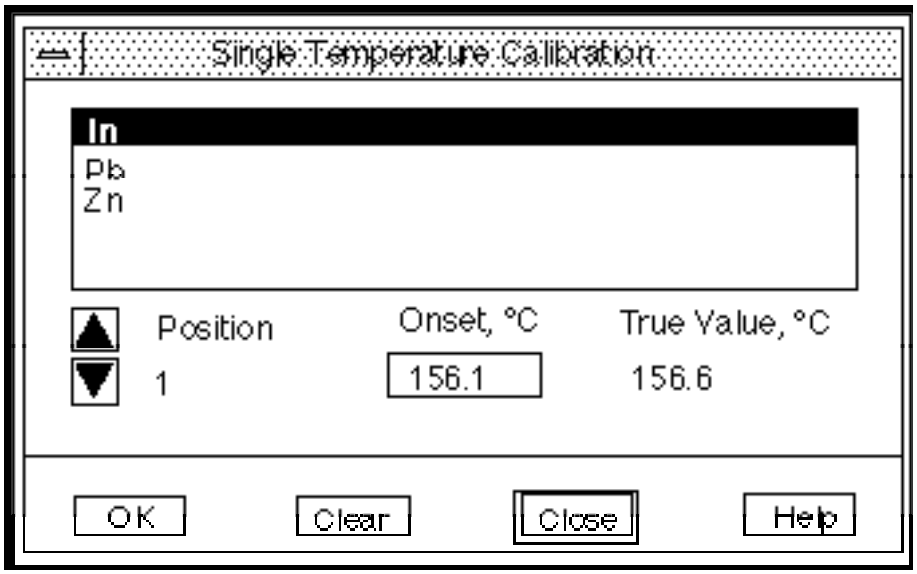


Fig. x: In the first row or position the Curie temperature has been entered automatically. OK at position 1 would only recalculate the A value of the Pt100. After `Close` an additional single temperature calibration performed with e.g. isatherm, enables recalculation of B as well (check position 2 and click OK).

After `OK` you get the `Temperature Calibration` box displaying the new A, B and C values. On the right in brackets you see the previous values that would remain active when quitting the box with `Cancel`. For your information the deviation of the new temperature scale from the one with the default Pt100 values is calculated at two temperatures: 25 and 500 °C.

With `OK` you accept the new calibration.

Note: When running more than one single temperature calibration, open the `Single Temperature Calibration` box after having finished the last standard. Press `OK` to activate the calculation of the Pt100 parameters based on several experiments. Make sure that you are at the last row (position) of the table produced. Only the values down to the actual position are considered.

The **procedure with manual entry** of the Curie temperature(s), e.g. obtained by the nickel check, is described as follows:

- Call `Calibration/Single Temp. Calib.` in the module control window and select the first calibration substance. Enter the measured Curie temperature. The true value is already shown for comparison.
- Click the arrow down to come to the next position.
- Select the next calibration substance and enter the measured Curie temperature. Go on until all measurements are entered and click the `OK` button. Only the rows up to the actual position are considered. `Clear` clears all entries.
- After `OK` you get the `Temperature Calibration` box displaying the new A, B and C values. On the right in brackets you see the previous values that would remain active when quitting the box with `Cancel`. For your information the deviation of the new temperature scale from the one with the standard Pt100 values is calculated at two temperatures: 25 and 500 °C.
- With `OK` you accept the new calibration. As a result of this calibration the temperature function of the Pt100 is corrected (the ordinate intercept, A, and - with more than 1 calibration standard - the slope, B, are recalculated, i.e. the non linearity of the temperature function is not changed).

If you prefer an interactive evaluation of Curie temperatures, develop methods with start temperatures approx. five times the value of the heating rate below the expected Curie temperature of the substance and approx. five times the heating rate above the expected Curie temperature of . Usual heating rates are 1…10 °C/min (select the rate you apply for your later work).

With `None` under `Miscellaneous/Calibration/Type` you suppress the automatic determination of the temperatures at the inflection point as well as the automatic entry into the `Single Temperature Calibration box.`

Examples:

Isatherm	(142.5 °C):	130 °C through 160 °C with 2 °C/min
Nickel	(375.0 °C)	340 °C through 410 °C with 5 °C/min.

Perform the experiments. In the evaluate window determine the inflection point of the TG step. Enter them as above mentioned.

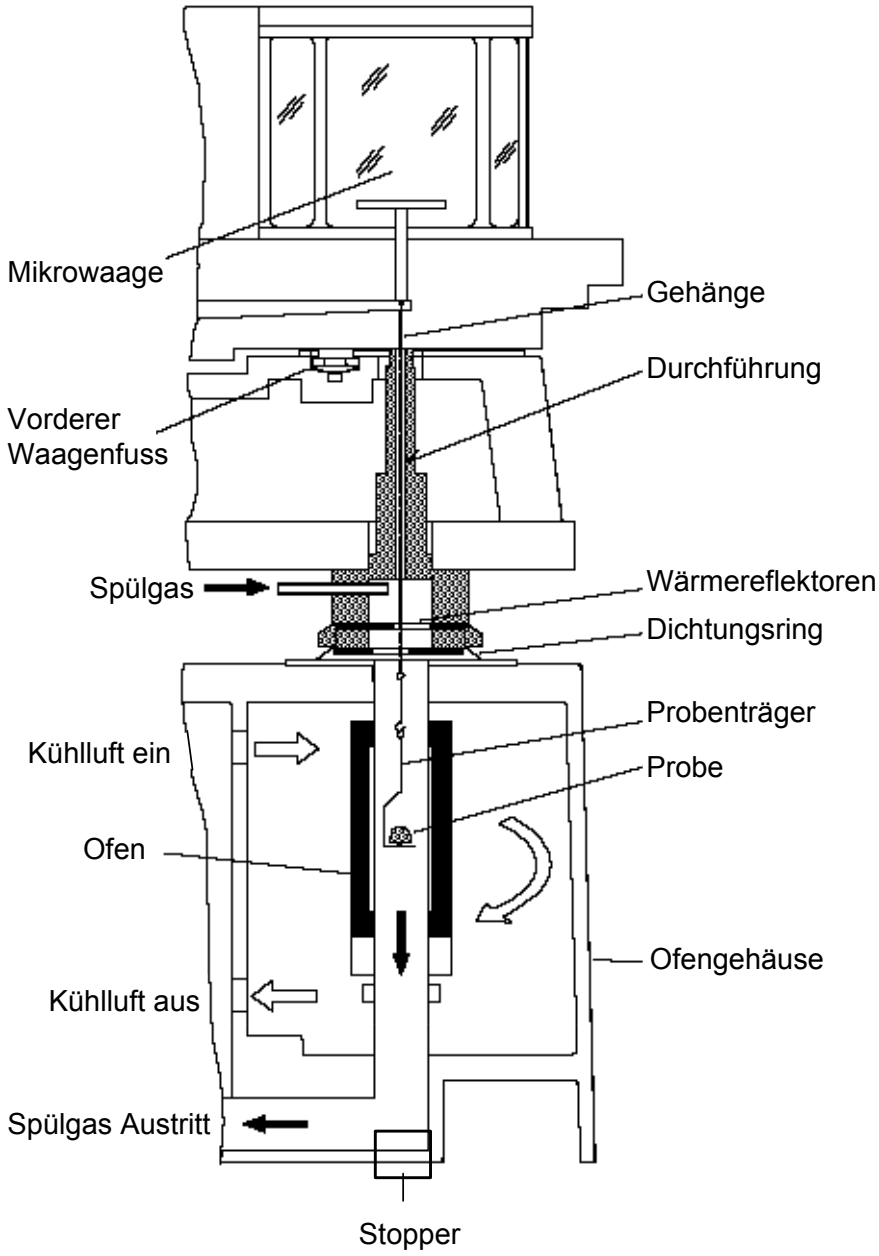
Remark: Several determinations with equal calibration substance give a mean value.

9.6 Description of the TG50

9.6.1 Construction of the TG50 Thermobalance

The platform resting on three columns carries the microbalance. The balance is described in its separate instruction manual.

The figure shows details of the construction of the furnace part and the suspension lead through between furnace and balance.



9.6.2 Temperature Equilibration

The temperature should follow a program predefined in the method. To ensure this the sample is first brought to the insert temperature, and subsequently the furnace temperature is controlled in a suitable manner by the TC15. The tau lag parameters A, B and C define the temperature function of the time constant, tau lag, between furnace and sample.

The settling period

During the settling period before the start of the first segment, (display: SETTLING), the sample is brought to the start temperature. The settling period depends on the initial temperature as is shown in the table settling time. The values given assume that the sample has the ambient temperature of approx. 25 °C at the moment of insertion, thus the settling time is zero when starting at 25 °C.

The following equation estimates the time necessary to bring the sample from ambient 25 °C to the isothermal furnace start temperature T:

$$t_{SETTLING} = \text{tau lag (T)} \bullet \ln (T - 25\ °C)$$

The equation only is valid for T ≥ 26 °C. With 25 < T < 26 °C the settling time is zero.

This settling time automatically precedes the measurement in order to ensure that the sample has reached the initial temperature to within one degree. The settling times for selected insert temperatures are tabulated below.

During heating to the insert temperature, the fast furnace control can appreciably overshoot the insert temperature. The sample itself is not heated above the insert temperature, however, owing to the slow temperature equilibration.

If the settling period is skipped (FORCED START by pressing OK during settling,) the sample does not necessarily reach the preset temperature at the start.

START TEMPERATURE	When ever possible use 25 °C. In this case the settling period is zero.
HEATING RATE	The heating rate depends on the application: - Rough screening 50 K/min - Screening 20 K/min - For good temperature homogeneity in the sample: 5 K/min
END TEMPERATURE	Use a method with a high enough end temperature. The measurement can be stopped early simply by pressing [RESET].The maximum value of the TG50 is 1000 °C.

9.6.3 The Temperature Control

The furnace temperature is controlled in such a way that the theoretical sample temperature follows the desired profile. The theoretical sample temperature is the temperature of an inert sample with the same heat capacity as the real sample. A real sample undergoes endo- or exothermal reactions causing temperature differences compared with the theoretical sample.

The time constant of the heat transfer from furnace to the sample is called tau lag and depends on temperature. The time constant is calculated as follows:

$$\text{tau lag} = A + BT + CT^2$$

where the default values of A, B and C are:

$A = 109$
$B = -0.1799\ T$
$C = 9.17\ e^{-5}\ T^2$

To ensure that the sample temperature follows the temperature program in a dynamic measurement, the furnace temperature must be higher by a certain amount. This temperature difference depends on tau lag and on the heating rate. The same applies to controlled cooling in an analogous manner. The furnace advance is calculated with the following equation:

$$\Delta T = T_{furnace} - T_{sample} = \text{tau lag} \bullet \beta$$

where β is the heating rate. Furnace and sample temperature during a dynamic measurement of 1 segment are shown graphically in the illustration.

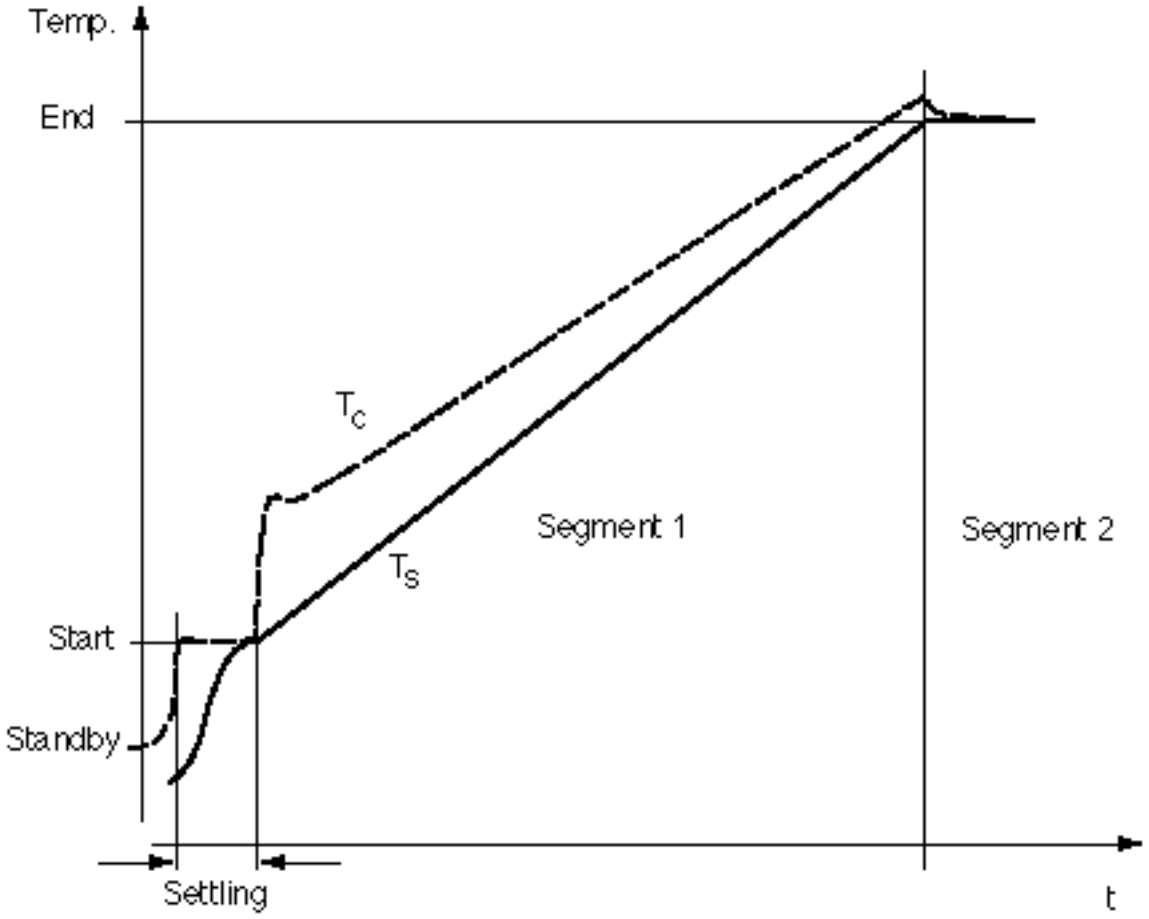


Table for estimating the settling time and the advance of the furnace temperature with the default tau lag parameters:

Temperature °C	SETTLING time	Advance °C		
	min	10 K/min	20 K/min	50 K/min
20	2.1	13	27	67
25	0	13	26	66
30	2.1	13	26	65
50	4.0	12	25	62
100	4.8	11	22	55
200	4.4	9	17	43
300	3.7	7	13	33
500	2.2	4	7	18
700	1.4	2	4	11
900	1.6	2	5	18

9.7 Maintenance

9.7.1 Maintenance of the balance

Details are to be found in the instruction manual for the balance.

9.7.2 Cleaning the Feedthrough to the balance

In general, condensation products do not affect later analyses. Nevertheless the reflector plates in the lead-through between furnace and balance should occasionally to be cleaned to ensure good heat reflection. After lowering the furnace and removal of the suspension, the entire lead-through with purge gas inlet can be removed by loosening the fixing screw with the allen key. The purge gas tubing and the sealing gasket are removed. The lead-through can now be rinsed with a solvent (e.g. alcohol, petrol) and rubbed with a cloth. It is important that the central opening in the lead-through is clean as well as the reflector plates, as otherwise the suspension can stick. Remove any dust fibres from the lead-through and the suspension chain.

9.7.3 Cleaning Pans and Sample Carrier

Pans and sample carrier made from platinum can be heated in a gas flame. Alumina pans are cleaned with strong acid and subsequently heated in a flame.

with correct usage of purge gas, the suspension should not become dirty. It can hovewer rinsed with a solvent (e.g. petrol) if necessary.

9.8 Malfunctions, Errors Messages, Warnings

TG50 Thermobalance

Fan doesn't run:	Power cable not plugged in.
Strong signal noise	The suspension is touching the sides of the passage hole or the furnace or the furnace wall. Depending on how the strong the oscillation is, the hanger can sometimes stick to the opening if the opening is contaminated with decomposition products (even if the hanger chain is well centered at the top). Or the support for the measuring cell is not free from vibrations. Or there are too strong air turbulences in the room (draught!). Or the plug at the lower end of the furnace is missing. Or the tube (approx. 1 m long) at the purge gas outlet is missing. Or the purge gas flow fluctuates too much Or the vibration and weighing process adapters of the microbalance do not have the optimum settings. Reset using MT5 RESET. Or the weighing chamber is not completely closed, or the weighing chamber cover is missing. Or the foam rubber seal is missing.
ERR.2 CL-CHANNEL:	The "current loop channel" (data line) to the balance does not work. Possible reasons are: • the balance is switched off or in standby • the cable to the TC15 is not properly plugged in • the channel parameters of the balance are wrong (see chapter 11.2.5 "Configuring the balance")

9.9 Specifications

TG50 Thermobalance

Temperature

Range	Room temperature to 1000 °C
Precision	± 2 °C
Heating and cooling rates	0…100 °C/min
Cooling time	
from 1000 to 100 °C	18 min
Cooling means	Air (fan)

Weight data

Weighing range, electrical	0…5100 mg
Resolution	1 µg to 99.999 mg, 10 µg to 999.999 mg, 100 µg above 1 g
Noise (50 °C isothermal)	4 µg peak/peak during 5 min.
Data output	Bidirectional data interface (RS-232C)

Sample chamber

Purge gas connector for inert and reactive gases. No corrosive gases may be used. Flammable gases may be used only with inert gas in a non-explosive mix.

Dimensions

TG50-MT5	
width x depth x height	250 x 450 x 450 mm
Weight	25 kg

9.10 Accessories