Differential Scanning Calorimetry (DSC)

Basic Theory &
Applications Training

Agenda

- Understanding DSC
- Experimental Design
- Calibration
- Optimization of DSC Conditions
- Interpretation of Undesirable Events in DSC Data
- Applications

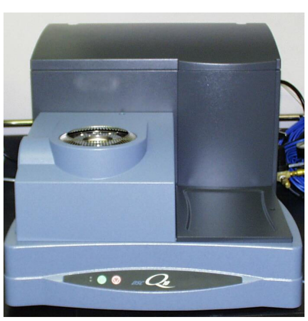
2900 Series DSC's

DSC 2010

DSC 2910

DSC 2920

First Generation Q Series™ DSCs



Q10

Q100

Q1000

Second Generation Q-Series™ DSCs

Q2000

Q200

AutoQ20

Q2000 is top-of-the-line, research grade with all options

Q200 is research grade and expandable

Q20 is a basic DSC – Available as an Auto Q20 & also Q20P

Understanding DSC - Agenda

- What does a DSC measure?
- How does a DSC make that measurement?
- How is a Tzero™ DSC different?
- Tzero Results
- Advanced Tzero

Agenda

- What does a DSC measure?
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DSC Training Course

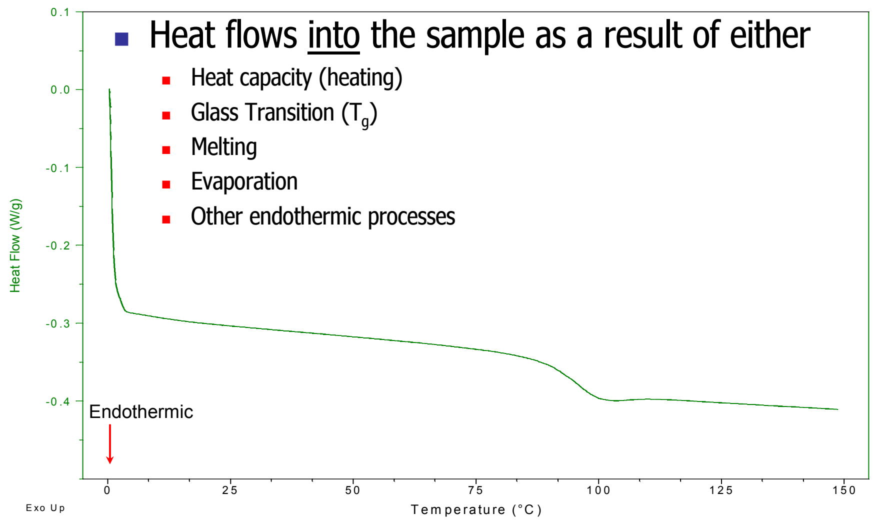
What Does a DSC Measure?

A DSC measures the difference in heat flow rate (mW = mJ/sec) between a sample and inert reference as a function of time and temperature

DSC Training Course

Endothermic Heat Flow

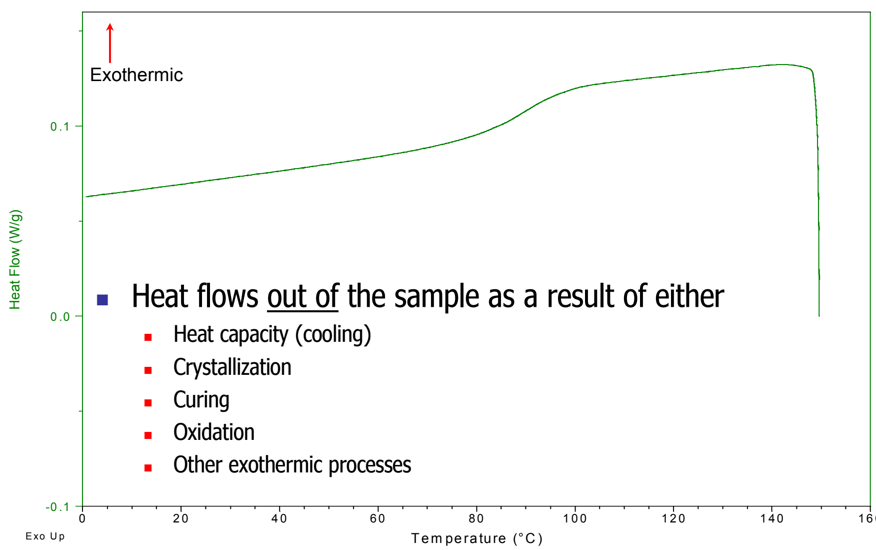
- Heat flows <u>into</u> the sample as a result of either
  - Heat capacity (heating)
  - Glass Transition (T_g)
  - Melting
  - Evaporation
  - Other endothermic processes



DSC Training Course

Exothermic Heat Flow

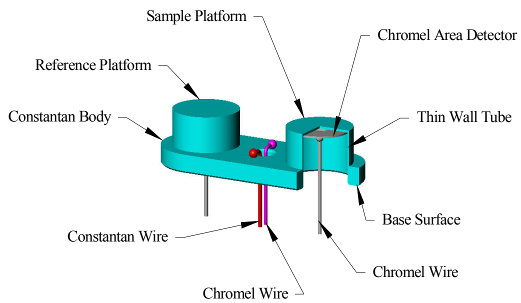
- Heat flows <u>out of</u> the sample as a result of either
  - Heat capacity (cooling)
  - Crystallization
  - Curing
  - Oxidation
  - Other exothermic processes



DSC Training Course

Temperature

- What temperature is being measured and displayed by the DSC?
  - Sensor Temp: used by most DSCs. It is measured at the sample platform with a thermocouple, thermopile or PRT.



Temperature

- What temperature is being measured and displayed by the DSC?
  - Pan Temp: calculated by TA Q1000/2000 based on pan material and shape
    - Uses weight of pan, resistance of pan, & thermoconductivity of purge gas
  - What about sample temperature?
    - The actual temperature of the sample is never measured by DSC

Temperature

- What temperatures are not typically being displayed?
  - Program Temp: the set-point temperature is usually not recorded. It is used to control furnace temperature
  - Furnace Temp: usually not recorded. It creates the temperature environment of the sample and reference

Understanding DSC Signals

Heat Flow

- Relative Heat Flow: measured by all DSCs except TA Q1000/2000. The absolute value of the signal is not relevant, only absolute changes are used.
- Absolute Heat Flow: used by Q1000/2000. Dividing the signal by the measured heating rate converts the heat flow signal into a heat capacity signal

DSC Heat Flow

$\frac{dH}{dt}$ = DSC heat flow signal

Cp = Sample Heat Capacity
= Sample Specific Heat x Sample Weight

$$\frac{dH}{dt} = Cp\frac{dT}{dt} + f(T,t)$$

$\frac{dT}{dt}$ = Heating Rate

$f(T,t)$ = Heat flow that is function of time at an absolute temperature (kinetic)

Agenda

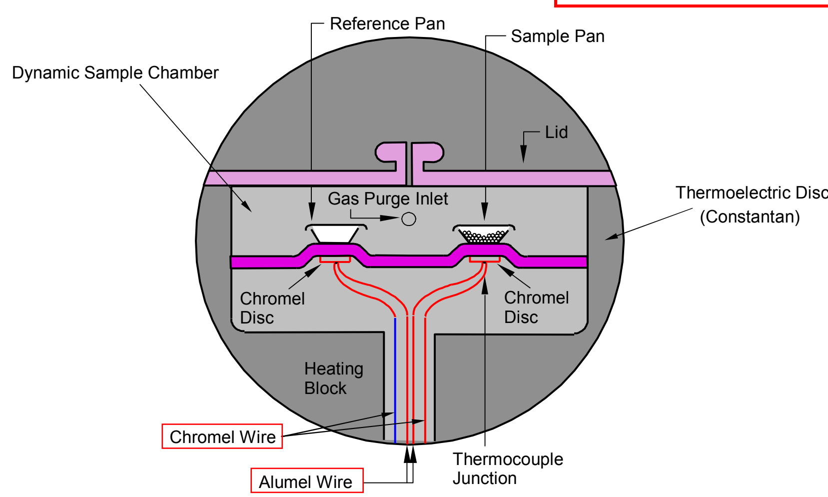
- What does a DSC measure?
- How does a DSC make that measurement?
- How is a Tzero™ DSC different?
- Tzero Results
- Advanced Tzero

How does a DSC Measure Heat Flow?

- DSC comprises two nominally identical calorimeters in a common enclosure that are assumed to be identical.
- Advantages of a twin calorimeter:
  - Noise reduction by cancellation of common mode noise.
  - Simplified heat flow rate measurement.
  - Cancellation of calorimeter and pan heat capacities.
  - Cancellation of heat leakages.

Heat Flux DSC Cell Schematic

2900 Series DSC



Perfectly Symmetrical?

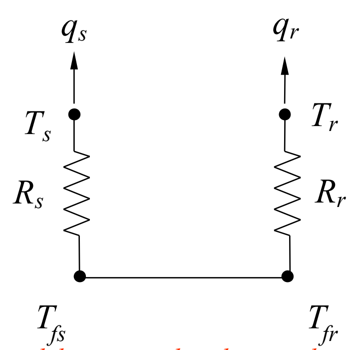
- The heat flow rate of an empty perfectly symmetrical twin calorimeter should be zero.
- However, it almost never is because the DSC is rarely symmetrical as assumed.
- The asymmetry is the inevitable result of manufacturing tolerances and is unavoidable.

For example, thermal resistance of the Tzero DSC cell is determined by the wall thickness of the "top hat" which is .005" (0.13mm). To achieve 1% thermal resistance imbalance would require manufacturing tolerance of .00005" (.00127mm).

Conventional DSC Measurements

2900 Series

Heat Flow Measurement Model



Heat Balance Equations

$$q_s = \frac{T_{fs} - T_s}{R_s} \qquad q_r = \frac{T_{fr} - T_r}{R_r}$$

Conventional DSC Heat Flow Rate Measurement

$$q = q_s - q_r$$

$$q = \frac{T_r - T_s}{R} = \frac{-\Delta T}{R}$$

This model assumes that the sample and reference calorimeter thermal resistances are identical, the temperature of the furnace at the sample and reference calorimeters are equal and does not include other known heat flows.

Conventional DSC - Assumptions

- The resistance between the sample sensor and the furnace equals the resistance between the reference sensor and the furnace
- Pan and calorimeter heat capacities are ignored
- Measured temperature equals sample temperature
- No heat exchange with the surroundings

Consequences of the Assumptions

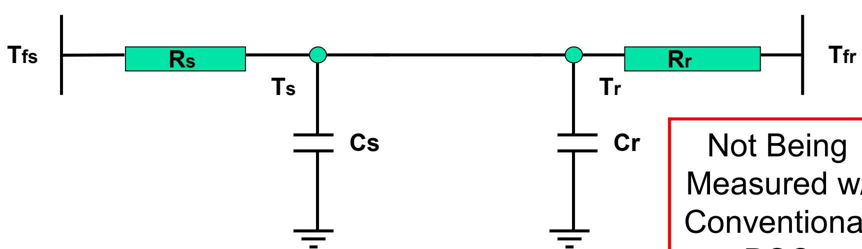
- Whenever the heating rate of the sample and reference calorimeters is not identical, the measured heat flow is not the actual sample heat flow rate. This occurs during transitions in standard DSC and always during MDSC®.
- Resolution suffers.
- Sensitivity suffers.
- MDSC® results are strongly period dependent, requiring long periods and slow heating rates.
- The heat flow baseline is usually curved and has large slope and offset.

Violations of Assumptions

Pan and calorimeter heat capacities are ignored

- Sample and reference heat capacities are assumed to be the same and to heat at the same rate.
- In general the sample and reference calorimeter heat capacities do not match contributing to non-zero empty DSC heat flow rate baseline.
- During transitions and MDSC® experiments the sample and reference heating rates differ and the measured heat flow rate is incorrect because the sample and reference sensor and pan heat capacities store or release heat at different rates.

Expanded Principle of Operation



Not Being Measured w/ Conventional DSC

$$Q = \frac{Ts - Tr}{R} + A + B + C$$

A: Thermal Resistance Imbalance

B: Thermal Capacitance Imbalance

C: Heating Rate Imbalance

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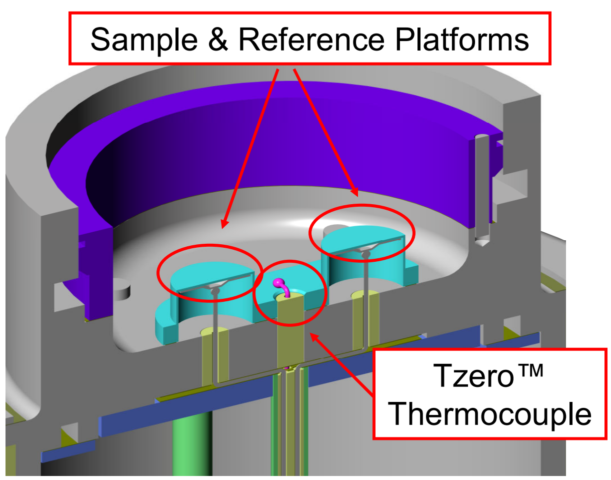
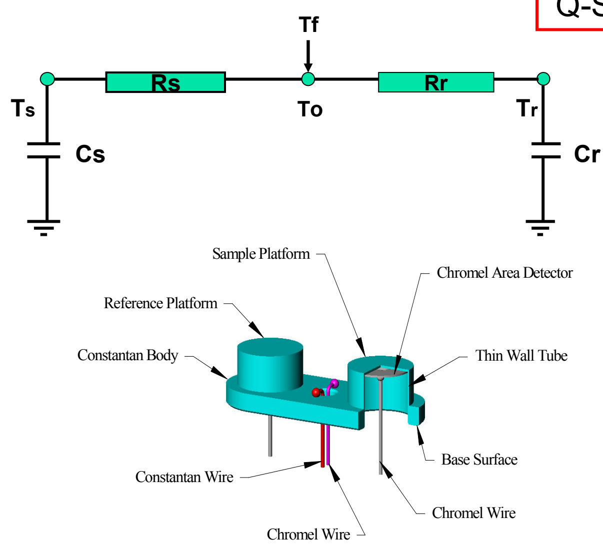
Q-Series DSC Schematic



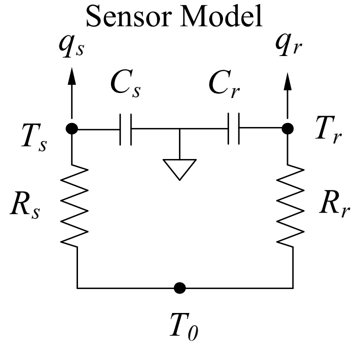
Q-Series Heat Flow Measurement

Q-Series DSC



Tzero™ Heat Flow Measurement

Heat Flow Sensor Model



Differential Temperatures

$$\Delta T = T_s - T_r \qquad \Delta T_0 = T_0 - T_s$$

Heat Flow Rate Equations

$$q_s = \frac{\Delta T_0}{R_s} - C_s \frac{dT}{dt}$$

$$q_r = \frac{\Delta T_0 + \Delta T}{R_r} - C_r \frac{dT}{dt}$$

The sample and reference calorimeter thermal resistances and heat capacities obtained from Tzero calibration are used in the heat flow rate measurements.

Tzero™ Heat Flow Measurement (T4)

$$q_{T4} = q_s - q_r$$

Thermal Resistance Imbalance

Heating Rate Difference

$$q_{T4} = -\frac{\Delta T}{R_r} + \Delta T_0\left(\frac{1}{R_s} - \frac{1}{R_r}\right) + (C_r - C_s)\frac{dT_s}{d\tau} - C_r\frac{d\Delta T}{d\tau}$$

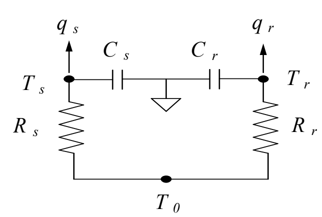
Principal DSC Heat Flow

Heat Capacity Imbalance

The four term Tzero heat flow rate measurement includes effects of the thermal resistance and heat capacity imbalances as well as the difference in the heating rates of the sample and reference calorimeters. When the assumptions of conventional DSC are applied, only the first term remains and the conventional heat flow rate measurement is obtained.

Tzero™ Heat Flow Equation

Heat Flow Sensor Model

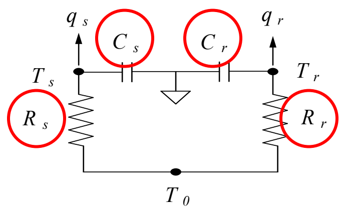


Besides the three temperatures (T_s, T_r, T_0); what other values do we need to calculate Heat Flow?

$$q = -\frac{\Delta T}{R_r} + \Delta T_0\left(\frac{1}{R_s} - \frac{1}{R_r}\right) + (C_r - C_s)\frac{dT_s}{d\tau} - C_r\frac{d\Delta T}{d\tau}$$

Tzero™ Heat Flow Equation

Heat Flow Sensor Model



Besides the three temperatures (T_s, T_r, T_0); what other values do we need to calculate Heat Flow?

How do we calculate these?

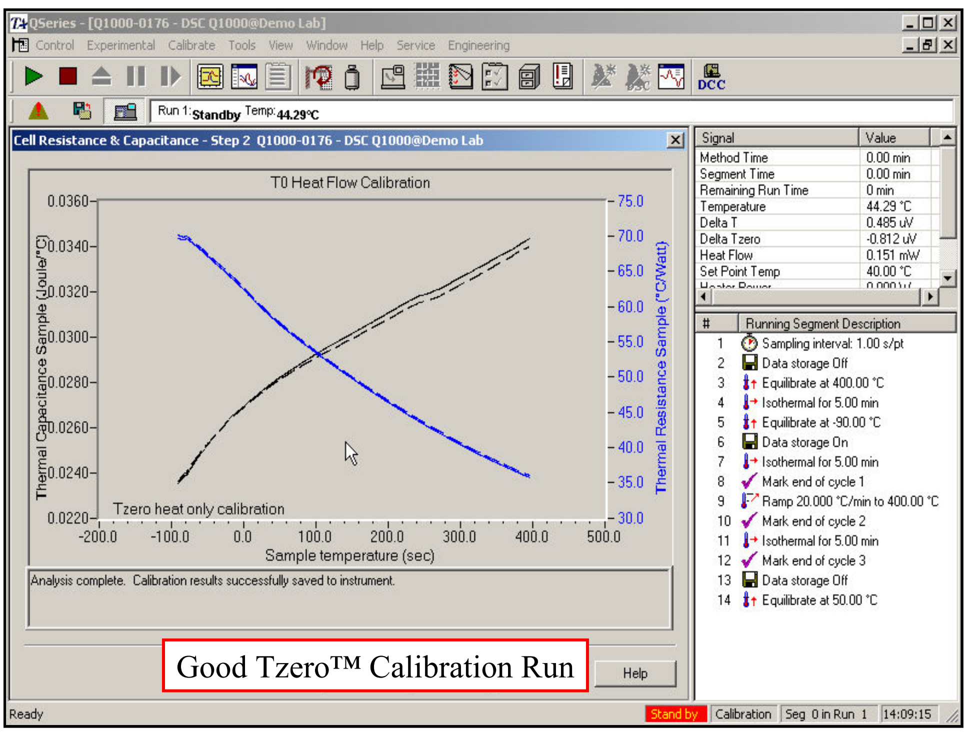
$$q = -\frac{\Delta T}{R_r} + \Delta T_0 \left(\frac{1}{R_s} - \frac{1}{R_r} \right) + \left(C_r - C_s \right) \frac{dT_s}{d\tau} - C_r \frac{d\Delta T}{d\tau}$$

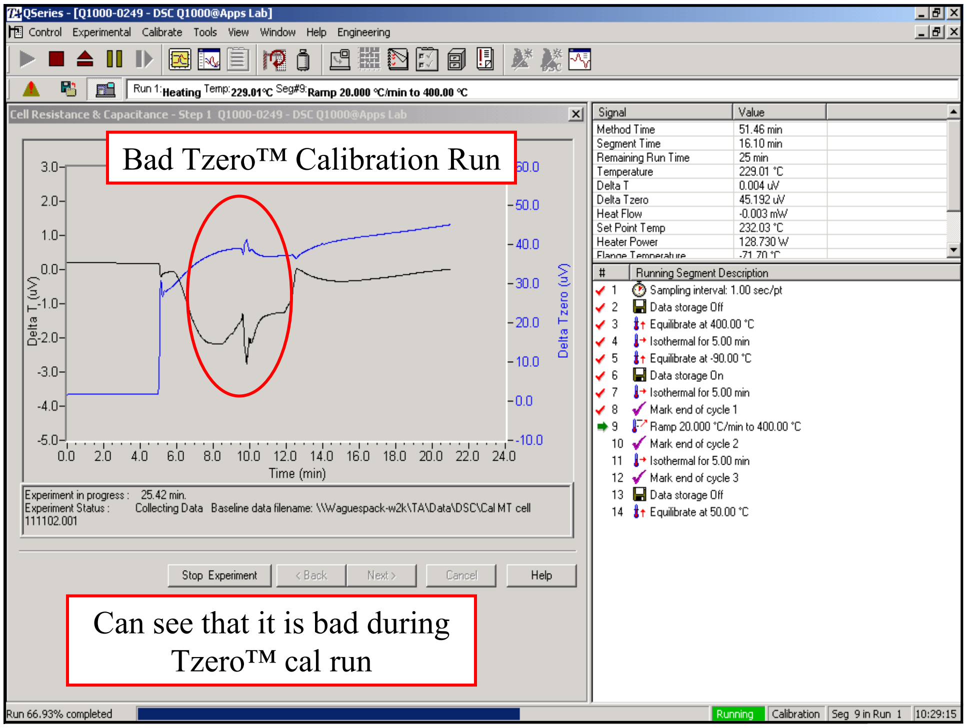
Measuring the C’s & R’s

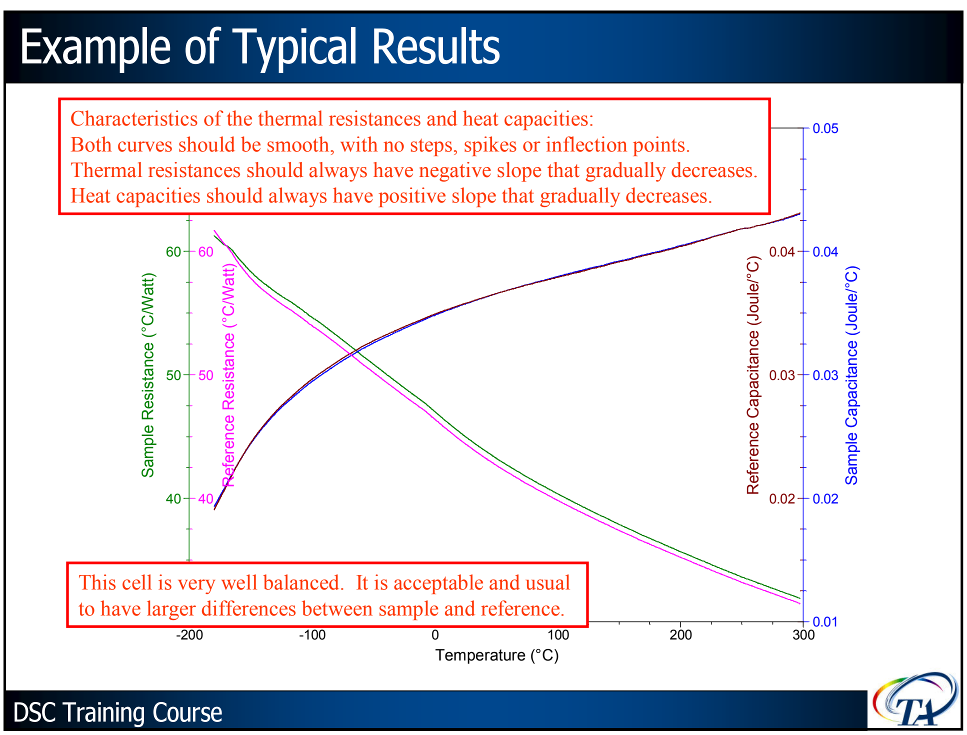
- Tzero™ Calibration calculates the C’s & R’s
- Calibration is a misnomer, THIS IS NOT A CALIBRATION, but rather a measurement of the Capacitance (C) and Resistance (R) of each DSC cell
- After determination of these values, they can be used in the Four Term Heat Flow Equation (T4) shown previously

A few words about the C's and R's

- The curves should be smooth and continuous, without evidence of noise or artifacts
- Capacitance values should increase with temperature (with a decreasing slope)
- Resistance values should decrease with temperature (also with a decreasing slope)
- It is not unusual for there to be a difference between the two sides, although often they are very close to identical




QSeries - [Q1000-0249 - DSC Q1000@Apps Lab]
Control Experimental Calibrate Tools View Window Help Engineering
Run 1: Heating Temp: 229.01°C Seg#9: Ramp 20.000 °C/min to 400.00 °C
Cell Resistance & Capacitance - Step 1 Q1000-0249 - DSC Q1000@Apps Lab
Bad Tzero™ Calibration Run
Delta T (uV)
Delta Tzero (uV)
Time (min)
Experiment in progress : 25.42 min.
Experiment Status : Collecting Data Baseline data filename: \\Waguespack-w2k\TA\Data\DSC\Cal MT cell 111102.001
Stop Experiment
< Back
Next >
Cancel
Help
Can see that it is bad during Tzero™ cal run
Signal
Value
Method Time 51.46 min
Segment Time 16.10 min
Remaining Run Time 25 min
Temperature 229.01 °C
Delta T 0.004 uV
Delta Tzero 45.192 uV
Heat Flow -0.003 mW
Set Point Temp 232.03 °C
Heater Power 128.730 W
Running Segment Description
1 Sampling interval: 1.00 sec/pt
2 Data storage Off
3 Equilibrate at 400.00 °C
4 Isothermal for 5.00 min
5 Equilibrate at -90.00 °C
6 Data storage On
7 Isothermal for 5.00 min
8 Mark end of cycle 1
9 Ramp 20.000 °C/min to 400.00 °C
10 Mark end of cycle 2
11 Isothermal for 5.00 min
12 Mark end of cycle 3
13 Data storage Off
14 Equilibrate at 50.00 °C
Run 66.93% completed
Running
Calibration
Seg 9 in Run 1
10:29:15


Example of Typical Results
Characteristics of the thermal resistances and heat capacities:
Both curves should be smooth, with no steps, spikes or inflection points.
Thermal resistances should always have negative slope that gradually decreases.
Heat capacities should always have positive slope that gradually decreases.
Sample Resistance (°C/Watt)
Reference Resistance (°C/Watt)
Reference Capacitance (Joule/°C)
Sample Capacitance (Joule/°C)
This cell is very well balanced. It is acceptable and usual to have larger differences between sample and reference.
Temperature (°C)
DSC Training Course

Agenda

- What does a DSC measure?
- How does a DSC make that measurement?
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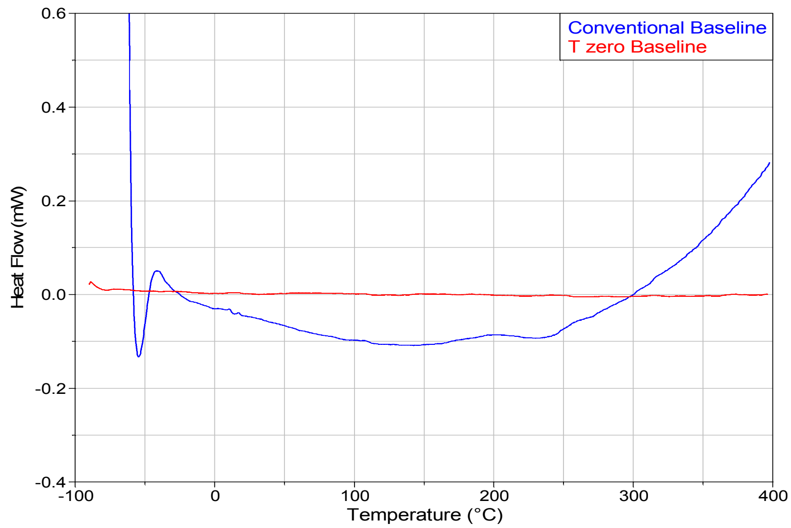
DSC Training Course

What does this do for us?

- By measuring the capacitance and resistance, we are no longer assuming the DSC cell is symmetrical
- Using these values in the four term equation, we see that nearly all aspects of DSC performance are improved by Tzero™ DSC.
  - Empty DSC baselines are straighter and closer to zero.
  - Resolution is enhanced.
  - Sensitivity is enhanced.
  - Frequency dependence of MDSC is greatly reduced.

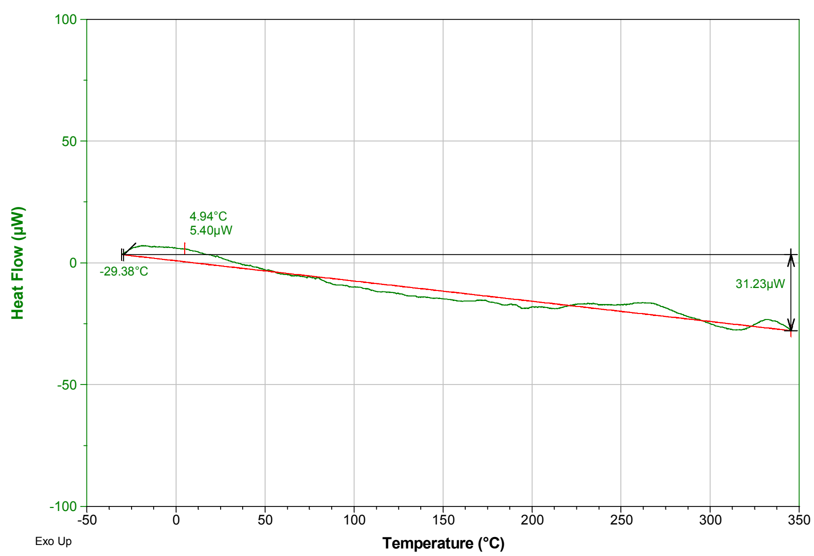
DSC Training Course

Tzero™ vs Conventional Baseline



DSC Training Course

Q2000 Quantified Baseline Performance



DSC Training Course

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Advanced Tzero™ Technology

- During transitions and MDSC experiments, the heating rates of the sample pan, sample calorimeter, reference pan and reference calorimeter may be very different.
- Sample pans have thermal resistance and heat capacity and sample and reference pans rarely have the same mass.
- Advanced Tzero includes the heat capacity of the pans and the heating rate differences between the sample and reference calorimeters and pans.
- Peaks are taller and sharper, hence both resolution and sensitivity are dramatically improved.

Advanced Tzero™ Model

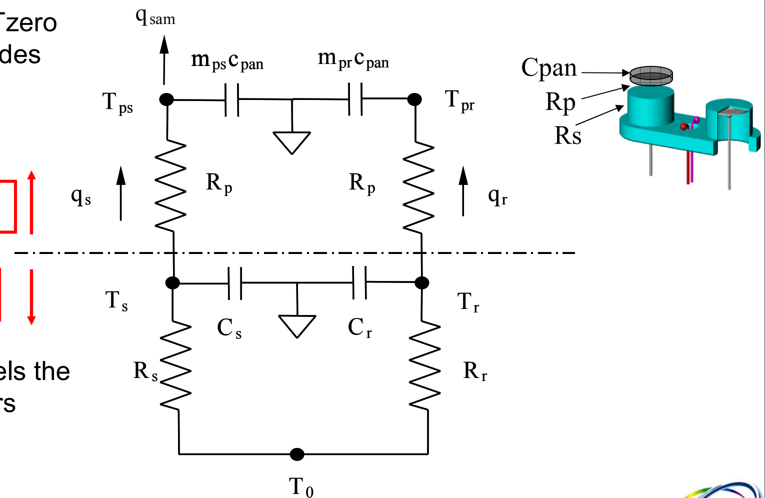
Advanced Tzero is a further refinement of the Tzero model and takes the measurement up to the sample pan, ***one step closer to the actual sample***

Advanced Tzero model includes the *pans*

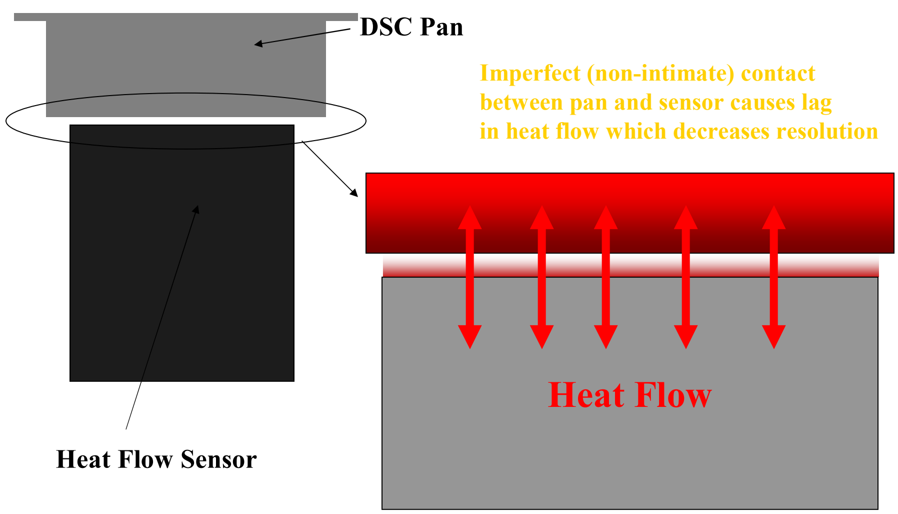
Q2000

Q200

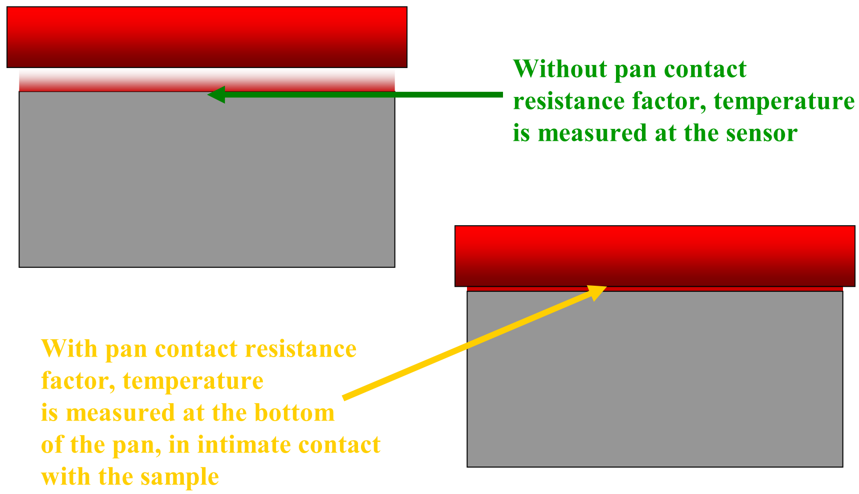
Tzero models the Calorimeters



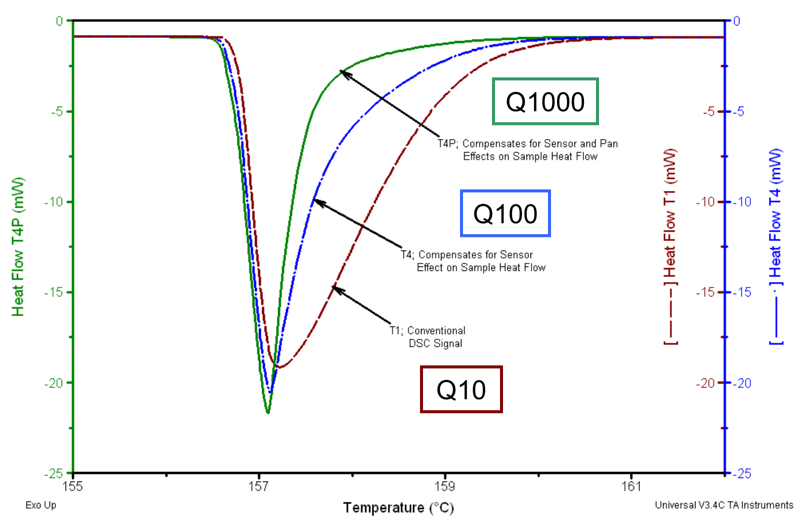
What is Pan Contact Resistance?



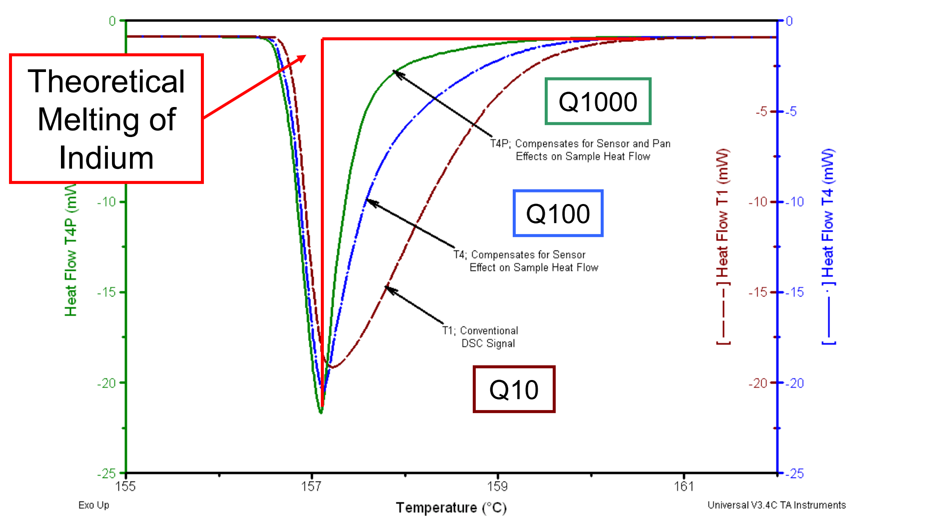
Result of Pan Contact Resistance Factor



Indium with Q-Series Heat Flow Signals

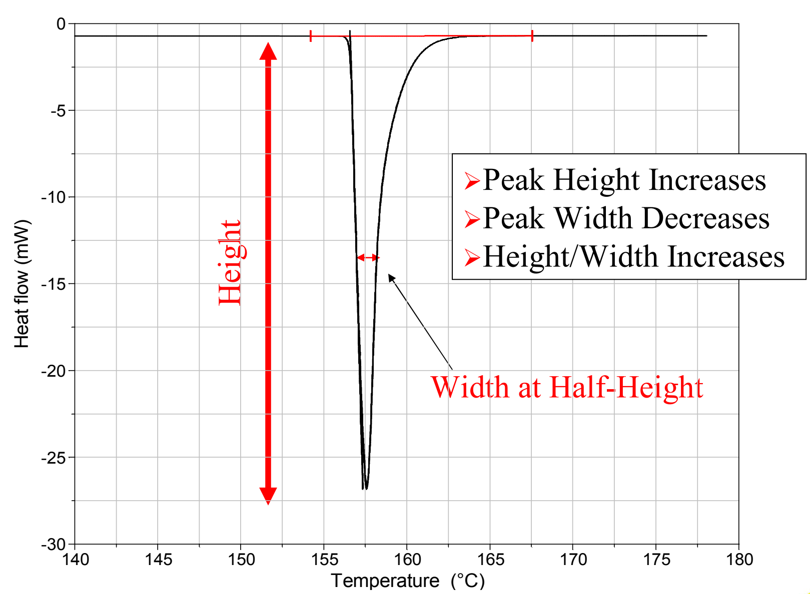


Indium with Q-Series Heat Flow Signals



DSC Training Course

Indium as a Measure of Sensitivity & Resolution



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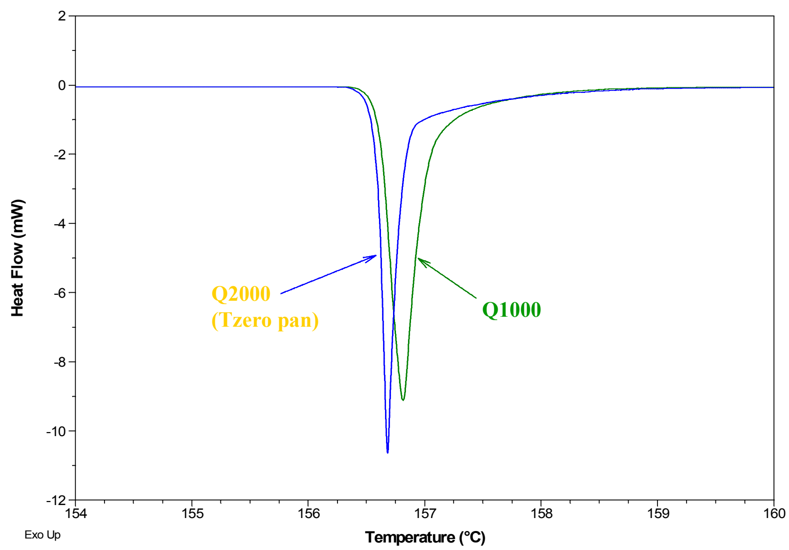
Improved Sensitivity/Resolution-Q2000



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Q-Series DSC Performance Comparison

	Q10/20	Q100/200	Q1000/2000
1st Generation Q-Series	7.5±0.4	20.8±2.1	36.3±4.4
2nd Generation Q-Series	**8.4±0.4**	**30±3.4**	**60±8**
Improvement	**12%**	**44%**	**65%**

DSC Training Course

Definitions

- **Amorphous Phase -** The portion of material whose molecules are randomly oriented in space. Liquids and glassy or rubbery solids. Thermosets and some thermoplastics

- **Crystalline Phase -** The portion of material whose molecules are regularly arranged into well defined structures consisting of repeat units. Very few polymers are 100% crystalline

- **Semi-crystalline Polymers -** Polymers whose solid phases are partially amorphous and partially crystalline. Most common thermoplastics are semi-crystalline

Definitions (cont.)

- **Melting –** The process of converting crystalline structure to a liquid amorphous structure

- **Thermodynamic Melting Temperature –** The temperature where a crystal would melt if it had a perfect structure (large crystal with no defects)

- **Metastable Crystals –** Crystals that melt at lower temperature due to small size (high surface area) and poor quality (large number of defects)

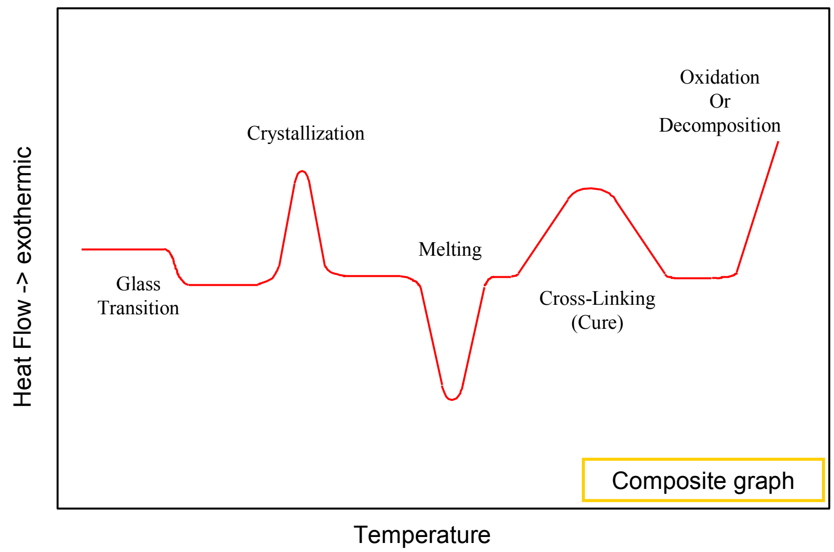
Definitions (cont.)

- **Crystal Perfection** – The process of small, less perfect crystals (metastable) melting at a temperature below their thermodynamic melting point and then (re) crystallizing into larger, more perfect crystals that will melt again at a higher temperature.
- **True Heat Capacity Baseline** – Often called the thermodynamic baseline, it is the measured baseline (usually in heat flow rate units of mW) with all crystallization and melting removed.
  - Assumes no interference from other latent heat such as polymerization, cure, evaporation etc. over the crystallization/melting range.

Definitions (cont.)

- **Crystallization –** The process of converting either solid amorphous structure (cold crystallization on heating) or liquid amorphous structure (cooling) to a more organized solid crystalline structure
- **Enthalpy of Melting/Crystallization** - The heat energy required for melting or released upon crystallization. This is calculated by integrating the area of the DSC peak on a time basis.

Typical DSC Transitions



Experimental Design

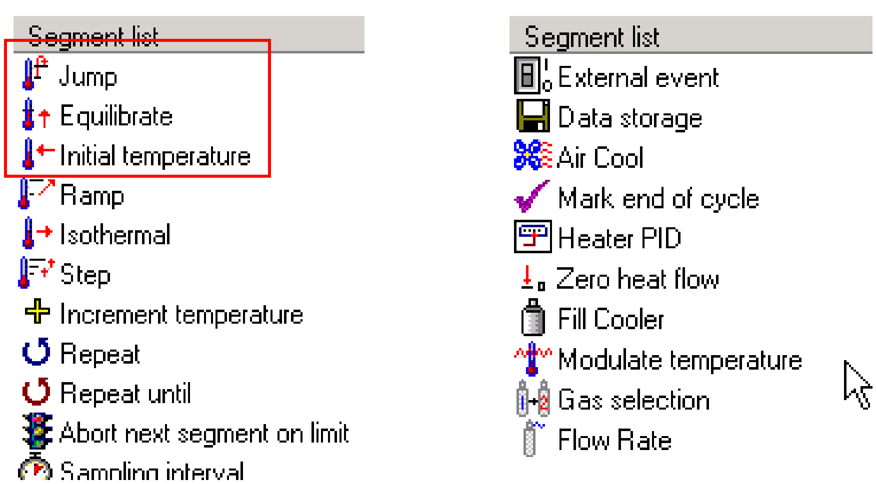
- Available Method Segments
- Method Design Rules
- Typical Methods (Examples)

Methods vs. Procedures

The logic of the instrument control software is based upon the concepts of *methods* and *procedures*.

- **METHODS** are the actual steps that the DSC executes during a run. The software provides custom templates built around types of experiments.
- **PROCEDURES** include, along with the *method*, all other options that the user sets in creating a run. For example, the data sampling interval, method end conditions, etc.

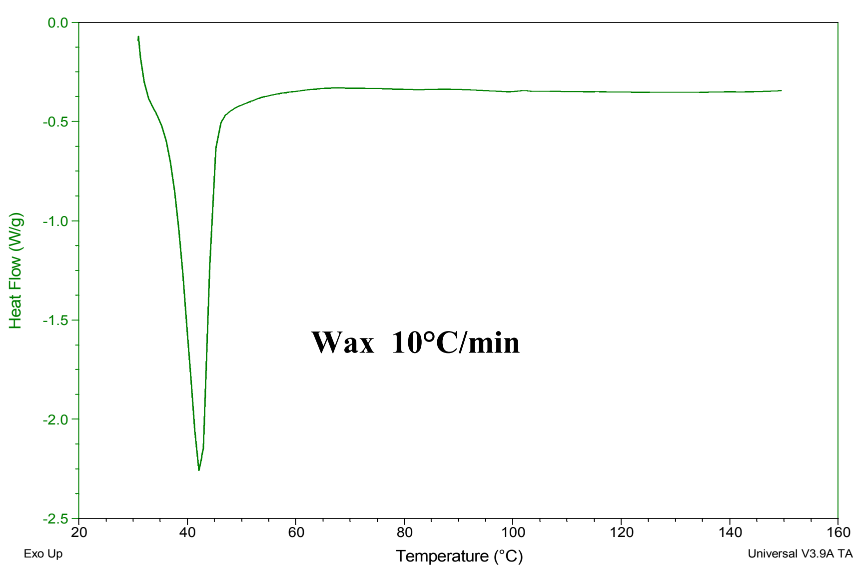
Q-Series DSC Segment List



Method Design Rules

- **Start Temperature**
  - Generally, the baseline should have two (2) minutes to completely stabilize prior to the transition of interest. Therefore, at 10°C/min., start at least 20°C below the transition onset temperature
- **End Temperature**
  - Allow a two (2) minute baseline after the transition of interest in order to correctly select integration or analysis limits
  - **Don't Decompose sample in DSC Cell**

Why have 2 min of baseline?



Heating/Cooling Methods

Typical Heating Method

1) Equilibrate at 0°C
2) Ramp 10°C/min. to 300°C

Typical Cooling Method

1) Equilibrate at 300°C
2) Ramp 10°C/min. to 25°C

Heat-Cool-Reheat Method

Typical Heat-Cool-Heat Method

1) Equilibrate @ 25°C
2) Ramp 10°C/min. to 300°C
3) Mark cycle end 0
4) Ramp 10°C/min. to 25°C
5) Mark cycle end 0
6) Ramp 10°C/min. to 300°C
7) Mark cycle end 0

Oxidative Stability (OIT) Method

OIT Method

1) Equilibrate at 60°C
2) Isothermal for 5.00 min.
3) Ramp 20°C/min. to 200°C
4) Isothermal for 5.00 min.
5) Select gas: 2
6) Abort next seg. if W/g > 1.0
7) Isothermal for 200.00 min.

Modulated® DSC Method

Typical MDSC Methods

1) Data storage: off
2) Equilibrate at -20°C
3) Modulate ±1°C every 60 seconds
4) Isothermal for 5.00 min.
5) Data storage: on
6) Ramp 3°C/min. to 300°C

DSC General Method Recommendations

- Determine decomposition temp
  - Stay below that temperature
- Run Heat-Cool-Heat @ 10°C/min
- Use specific segments as needed, i.e. gas switch, abort, etc.
- Modify heating rate based on what you're looking for

Calibration & Sample Preparation

- Instrument Calibration
  - Q200 & Q2000
    - Cell Constant & Temperature
  - Q20 & 2900s
    - Baseline
    - Cell Constant & Temperature
- Miscellaneous
  - Purge Gas
  - Cooling Accessories
  - Environment
- Sample Preparation
- Selecting Experimental Conditions

General Calibration Issues

- Calibration
  - Use Calibration Mode
  - Calibrate upon installation
  - Re-calibrate every ????
- Verification
  - Determine how often to verify data
  - Run a standard as a sample (std mode)
  - Compare results vs. known
  - If results are within your tolerance – system checks out and doesn't re-need calibration
  - If results are out of tolerance, then re-calibrate

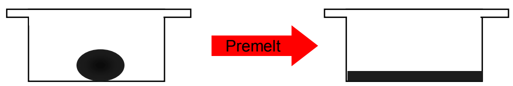
Heat Flow Calibration

- Differential Heat Flow (ASTM E968)
- Heat of fusion (melting) standards
- Heat capacity (no transition)

- Miscellaneous
  - Use specific purge gas at specified rate
  - Calibrate w/cooling accessory functioning if it will be used to run samples
  - Single point used for heat of fusion
  - Calibration should not change w/heating rate

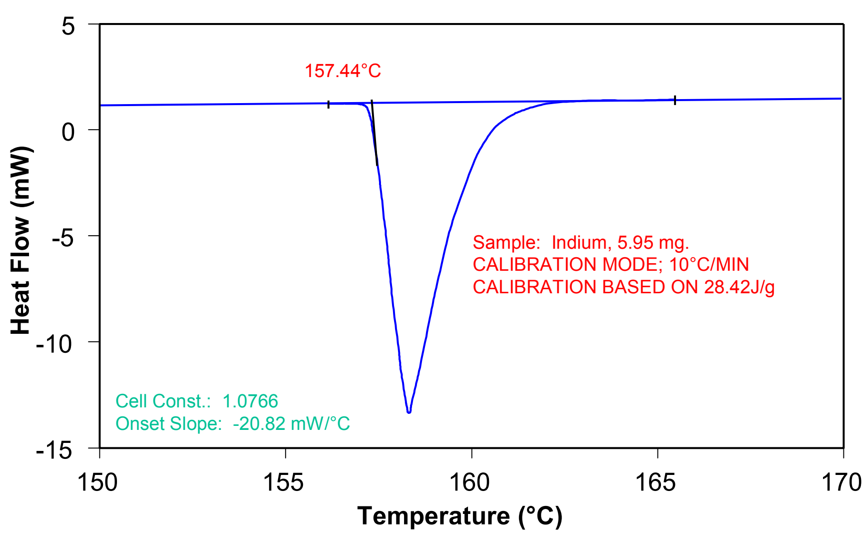
Heat Flow Calibration

- Prepare a 1-3mg sample of indium and premelt prior to first use



- Verify at least once a month
- Typical values for cell constant:
  - 1.0 to 1.2 (in N_2)

Calorimetric Calibration

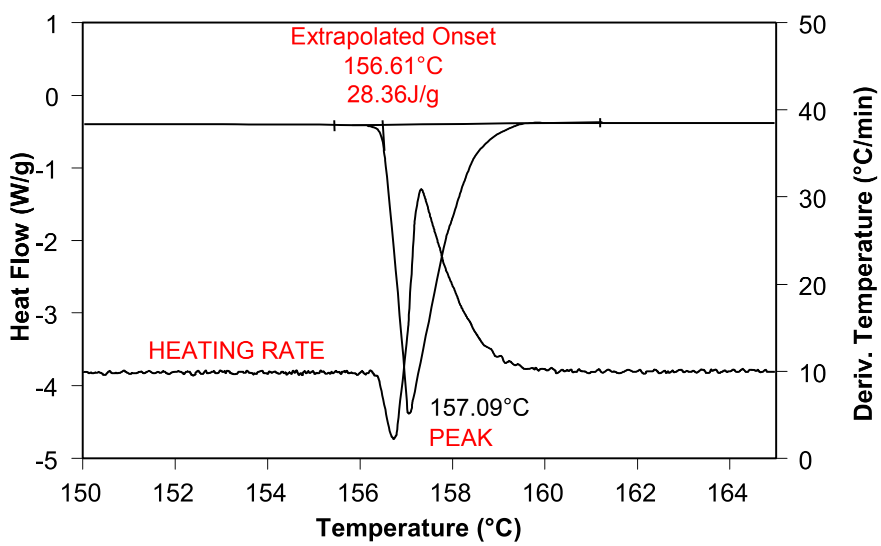


Temperature Calibration

- ASTM Method E967
  - Pure metals (indium, lead, etc.) typically used
  - Extrapolated onset is used as melting temperature
  - Sample is fully melted at the peak

DSC Training Course

Temperature Calibration



DSC Training Course

Temperature Calibration

- Verify at least once a month
- Maximum of five points
- Use tin, lead, and zinc one time only

Recommended Temperature & Enthalpy Standards

Enthalpy (cell constant)

- **Benzoic acid (147.3 J/g) Tm = 123°C**
- **Urea (241.8 J/g) Tm = 133°C**
- **Indium (28.45 J/g) Tm = 156.6°C**
- **Anthracene (161.9 J/g) Tm = 216°C**

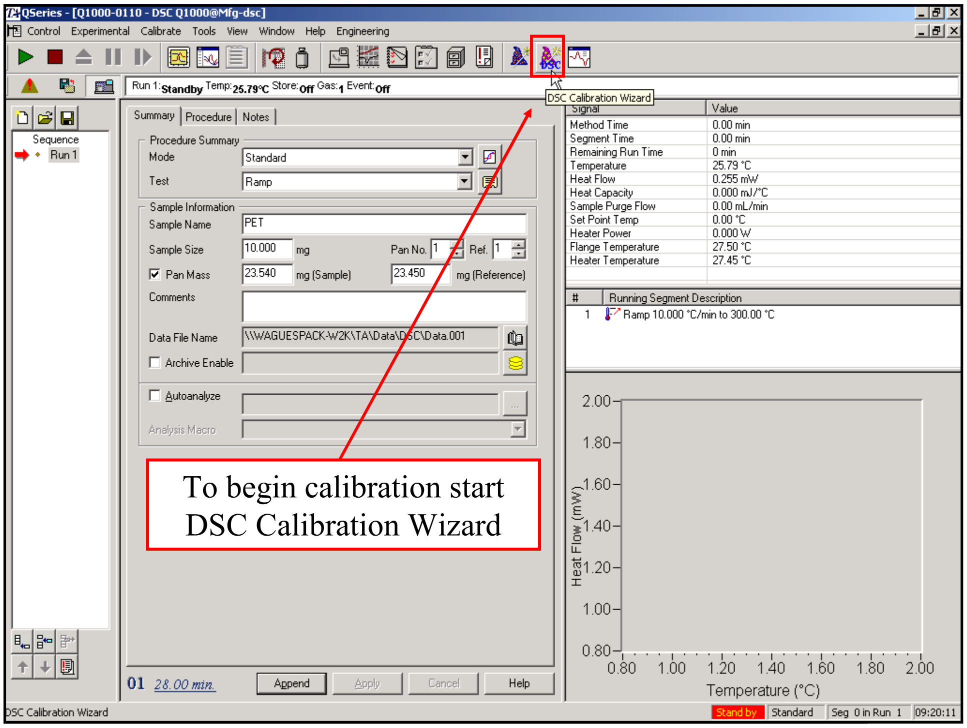
Temperature

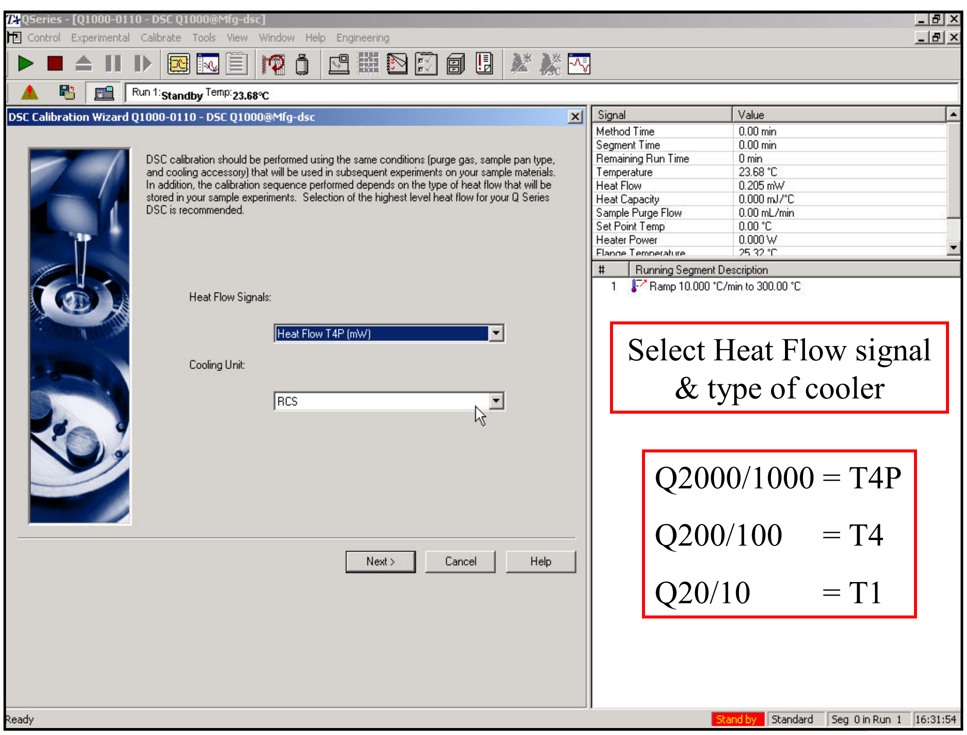
- **Cyclopentane* -150.77°C**
- **Cyclopentane* -135.09°C**
- **Cyclopentane* -93.43°C**
- **Cyclohexane# -83°C**
- **Water# 0°C**
- **Gallium# 29.76°C**
- **Phenyl Ether# 30°C**
- **p-NitrotolueneE 51.45°C**
- **NaphthaleneE 80.25°C**
- **Indium# 156.60°C**
- **Tin# 231.95°C**
- **Lead* 327.46°C**
- **Zinc# 419.53°C**

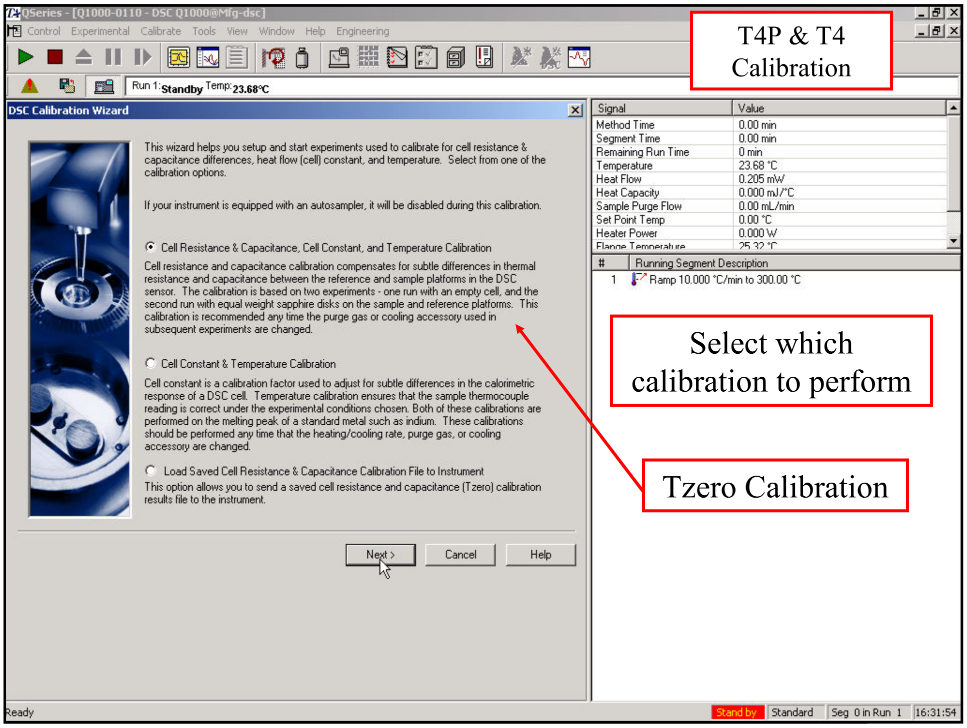
* GEFTA recommended
Thermochim. Acta, 219 (**1993**) 333.

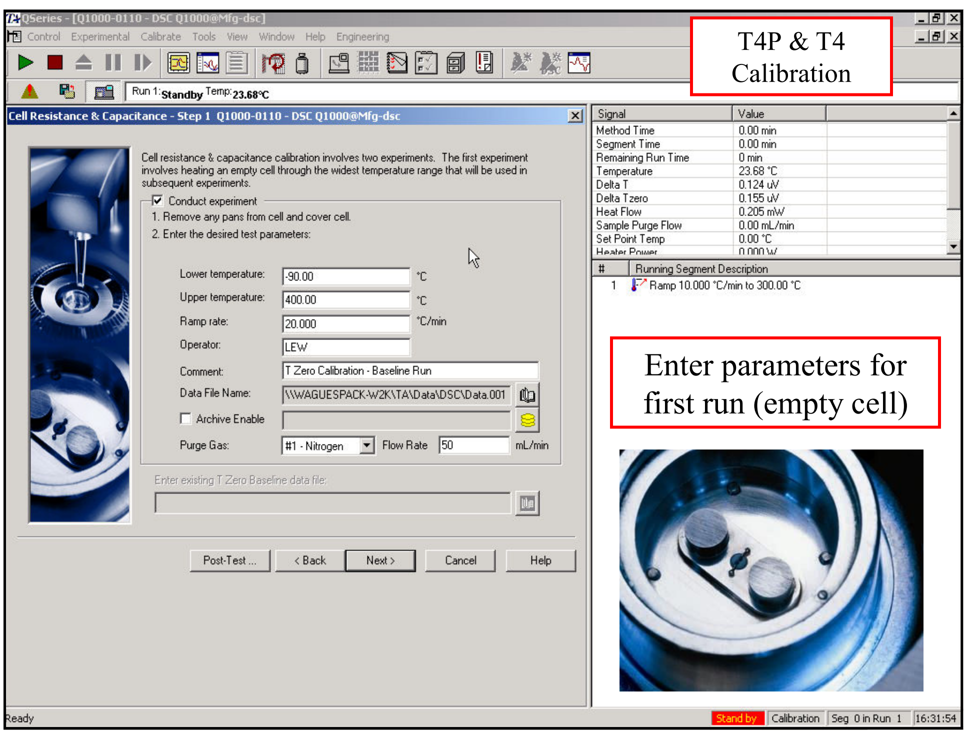
\# ITS 90 Fixed Point

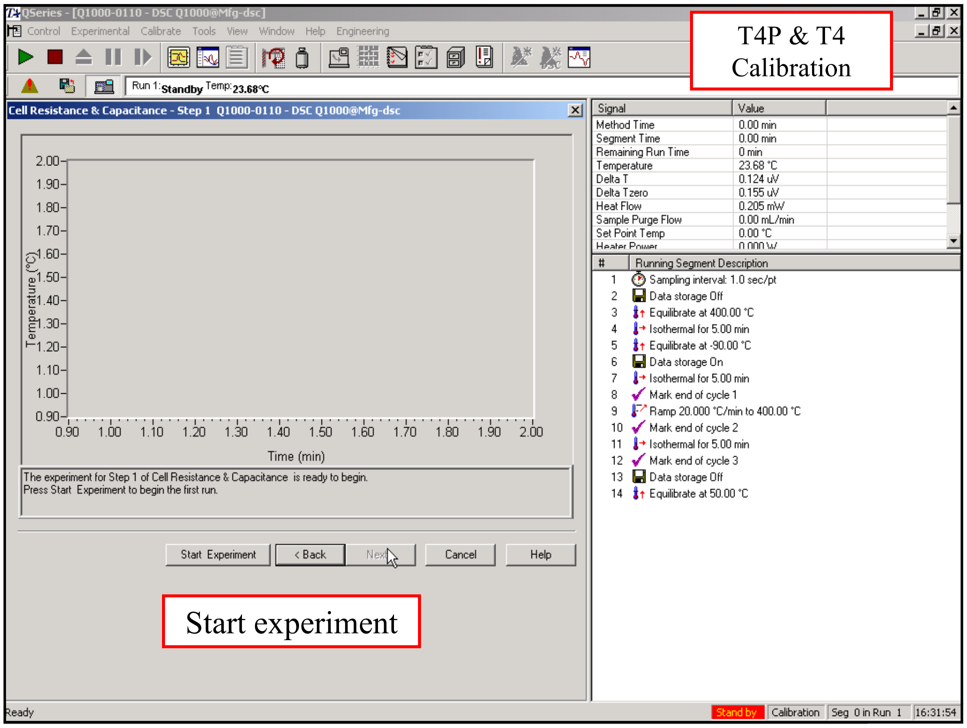
E Zone refined organic compound (sublimes)

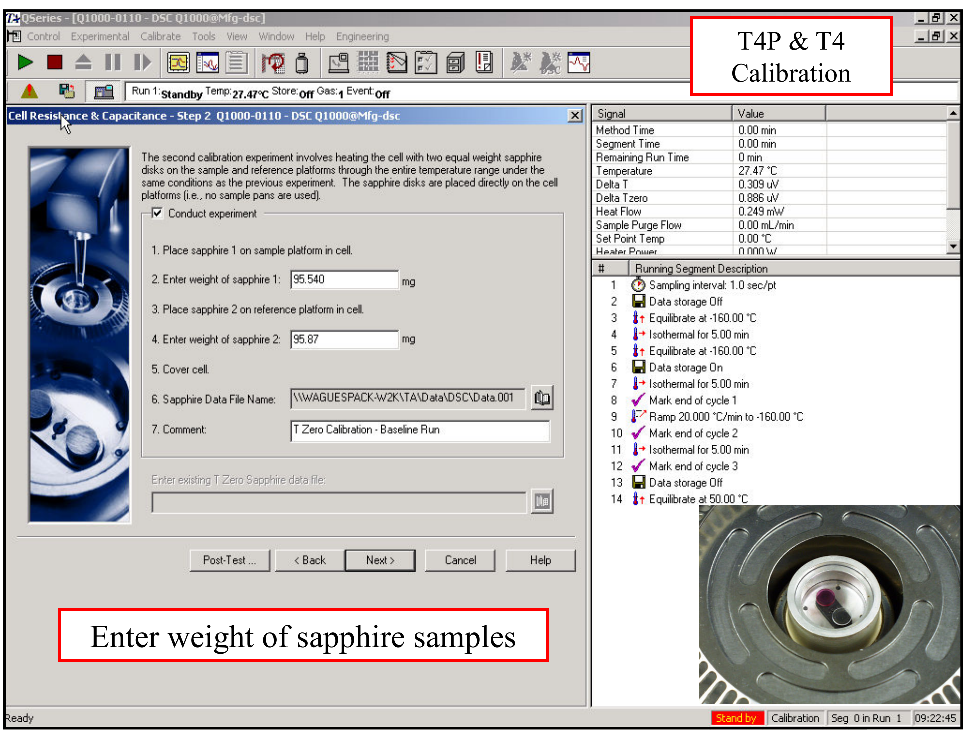

QSeries - [Q1000-0110 - DSC Q1000@Mfg-dsc]
DSC Calibration Wizard
To begin calibration start DSC Calibration Wizard
Procedure Summary
Mode
Standard
Test
Ramp
Sample Information
Sample Name
PET
Ramp 10.000 °C/min to 300.00 °C
Heat Flow (mW)
Temperature (°C)

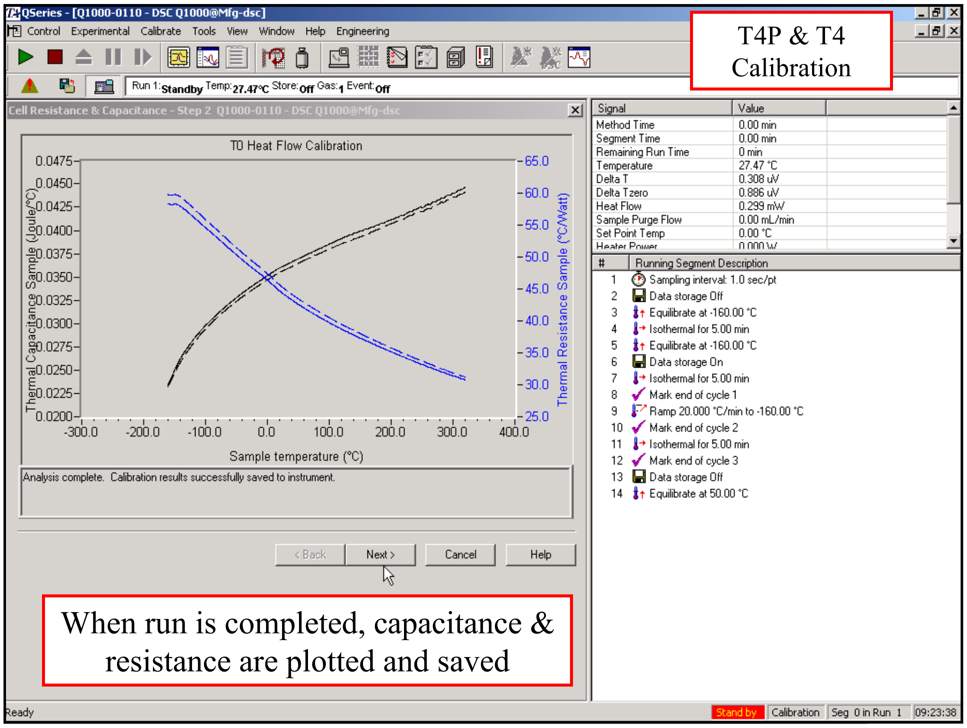

DSC Calibration Wizard Q1000-0110 - DSC Q1000@Mfg-dsc
DSC calibration should be performed using the same conditions (purge gas, sample pan type, and cooling accessory) that will be used in subsequent experiments on your sample materials. In addition, the calibration sequence performed depends on the type of heat flow that will be stored in your sample experiments. Selection of the highest level heat flow for your Q Series DSC is recommended.
Heat Flow Signals:
Heat Flow T4P (mW)
Cooling Unit:
RCS
Next >
Cancel
Help
Select Heat Flow signal & type of cooler
Q2000/1000 = T4P
Q200/100 = T4
Q20/10 = T1

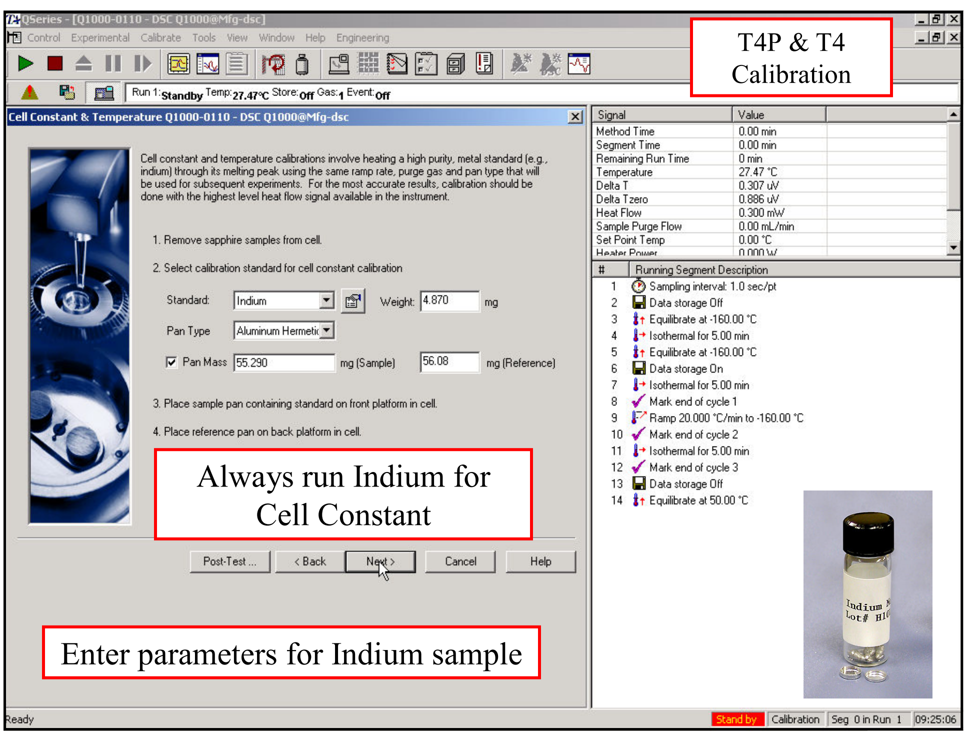

QSeries - [Q1000-0110 - DSC Q1000@Mfg-dsc]
Control Experimental Calibrate Tools View Window Help Engineering
T4P & T4
Calibration
Run 1: Standby Temp: 23.68°C
DSC Calibration Wizard
This wizard helps you setup and start experiments used to calibrate for cell resistance & capacitance differences, heat flow (cell) constant, and temperature. Select from one of the calibration options.
If your instrument is equipped with an autosampler, it will be disabled during this calibration.
Cell Resistance & Capacitance, Cell Constant, and Temperature Calibration
Cell resistance and capacitance calibration compensates for subtle differences in thermal resistance and capacitance between the reference and sample platforms in the DSC sensor. The calibration is based on two experiments - one run with an empty cell, and the second run with equal weight sapphire disks on the sample and reference platforms. This calibration is recommended any time the purge gas or cooling accessory used in subsequent experiments are changed.
Cell Constant & Temperature Calibration
Cell constant is a calibration factor used to adjust for subtle differences in the calorimetric response of a DSC cell. Temperature calibration ensures that the sample thermocouple reading is correct under the experimental conditions chosen. Both of these calibrations are performed on the melting peak of a standard metal such as indium. These calibrations should be performed any time that the heating/cooling rate, purge gas, or cooling accessory are changed.
Load Saved Cell Resistance & Capacitance Calibration File to Instrument
This option allows you to send a saved cell resistance and capacitance (Tzero) calibration results file to the instrument.
Next >
Cancel
Help
Signal
Value
Method Time
0.00 min
Segment Time
0.00 min
Remaining Run Time
0 min
Temperature
23.68 °C
Heat Flow
0.205 mW
Heat Capacity
0.000 mJ/°C
Sample Purge Flow
0.00 mL/min
Set Point Temp
0.00 °C
Heater Power
0.000 W
Running Segment Description
1 Ramp 10.000 °C/min to 300.00 °C
Select which calibration to perform
Tzero Calibration
Ready
Stand by
Standard
Seg 0 in Run 1
16:31:54

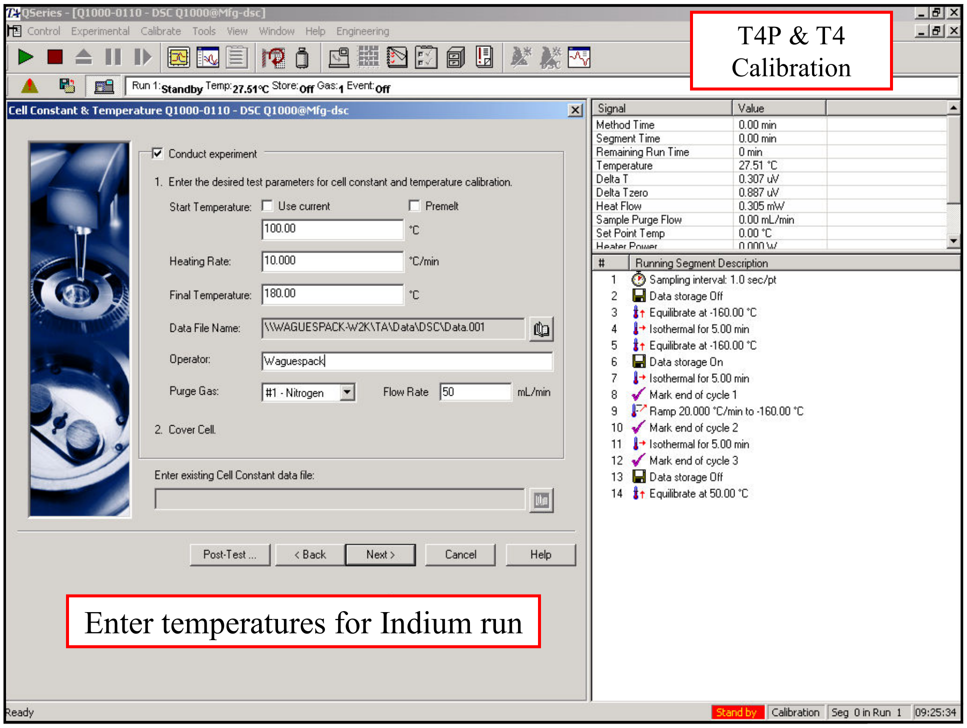

QSeries - [Q1000-0110 - DSC Q1000@Mfg-dsc]
Control Experimental Calibrate Tools View Window Help Engineering
T4P & T4
Calibration
Run 1: Standby Temp: 23.68°C
Cell Resistance & Capacitance - Step 1 Q1000-0110 - DSC Q1000@Mfg-dsc
Cell resistance & capacitance calibration involves two experiments. The first experiment involves heating an empty cell through the widest temperature range that will be used in subsequent experiments.
Conduct experiment
1. Remove any pans from cell and cover cell.
2. Enter the desired test parameters:
Lower temperature: -90.00 °C
Upper temperature: 400.00 °C
Ramp rate: 20.000 °C/min
Operator: LEW
Comment: T Zero Calibration - Baseline Run
Data File Name: \\WAGUESPACK-W2K\TA\Data\DSC\Data.001
Archive Enable
Purge Gas: #1 - Nitrogen Flow Rate 50 mL/min
Enter existing T Zero Baseline data file:
Post-Test ...
< Back
Next >
Cancel
Help
Signal
Value
Method Time
0.00 min
Segment Time
0.00 min
Remaining Run Time
0 min
Temperature
23.68 °C
Delta T
0.124 uV
Delta Tzero
0.155 uV
Heat Flow
0.205 mW
Sample Purge Flow
0.00 mL/min
Set Point Temp
0.00 °C
Running Segment Description
1 Ramp 10.000 °C/min to 300.00 °C
Enter parameters for first run (empty cell)
Ready
Stand by
Calibration
Seg 0 in Run 1
16:31:54

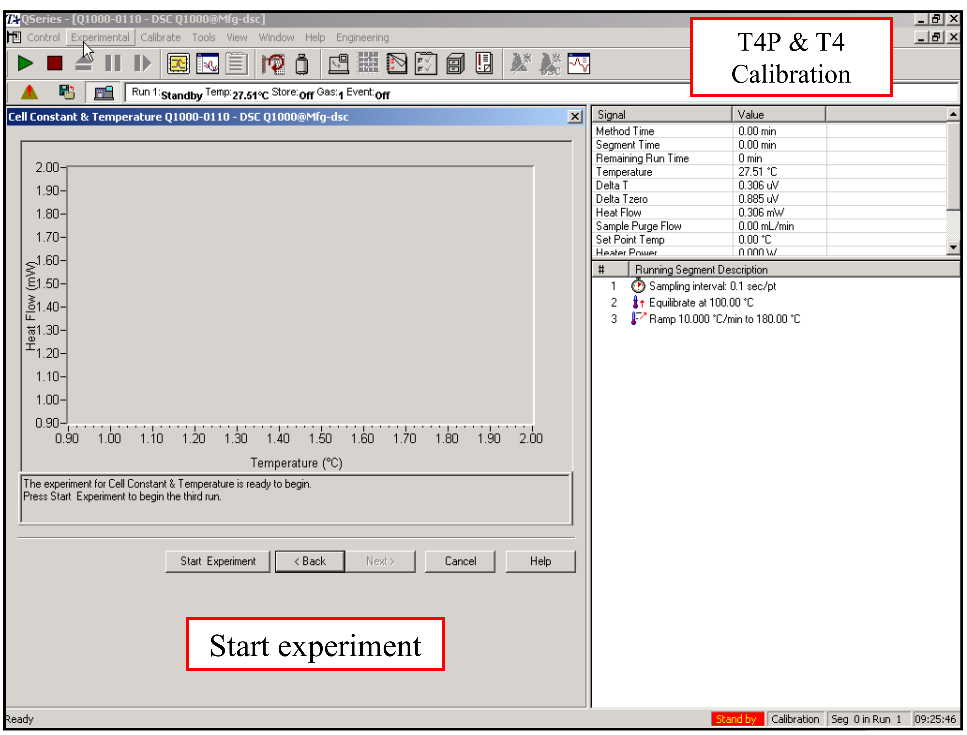

QSeries - [Q1000-0110 - DSC Q1000@Mfg-dsc]
Control Experimental Calibrate Tools View Window Help Engineering
T4P & T4 Calibration
Run 1: Standby Temp: 23.68°C
Cell Resistance & Capacitance - Step 1 Q1000-0110 - DSC Q1000@Mfg-dsc
Temperature (°C)
Time (min)
The experiment for Step 1 of Cell Resistance & Capacitance is ready to begin.
Press Start Experiment to begin the first run.
Start Experiment
< Back
Next
Cancel
Help
Start experiment
Signal
Value
Method Time 0.00 min
Segment Time 0.00 min
Remaining Run Time 0 min
Temperature 23.68 °C
Delta T 0.124 uV
Delta Tzero 0.155 uV
Heat Flow 0.205 mW
Sample Purge Flow 0.00 mL/min
Set Point Temp 0.00 °C
Running Segment Description
1 Sampling interval: 1.0 sec/pt
2 Data storage Off
3 Equilibrate at 400.00 °C
4 Isothermal for 5.00 min
5 Equilibrate at -90.00 °C
6 Data storage On
7 Isothermal for 5.00 min
8 Mark end of cycle 1
9 Ramp 20.000 °C/min to 400.00 °C
10 Mark end of cycle 2
11 Isothermal for 5.00 min
12 Mark end of cycle 3
13 Data storage Off
14 Equilibrate at 50.00 °C
Ready
Stand by
Calibration
Seg 0 in Run 1
16:31:54

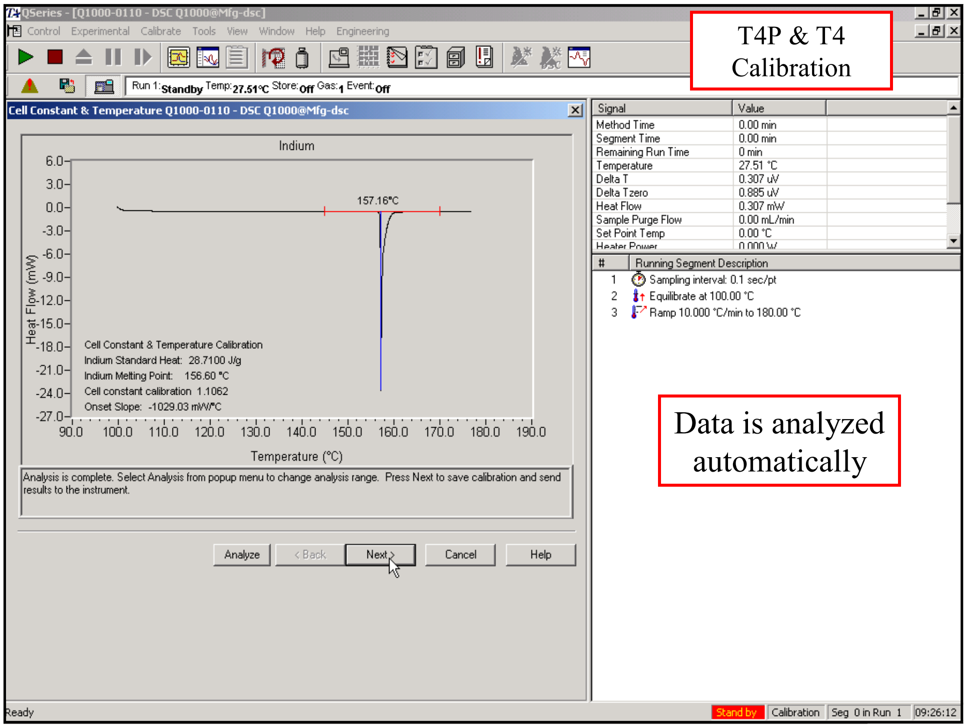

QSeries - [Q1000-0110 - DSC Q1000@Mfg-dsc]
Control Experimental Calibrate Tools View Window Help Engineering
T4P & T4 Calibration
Run 1: Standby Temp: 27.47°C Store: Off Gas: 1 Event: Off
Cell Resistance & Capacitance - Step 2 Q1000-0110 - DSC Q1000@Mfg-dsc
The second calibration experiment involves heating the cell with two equal weight sapphire disks on the sample and reference platforms through the entire temperature range under the same conditions as the previous experiment. The sapphire disks are placed directly on the cell platforms (i.e., no sample pans are used).
Conduct experiment
1. Place sapphire 1 on sample platform in cell.
2. Enter weight of sapphire 1: 95.540 mg
3. Place sapphire 2 on reference platform in cell.
4. Enter weight of sapphire 2: 95.87 mg
5. Cover cell.
6. Sapphire Data File Name: \\WAGUESPACK-W2K\TA\Data\DSC\Data.001
7. Comment: T Zero Calibration - Baseline Run
Enter existing T Zero Sapphire data file:
Post-Test ...
< Back
Next >
Cancel
Help
Enter weight of sapphire samples
Signal
Value
Method Time 0.00 min
Segment Time 0.00 min
Remaining Run Time 0 min
Temperature 27.47 °C
Delta T 0.309 uV
Delta Tzero 0.886 uV
Heat Flow 0.249 mW
Sample Purge Flow 0.00 mL/min
Set Point Temp 0.00 °C
Running Segment Description
1 Sampling interval: 1.0 sec/pt
2 Data storage Off
3 Equilibrate at -160.00 °C
4 Isothermal for 5.00 min
5 Equilibrate at -160.00 °C
6 Data storage On
7 Isothermal for 5.00 min
8 Mark end of cycle 1
9 Ramp 20.000 °C/min to -160.00 °C
10 Mark end of cycle 2
11 Isothermal for 5.00 min
12 Mark end of cycle 3
13 Data storage Off
14 Equilibrate at 50.00 °C
Ready
Stand by
Calibration
Seg 0 in Run 1
09:22:45

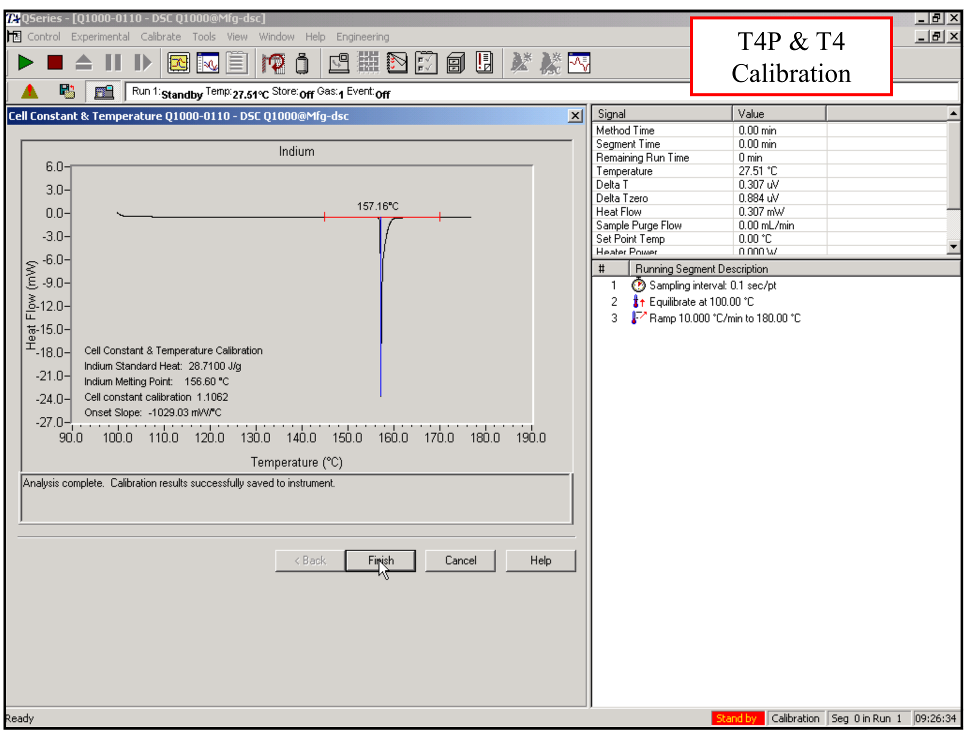

T4P & T4
Calibration
Cell Resistance & Capacitance - Step 2 Q1000-0110 - DSC Q1000@Mfg-dsc
T0 Heat Flow Calibration
Thermal Capacitance Sample (Joule/°C)
Thermal Resistance Sample (°C/Watt)
Sample temperature (°C)
Analysis complete. Calibration results successfully saved to instrument.
< Back
Next >
Cancel
Help
When run is completed, capacitance & resistance are plotted and saved


T4P & T4
Calibration
Cell Constant & Temperature Q1000-0110 - DSC Q1000@Mfg-dsc
Cell constant and temperature calibrations involve heating a high purity, metal standard (e.g., indium) through its melting peak using the same ramp rate, purge gas and pan type that will be used for subsequent experiments. For the most accurate results, calibration should be done with the highest level heat flow signal available in the instrument.
1. Remove sapphire samples from cell.
2. Select calibration standard for cell constant calibration
Standard: Indium
Weight: 4.870 mg
Pan Type Aluminum Hermetic
Pan Mass 55.290 mg (Sample) 56.08 mg (Reference)
3. Place sample pan containing standard on front platform in cell.
4. Place reference pan on back platform in cell.
Always run Indium for Cell Constant
Post-Test ...
< Back
Next >
Cancel
Help
Enter parameters for Indium sample


T4P & T4 Calibration
Cell Constant & Temperature Q1000-0110 - DSC Q1000@Mfg-dsc
Conduct experiment
1. Enter the desired test parameters for cell constant and temperature calibration.
Start Temperature:
Use current
Premelt
100.00
Heating Rate:
10.000
Final Temperature:
180.00
Data File Name:
\\WAGUESPACK-W2K\TA\Data\DSC\Data.001
Operator:
Waguespack
Purge Gas:
#1 - Nitrogen
Flow Rate
50
2. Cover Cell.
Enter existing Cell Constant data file:
Post-Test ...
< Back
Next >
Cancel
Help
Enter temperatures for Indium run
Signal
Value
Running Segment Description
Sampling interval: 1.0 sec/pt
Data storage Off
Equilibrate at -160.00 °C
Isothermal for 5.00 min
Equilibrate at -160.00 °C
Data storage On
Isothermal for 5.00 min
Mark end of cycle 1
Ramp 20.000 °C/min to -160.00 °C
Mark end of cycle 2
Isothermal for 5.00 min
Mark end of cycle 3
Data storage Off
Equilibrate at 50.00 °C


T4P & T4 Calibration
Cell Constant & Temperature Q1000-0110 - DSC Q1000@Mfg-dsc
Heat Flow (mW)
Temperature (°C)
The experiment for Cell Constant & Temperature is ready to begin.
Press Start Experiment to begin the third run.
Start Experiment
< Back
Next >
Cancel
Help
Start experiment
Running Segment Description
Sampling interval: 0.1 sec/pt
Equilibrate at 100.00 °C
Ramp 10.000 °C/min to 180.00 °C

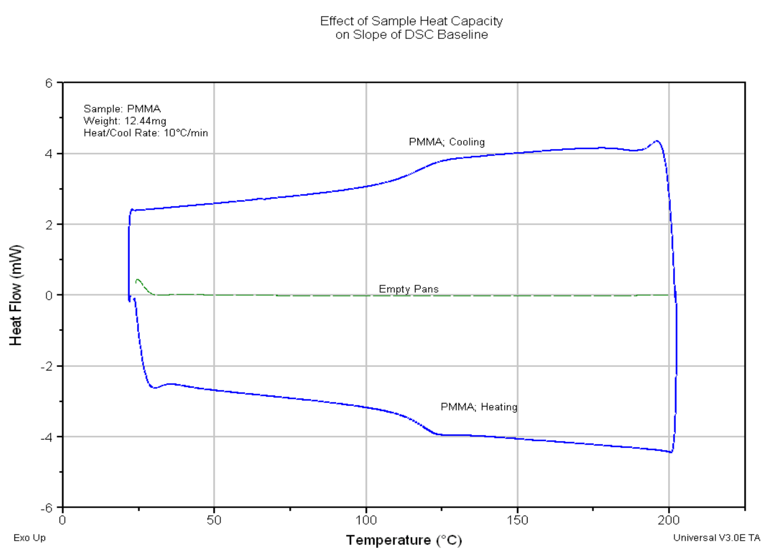

T4P & T4 Calibration
Data is analyzed automatically
QSeries - [Q1000-0110 - DSC Q1000@Mfg-dsc]
Control Experimental Calibrate Tools View Window Help Engineering
Run 1: Standby Temp: 27.51°C Store: Off Gas: 1 Event: Off
Cell Constant & Temperature Q1000-0110 - DSC Q1000@Mfg-dsc
Indium
157.16°C
Heat Flow (mW)
Temperature (°C)
Cell Constant & Temperature Calibration
Indium Standard Heat: 28.7100 J/g
Indium Melting Point: 156.60 °C
Cell constant calibration 1.1062
Onset Slope: -1029.03 mW/°C
Analysis is complete. Select Analysis from popup menu to change analysis range. Press Next to save calibration and send results to the instrument.
Analyze
< Back
Next >
Cancel
Help
Signal
Value
Method Time 0.00 min
Segment Time 0.00 min
Remaining Run Time 0 min
Temperature 27.51 °C
Delta T 0.307 uV
Delta Tzero 0.885 uV
Heat Flow 0.307 mW
Sample Purge Flow 0.00 mL/min
Set Point Temp 0.00 °C
Running Segment Description
1 Sampling interval: 0.1 sec/pt
2 Equilibrate at 100.00 °C
3 Ramp 10.000 °C/min to 180.00 °C
Ready
Stand by
Calibration
Seg 0 in Run 1
09:26:12


T4P & T4 Calibration
QSeries - [Q1000-0110 - DSC Q1000@Mfg-dsc]
Control Experimental Calibrate Tools View Window Help Engineering
Run 1: Standby Temp: 27.51°C Store: Off Gas: 1 Event: Off
Cell Constant & Temperature Q1000-0110 - DSC Q1000@Mfg-dsc
Indium
157.16°C
Heat Flow (mW)
Temperature (°C)
Cell Constant & Temperature Calibration
Indium Standard Heat: 28.7100 J/g
Indium Melting Point: 156.60 °C
Cell constant calibration 1.1062
Onset Slope: -1029.03 mW/°C
Analysis complete. Calibration results successfully saved to instrument.
< Back
Finish
Cancel
Help
Signal
Value
Method Time 0.00 min
Segment Time 0.00 min
Remaining Run Time 0 min
Temperature 27.51 °C
Delta T 0.307 uV
Delta Tzero 0.884 uV
Heat Flow 0.307 mW
Sample Purge Flow 0.00 mL/min
Set Point Temp 0.00 °C
Running Segment Description
1 Sampling interval: 0.1 sec/pt
2 Equilibrate at 100.00 °C
3 Ramp 10.000 °C/min to 180.00 °C
Ready
Stand by
Calibration
Seg 0 in Run 1
09:26:34

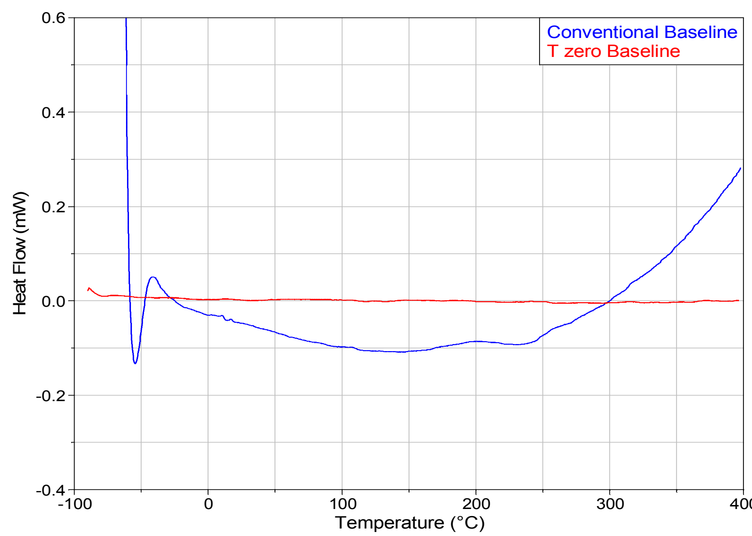
Baseline Calibration

- **Slope** — **Q20 & 2900s Only**
  - Calibration should provide flat baseline with empty cell
  - Polymers should always have an endothermic slope due to increasing heat capacity with increasing temperature
- **Curvature**
  - Not normally part of calibration procedure
  - Can be eliminated if necessary with baseline subtraction
  - Curvature can cause errors in analyses

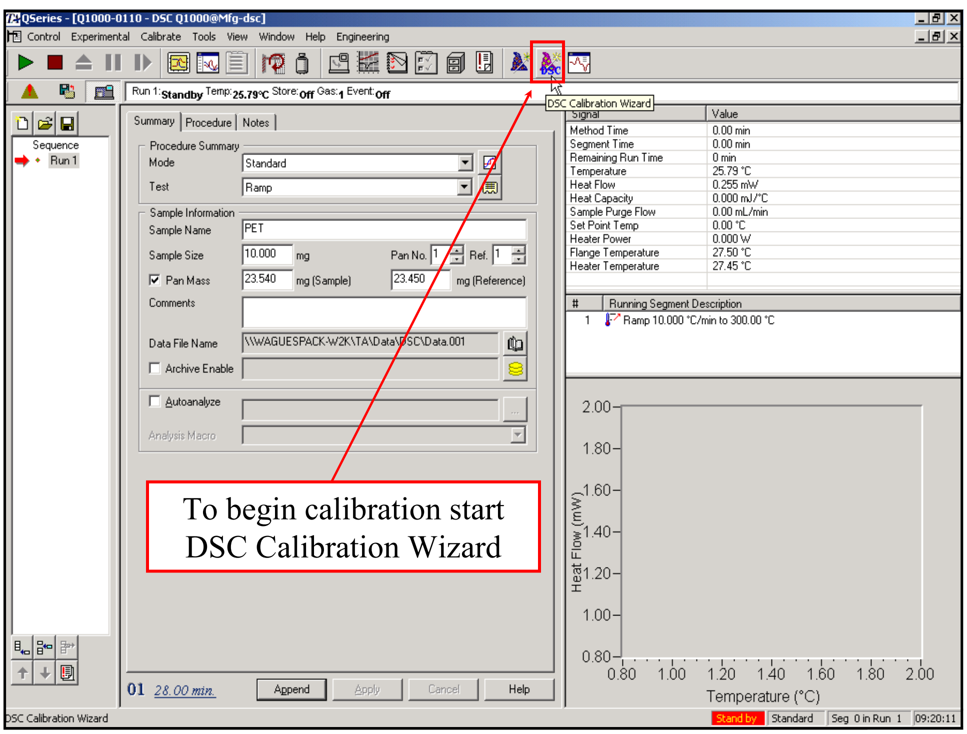
Baseline Slope due to Heat Capacity

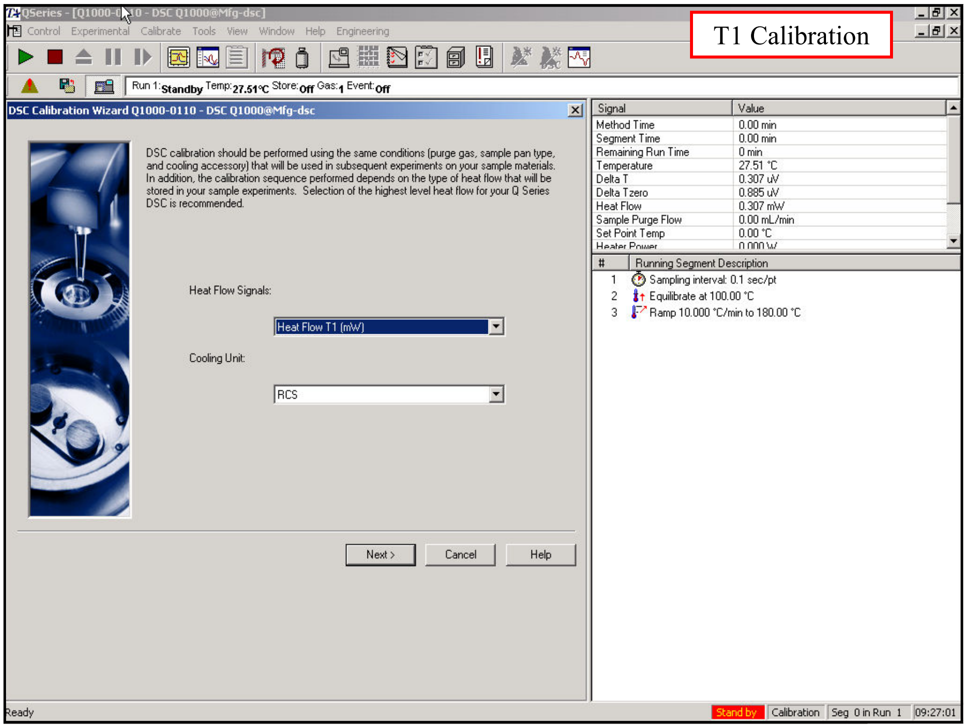


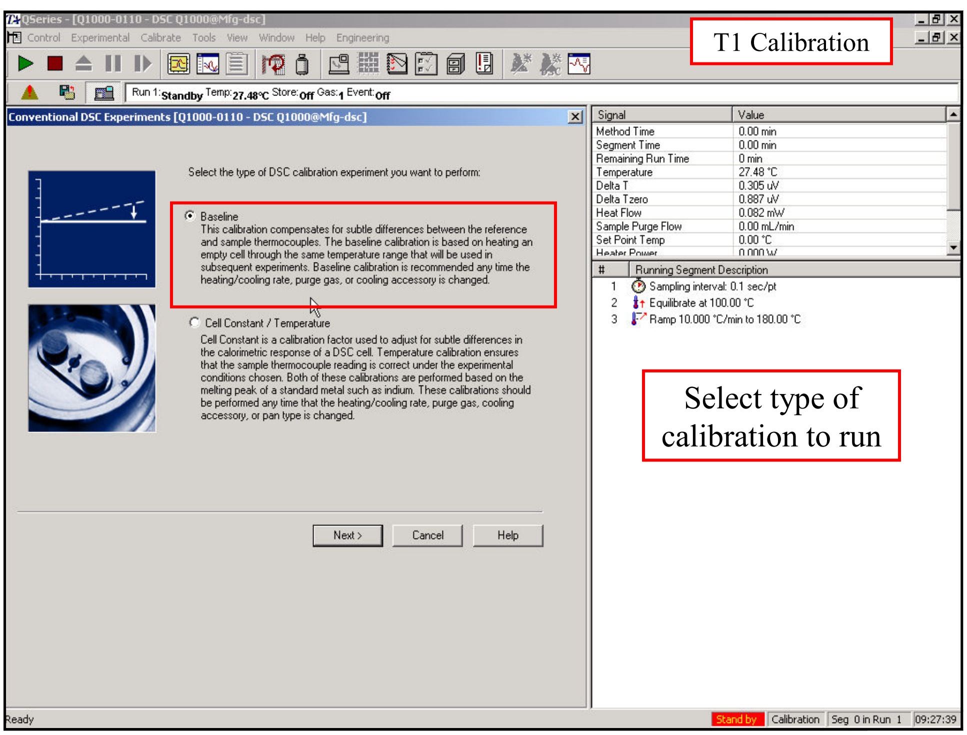
Baseline Curvature

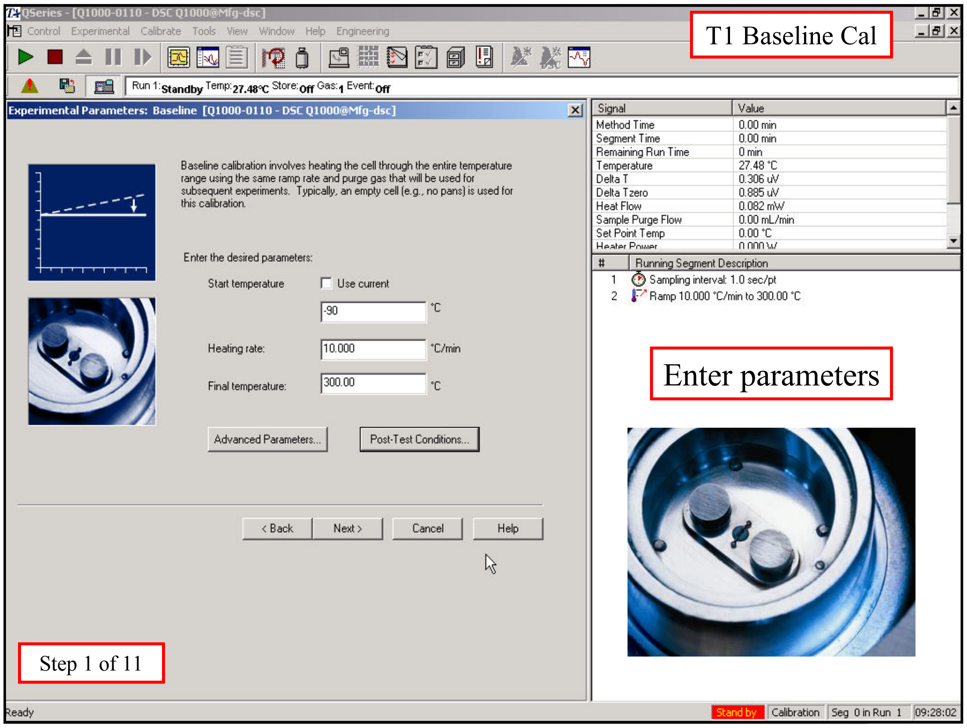


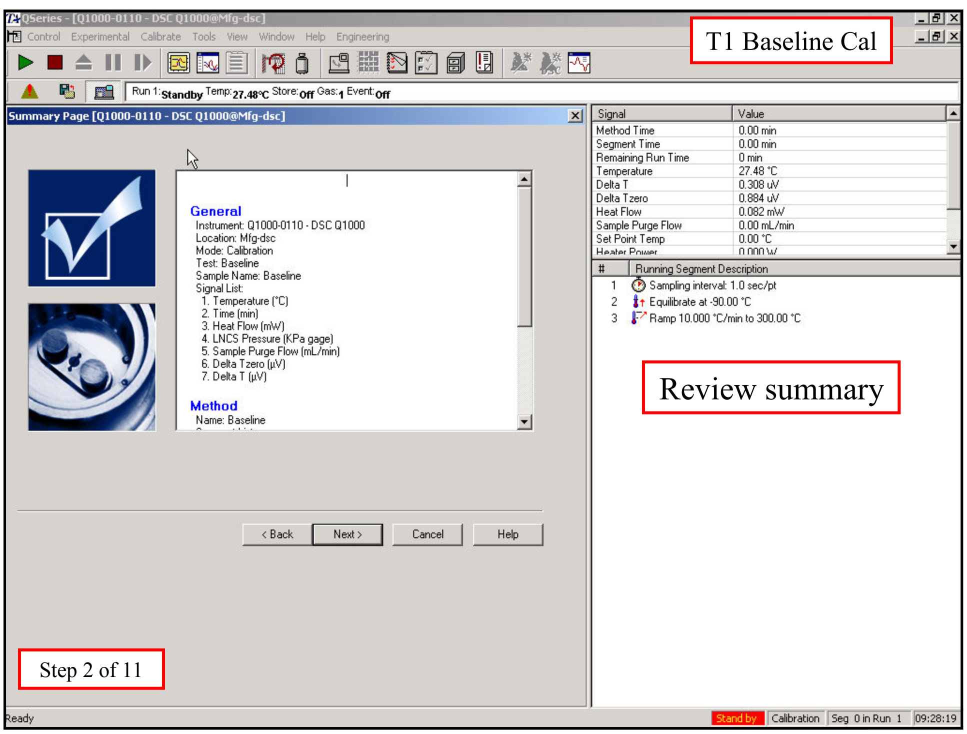
DSC Training Course

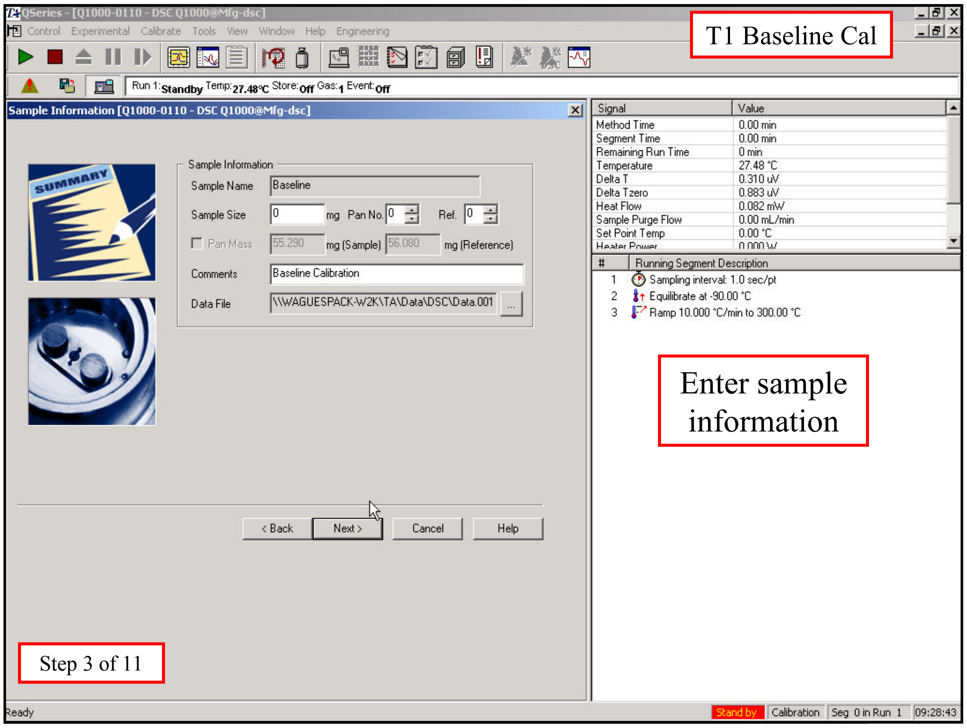


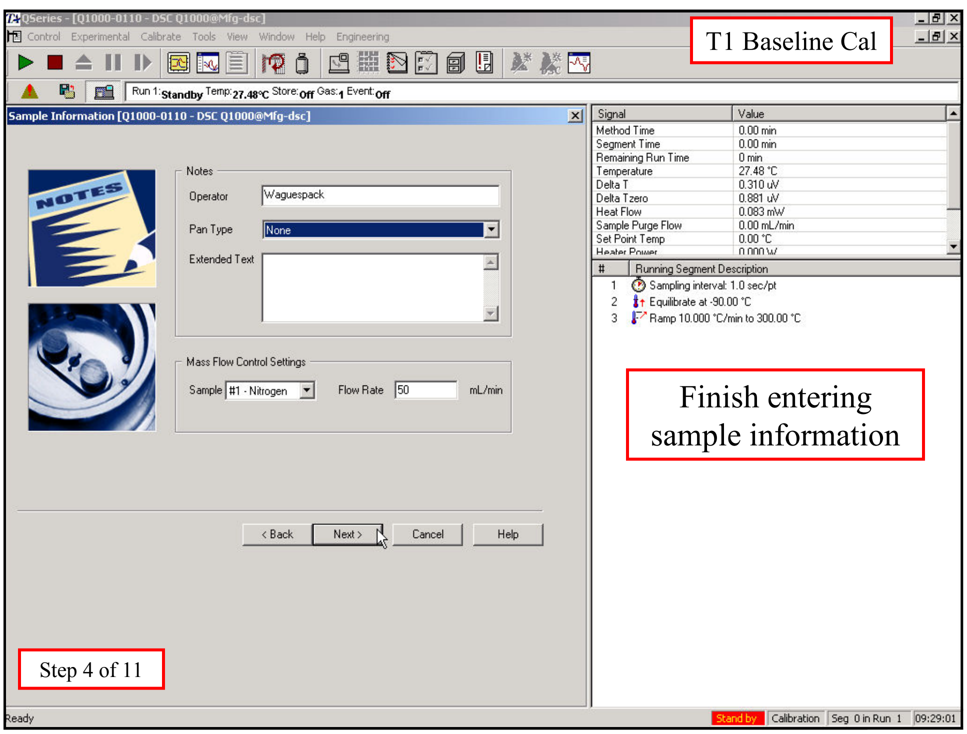

T1 Calibration
DSC Calibration Wizard Q1000-0110 - DSC Q1000@Mfg-dsc
DSC calibration should be performed using the same conditions (purge gas, sample pan type, and cooling accessory) that will be used in subsequent experiments on your sample materials. In addition, the calibration sequence performed depends on the type of heat flow that will be stored in your sample experiments. Selection of the highest level heat flow for your Q Series DSC is recommended.
Heat Flow Signals:
Heat Flow T1 (mW)
Cooling Unit:
RCS
Next >
Cancel
Help
Signal
Value
Running Segment Description
Sampling interval: 0.1 sec/pt
Equilibrate at 100.00 °C
Ramp 10.000 °C/min to 180.00 °C

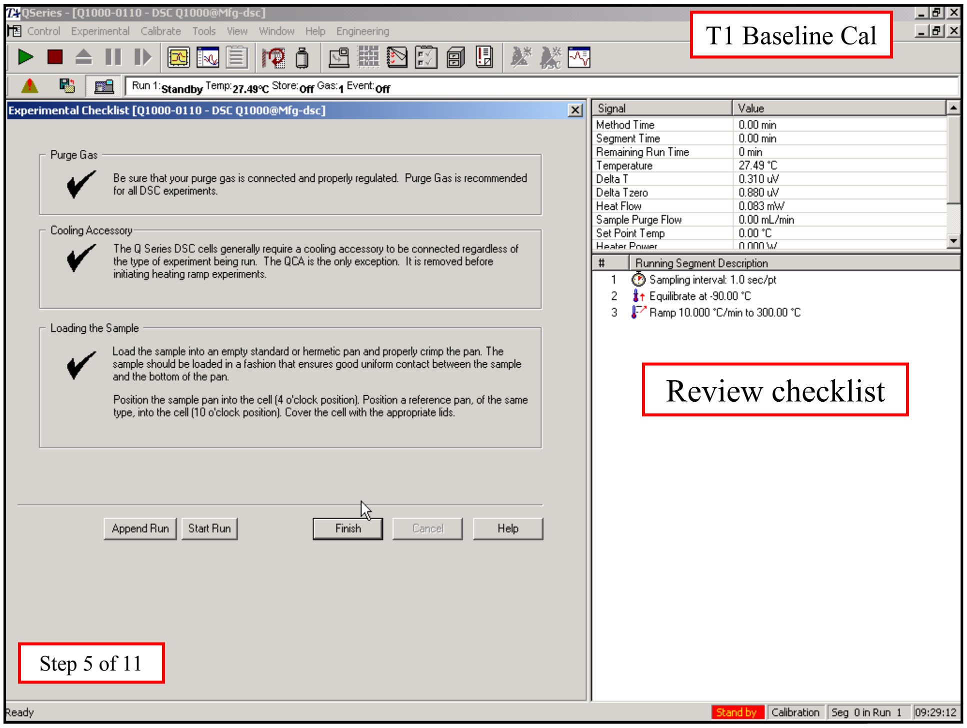

T1 Calibration
Conventional DSC Experiments [Q1000-0110 - DSC Q1000@Mfg-dsc]
Select the type of DSC calibration experiment you want to perform:
Baseline
This calibration compensates for subtle differences between the reference and sample thermocouples. The baseline calibration is based on heating an empty cell through the same temperature range that will be used in subsequent experiments. Baseline calibration is recommended any time the heating/cooling rate, purge gas, or cooling accessory is changed.
Cell Constant / Temperature
Cell Constant is a calibration factor used to adjust for subtle differences in the calorimetric response of a DSC cell. Temperature calibration ensures that the sample thermocouple reading is correct under the experimental conditions chosen. Both of these calibrations are performed based on the melting peak of a standard metal such as indium. These calibrations should be performed any time that the heating/cooling rate, purge gas, cooling accessory, or pan type is changed.
Next >
Cancel
Help
Select type of calibration to run

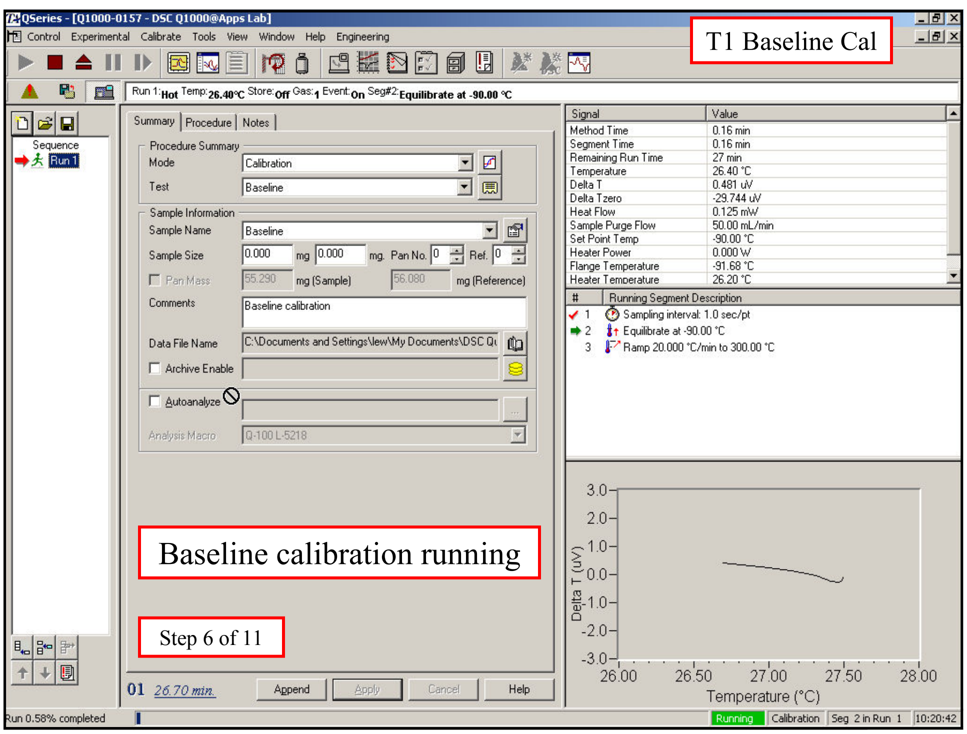

T1 Baseline Cal
Experimental Parameters: Baseline [Q1000-0110 - DSC Q1000@Mfg-dsc]
Baseline calibration involves heating the cell through the entire temperature range using the same ramp rate and purge gas that will be used for subsequent experiments. Typically, an empty cell (e.g., no pans) is used for this calibration.
Enter the desired parameters:
Start temperature
Use current
-90
Heating rate:
10.000
Final temperature:
300.00
Advanced Parameters...
Post-Test Conditions...
< Back
Next >
Cancel
Help
Enter parameters
Step 1 of 11

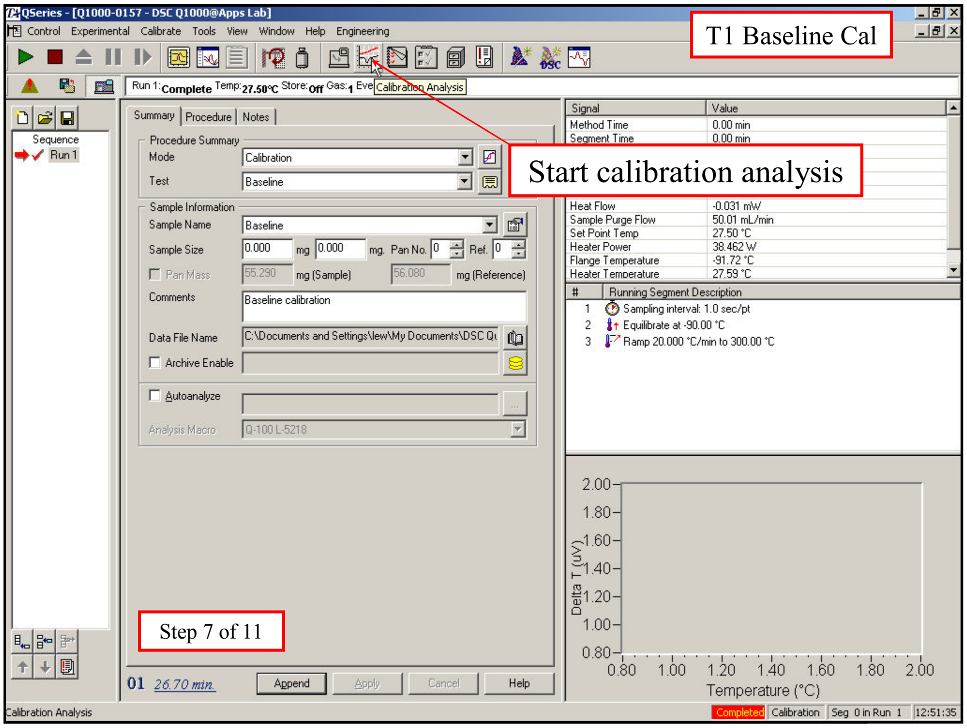

T1 Baseline Cal
Summary Page [Q1000-0110 - DSC Q1000@Mfg-dsc]
General
Instrument: Q1000-0110 - DSC Q1000
Location: Mfg-dsc
Mode: Calibration
Test: Baseline
Sample Name: Baseline
Signal List:
1. Temperature (°C)
2. Time (min)
3. Heat Flow (mW)
4. LNCS Pressure (KPa gage)
5. Sample Purge Flow (mL/min)
6. Delta Tzero (µV)
7. Delta T (µV)
Method
Name: Baseline
< Back
Next >
Cancel
Help
Review summary
Step 2 of 11


T1 Baseline Cal
Sample Information [Q1000-0110 - DSC Q1000@Mfg-dsc]
Sample Information
Sample Name Baseline
Sample Size 0 mg Pan No. 0 Ref. 0
Pan Mass 55.290 mg (Sample) 56.080 mg (Reference)
Comments Baseline Calibration
Data File \\WAGUESPACK-W2K\TA\Data\DSC\Data.001
< Back
Next >
Cancel
Help
Enter sample information
Step 3 of 11

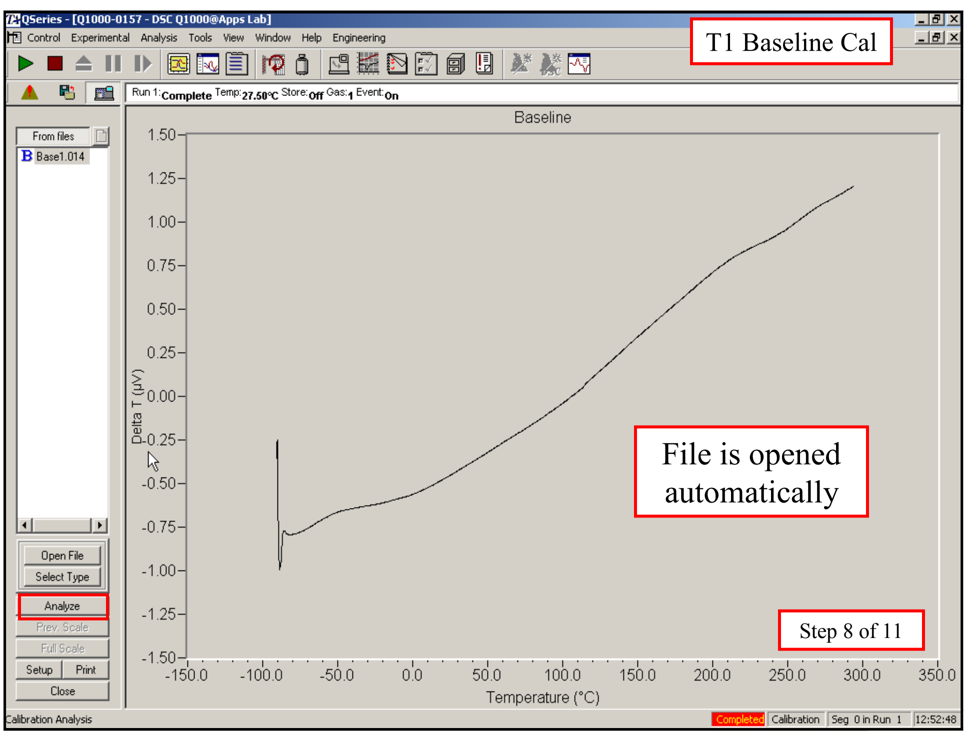

T1 Baseline Cal
Sample Information [Q1000-0110 - DSC Q1000@Mfg-dsc]
Notes
Operator Waguespack
Pan Type None
Extended Text
Mass Flow Control Settings
Sample #1 - Nitrogen Flow Rate 50 mL/min
< Back
Next >
Cancel
Help
Finish entering sample information
Step 4 of 11


T1 Baseline Cal
Experimental Checklist [Q1000-0110 - DSC Q1000@Mfg-dsc]
Purge Gas
Be sure that your purge gas is connected and properly regulated. Purge Gas is recommended for all DSC experiments.
Cooling Accessory
The Q Series DSC cells generally require a cooling accessory to be connected regardless of the type of experiment being run. The QCA is the only exception. It is removed before initiating heating ramp experiments.
Loading the Sample
Load the sample into an empty standard or hermetic pan and properly crimp the pan. The sample should be loaded in a fashion that ensures good uniform contact between the sample and the bottom of the pan.
Position the sample pan into the cell (4 o'clock position). Position a reference pan, of the same type, into the cell (10 o'clock position). Cover the cell with the appropriate lids.
Append Run
Start Run
Finish
Cancel
Help
Review checklist
Step 5 of 11

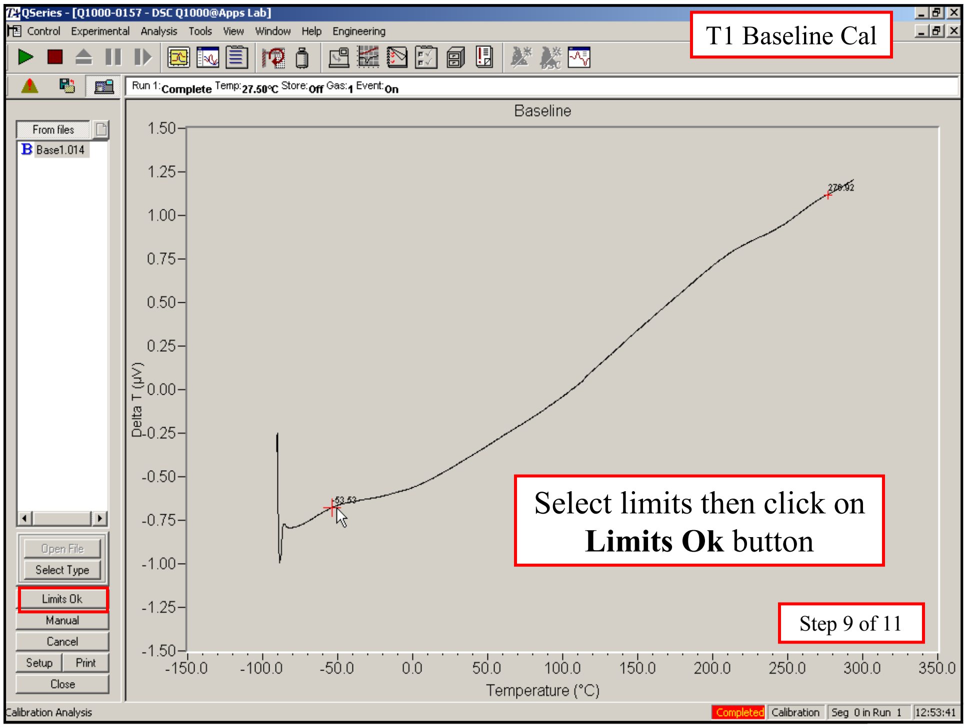

T1 Baseline Cal
Procedure Summary
Mode Calibration
Test Baseline
Sample Information
Sample Name Baseline
Comments Baseline calibration
Baseline calibration running
Step 6 of 11
Delta T (uV)
Temperature (°C)

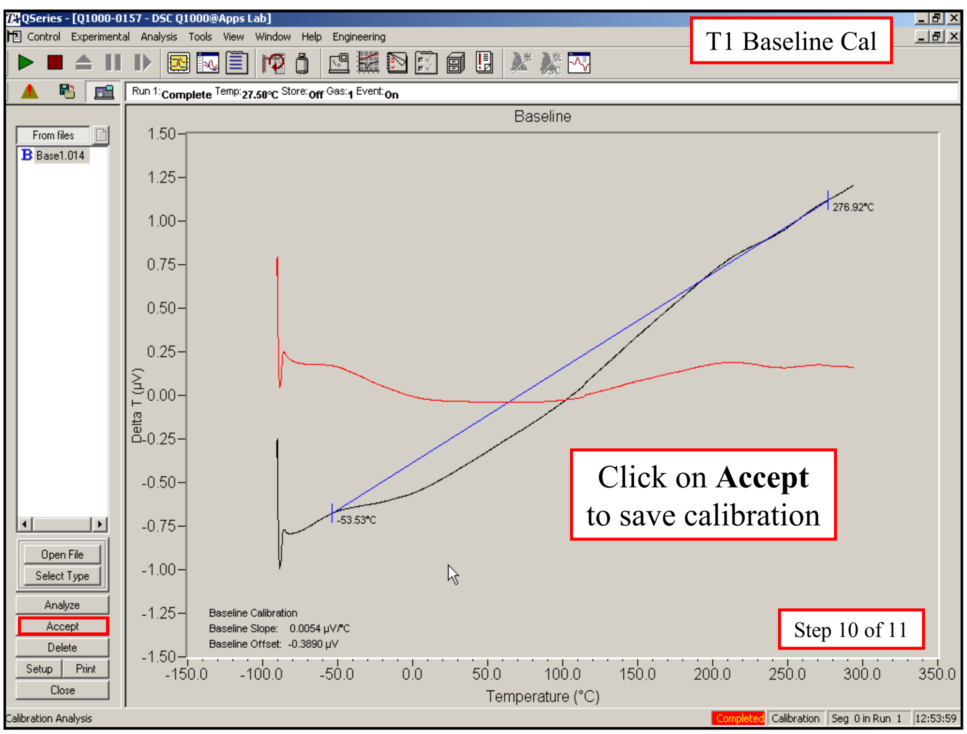


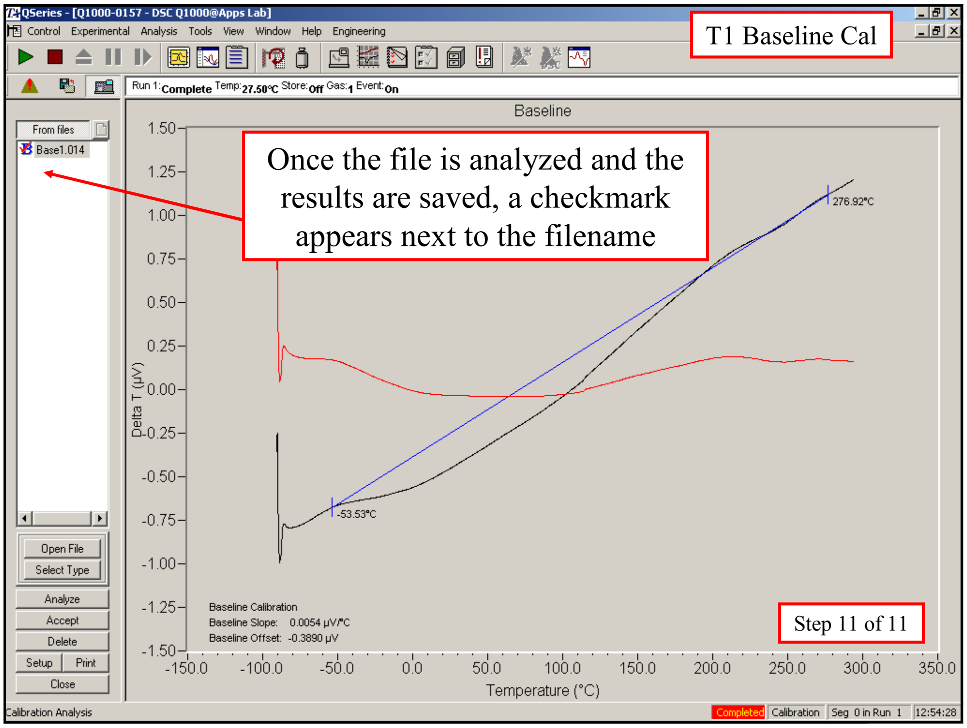
T1 Baseline Cal
Start calibration analysis
Step 7 of 11



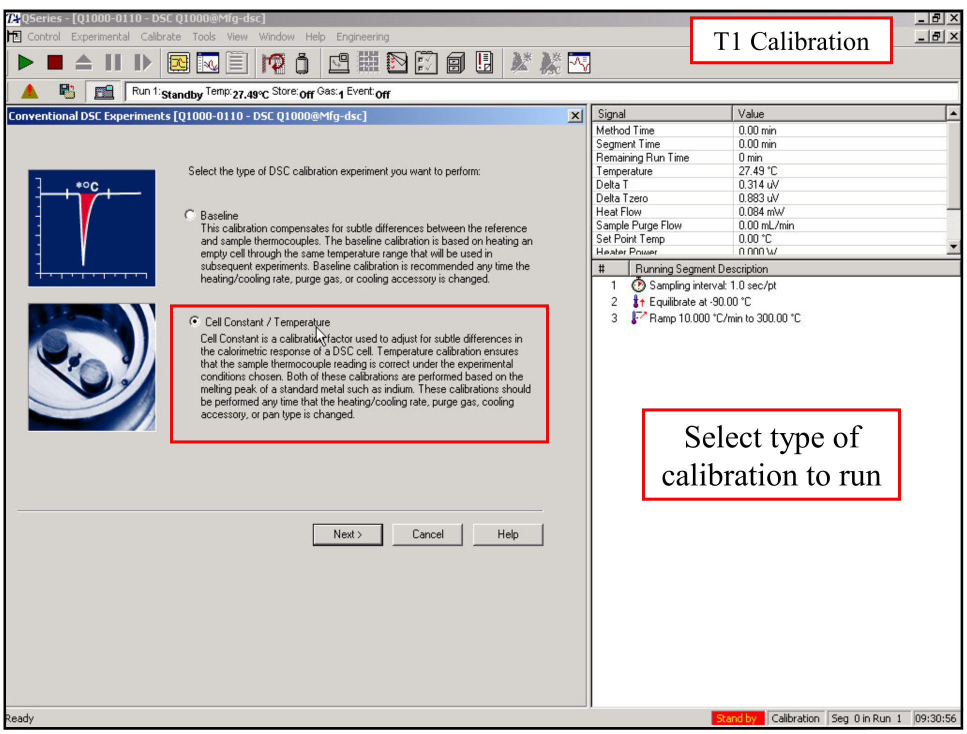
T1 Baseline Cal
File is opened automatically
Step 8 of 11


QSeries - [Q1000-0157 - DSC Q1000@Apps Lab]
T1 Baseline Cal
Baseline
Delta T (µV)
Temperature (°C)
Select limits then click on **Limits Ok** button
Step 9 of 11
From files
Base1.014
Open File
Select Type
Limits Ok
Manual
Cancel
Setup
Print
Close
Calibration Analysis

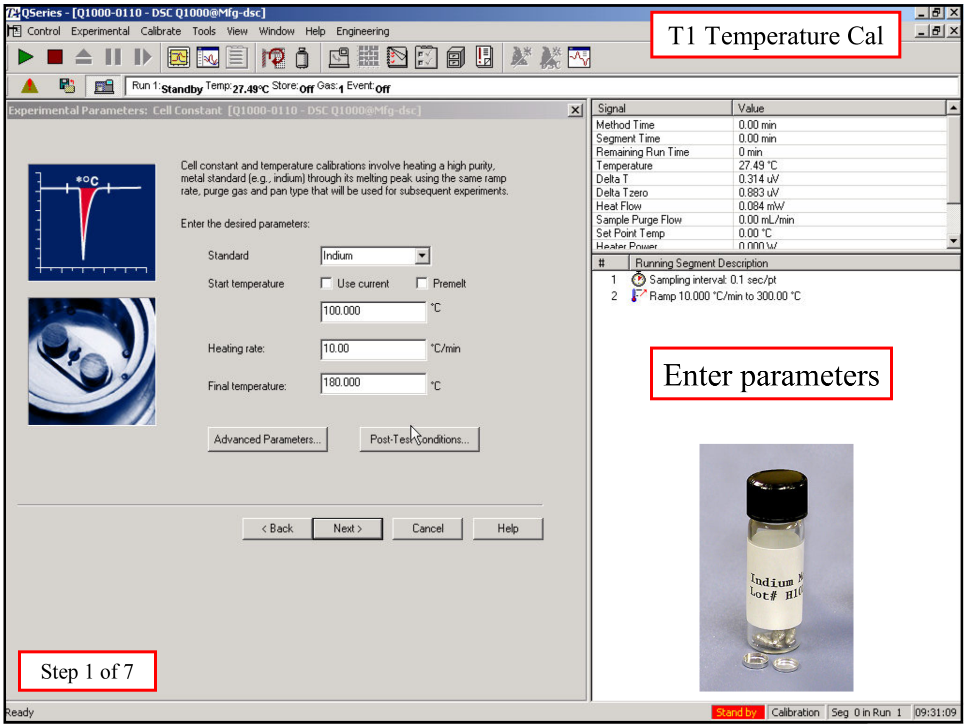

QSeries - [Q1000-0157 - DSC Q1000@Apps Lab]
T1 Baseline Cal
Baseline
Delta T (µV)
Temperature (°C)
276.92°C
-53.53°C
Click on **Accept** to save calibration
Baseline Calibration
Baseline Slope: 0.0054 µV/°C
Baseline Offset: -0.3890 µV
Step 10 of 11
From files
Base1.014
Open File
Select Type
Analyze
Accept
Delete
Setup
Print
Close
Calibration Analysis

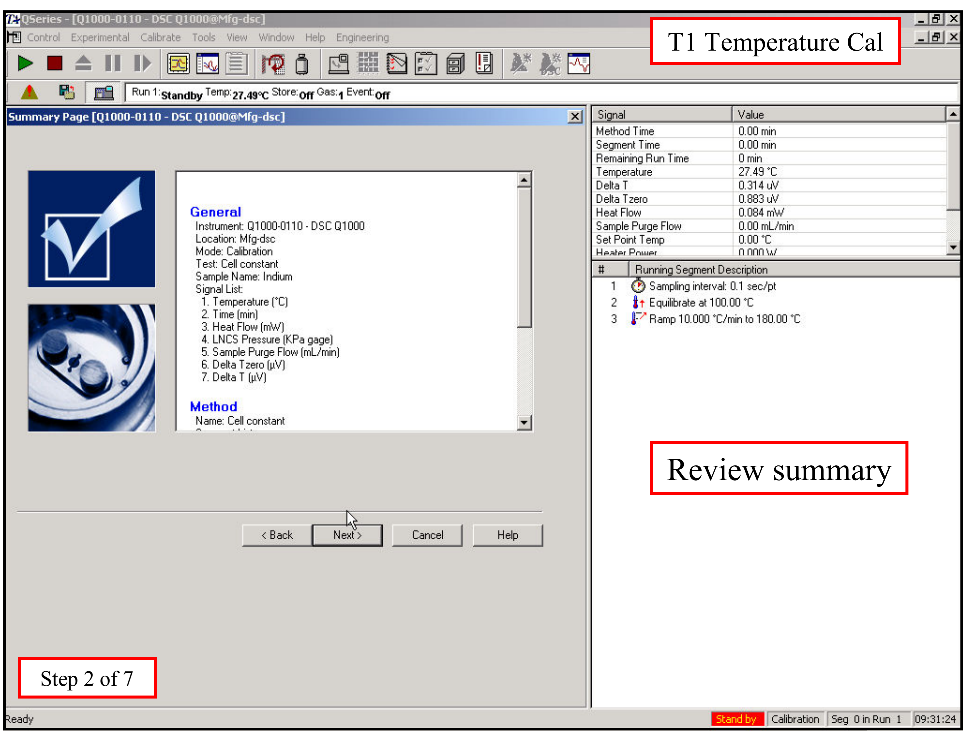


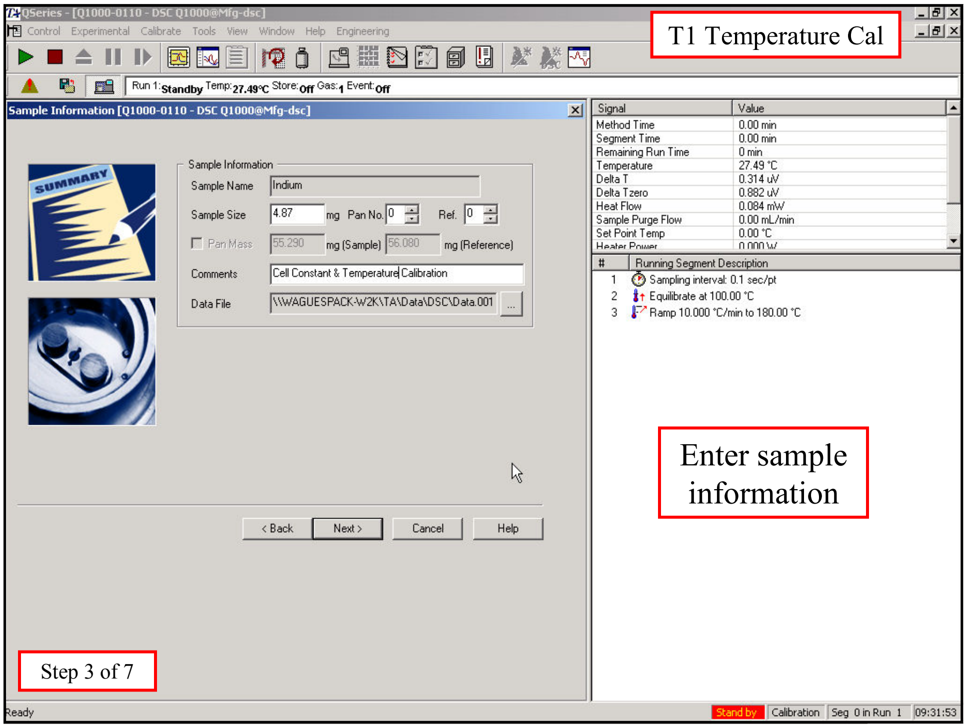
T1 Baseline Cal
Once the file is analyzed and the results are saved, a checkmark appears next to the filename
Baseline
Delta T (µV)
Temperature (°C)
276.92°C
-53.53°C
Baseline Calibration
Baseline Slope: 0.0054 µV/°C
Baseline Offset: -0.3890 µV
Step 11 of 11
Base1.014
Open File
Select Type
Analyze
Accept
Delete
Setup
Print
Close
Calibration Analysis

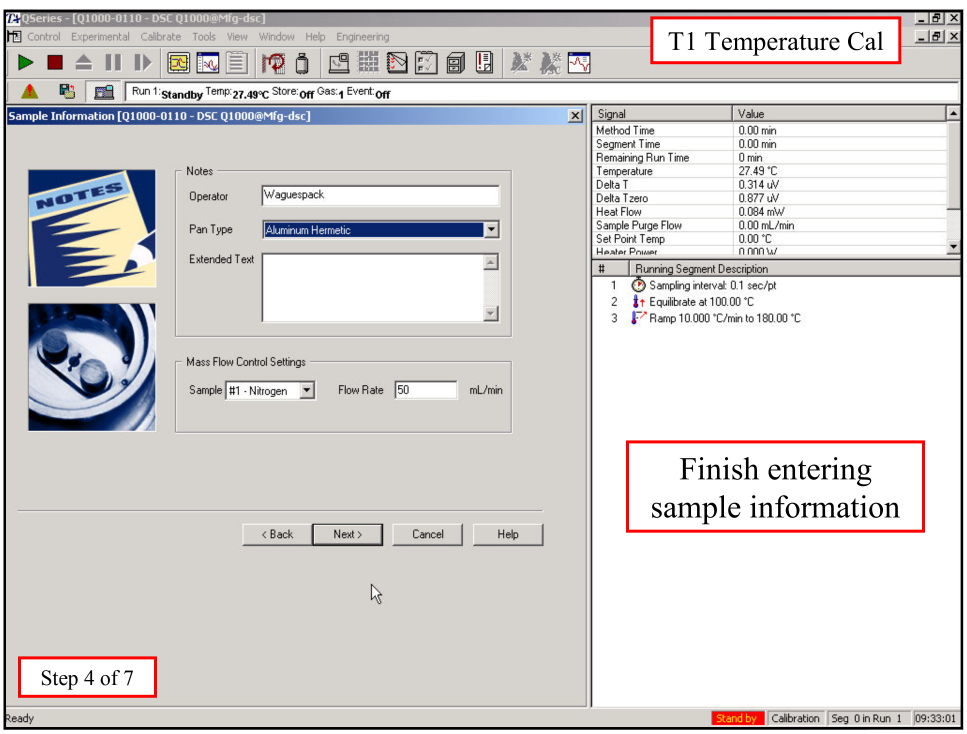


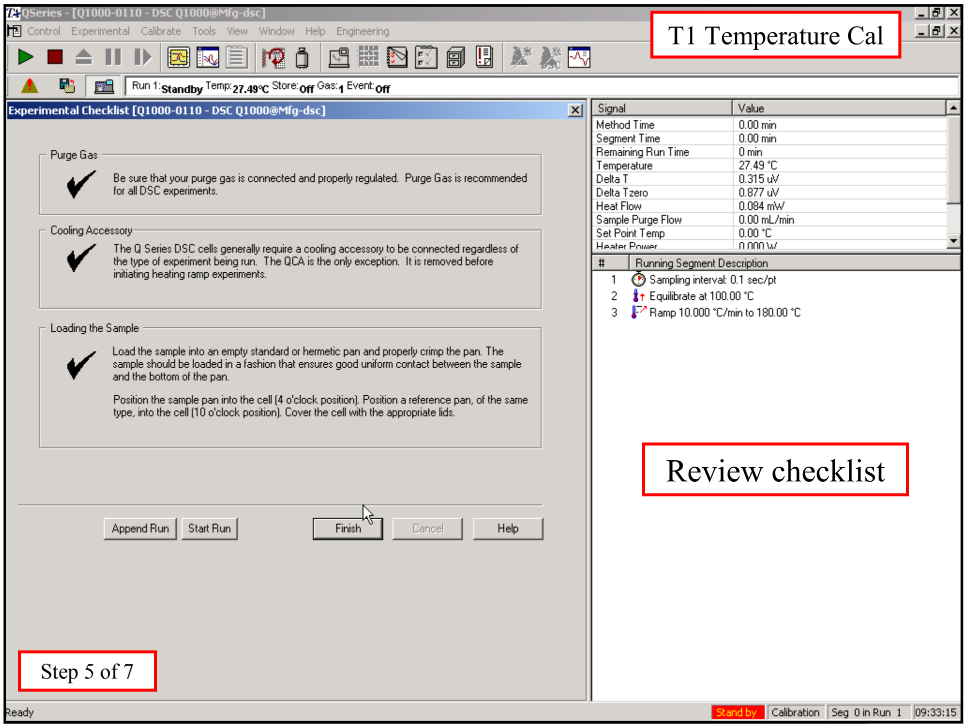
T1 Calibration
Conventional DSC Experiments [Q1000-0110 - DSC Q1000@Mfg-dsc]
Select the type of DSC calibration experiment you want to perform:
Baseline
This calibration compensates for subtle differences between the reference and sample thermocouples. The baseline calibration is based on heating an empty cell through the same temperature range that will be used in subsequent experiments. Baseline calibration is recommended any time the heating/cooling rate, purge gas, or cooling accessory is changed.
Cell Constant / Temperature
Cell Constant is a calibration factor used to adjust for subtle differences in the calorimetric response of a DSC cell. Temperature calibration ensures that the sample thermocouple reading is correct under the experimental conditions chosen. Both of these calibrations are performed based on the melting peak of a standard metal such as indium. These calibrations should be performed any time that the heating/cooling rate, purge gas, cooling accessory, or pan type is changed.
Next >
Cancel
Help
Select type of calibration to run
Running Segment Description
Sampling interval 1.0 sec/pt
Equilibrate at -90.00 °C
Ramp 10.000 °C/min to 300.00 °C

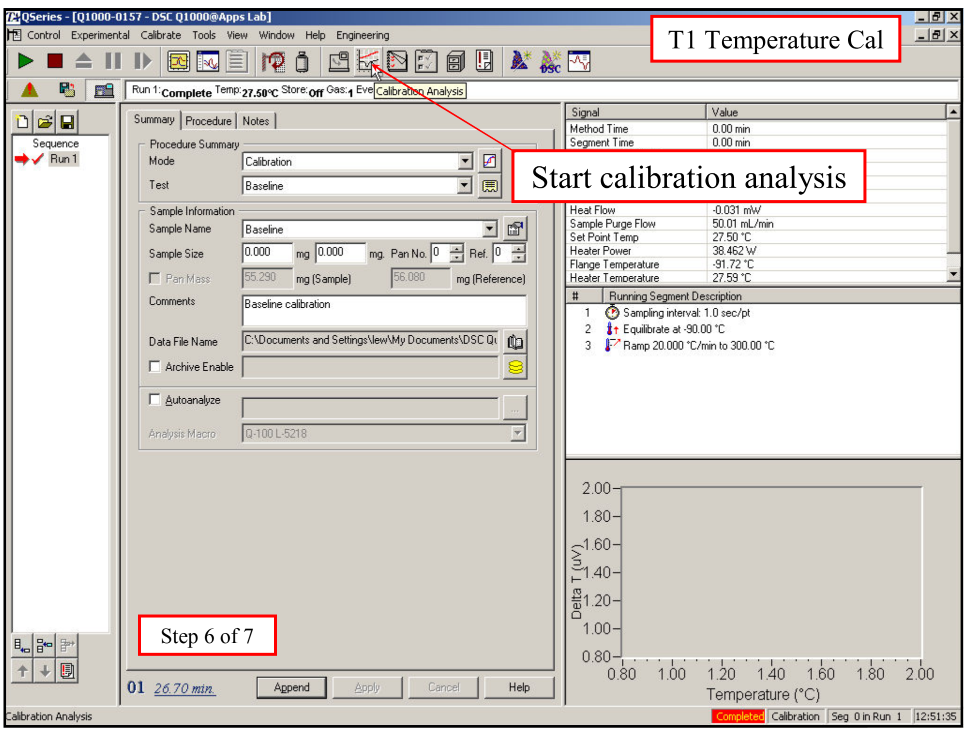

QSeries - [Q1000-0110 - DSC Q1000@Mfg-dsc]
Control Experimental Calibrate Tools View Window Help Engineering
T1 Temperature Cal
Run 1: Standby Temp: 27.49°C Store: Off Gas: 1 Event: Off
Experimental Parameters: Cell Constant [Q1000-0110 - DSC Q1000@Mfg-dsc]
Cell constant and temperature calibrations involve heating a high purity, metal standard (e.g., indium) through its melting peak using the same ramp rate, purge gas and pan type that will be used for subsequent experiments.
Enter the desired parameters:
Standard Indium
Start temperature Use current Premelt
100.000 °C
Heating rate: 10.00 °C/min
Final temperature: 180.000 °C
Advanced Parameters...
Post-Test Conditions...
< Back Next > Cancel Help
Step 1 of 7
Signal Value
Method Time 0.00 min
Segment Time 0.00 min
Remaining Run Time 0 min
Temperature 27.49 °C
Delta T 0.314 uV
Delta Tzero 0.883 uV
Heat Flow 0.084 mW
Sample Purge Flow 0.00 mL/min
Set Point Temp 0.00 °C
Running Segment Description
1 Sampling interval: 0.1 sec/pt
2 Ramp 10.000 °C/min to 300.00 °C
Enter parameters
Ready
Stand by Calibration Seg 0 in Run 1 09:31:09

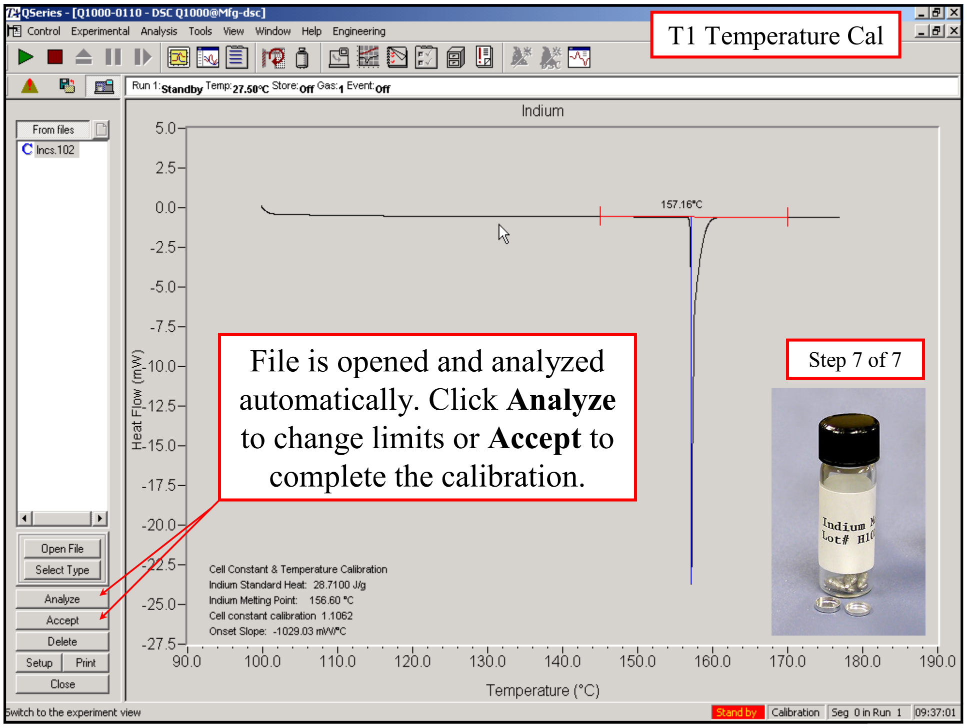

QSeries - [Q1000-0110 - DSC Q1000@Mfg-dsc]
Control Experimental Calibrate Tools View Window Help Engineering
T1 Temperature Cal
Run 1: Standby Temp: 27.49°C Store: Off Gas: 1 Event: Off
Summary Page [Q1000-0110 - DSC Q1000@Mfg-dsc]
General
Instrument: Q1000-0110 - DSC Q1000
Location: Mfg-dsc
Mode: Calibration
Test: Cell constant
Sample Name: Indium
Signal List:
1. Temperature (°C)
2. Time (min)
3. Heat Flow (mW)
4. LNCS Pressure (KPa gage)
5. Sample Purge Flow (mL/min)
6. Delta Tzero (µV)
7. Delta T (µV)
Method
Name: Cell constant
< Back Next > Cancel Help
Step 2 of 7
Signal Value
Method Time 0.00 min
Segment Time 0.00 min
Remaining Run Time 0 min
Temperature 27.49 °C
Delta T 0.314 uV
Delta Tzero 0.883 uV
Heat Flow 0.084 mW
Sample Purge Flow 0.00 mL/min
Set Point Temp 0.00 °C
Running Segment Description
1 Sampling interval: 0.1 sec/pt
2 Equilibrate at 100.00 °C
3 Ramp 10.000 °C/min to 180.00 °C
Review summary
Ready
Stand by Calibration Seg 0 in Run 1 09:31:24


T1 Temperature Cal
Sample Information [Q1000-0110 - DSC Q1000@Mfg-dsc]
Sample Information
Sample Name
Indium
Sample Size
4.87
mg
Pan No.
Ref.
Pan Mass
55.290
mg (Sample)
56.080
mg (Reference)
Comments
Cell Constant & Temperature Calibration
Data File
\\WAGUESPACK-W2K\TA\Data\DSC\Data.001
< Back
Next >
Cancel
Help
Signal
Value
Method Time
0.00 min
Segment Time
0.00 min
Remaining Run Time
0 min
Temperature
27.49 °C
Delta T
0.314 uV
Delta Tzero
0.882 uV
Heat Flow
0.084 mW
Sample Purge Flow
0.00 mL/min
Set Point Temp
0.00 °C
Running Segment Description
1 Sampling interval: 0.1 sec/pt
2 Equilibrate at 100.00 °C
3 Ramp 10.000 °C/min to 180.00 °C
Enter sample information
Step 3 of 7
Ready
Stand by
Calibration
Seg 0 in Run 1
09:31:53


T1 Temperature Cal
Sample Information [Q1000-0110 - DSC Q1000@Mfg-dsc]
Notes
Operator
Waguespack
Pan Type
Aluminum Hermetic
Extended Text
Mass Flow Control Settings
Sample
#1 - Nitrogen
Flow Rate
50
mL/min
< Back
Next >
Cancel
Help
Signal
Value
Method Time
0.00 min
Segment Time
0.00 min
Remaining Run Time
0 min
Temperature
27.49 °C
Delta T
0.314 uV
Delta Tzero
0.877 uV
Heat Flow
0.084 mW
Sample Purge Flow
0.00 mL/min
Set Point Temp
0.00 °C
Running Segment Description
1 Sampling interval: 0.1 sec/pt
2 Equilibrate at 100.00 °C
3 Ramp 10.000 °C/min to 180.00 °C
Finish entering sample information
Step 4 of 7
Ready
Stand by
Calibration
Seg 0 in Run 1
09:33:01


T1 Temperature Cal
Review checklist
Step 5 of 7
Experimental Checklist [Q1000-0110 - DSC Q1000@Mfg-dsc]
Purge Gas
Be sure that your purge gas is connected and properly regulated. Purge Gas is recommended for all DSC experiments.
Cooling Accessory
The Q Series DSC cells generally require a cooling accessory to be connected regardless of the type of experiment being run. The QCA is the only exception. It is removed before initiating heating ramp experiments.
Loading the Sample
Load the sample into an empty standard or hermetic pan and properly crimp the pan. The sample should be loaded in a fashion that ensures good uniform contact between the sample and the bottom of the pan.
Position the sample pan into the cell (4 o'clock position). Position a reference pan, of the same type, into the cell (10 o'clock position). Cover the cell with the appropriate lids.
Append Run
Start Run
Finish
Cancel
Help


T1 Temperature Cal
Start calibration analysis
Step 6 of 7
Calibration Analysis
Mode
Calibration
Test
Baseline
Sample Name
Baseline
Comments
Baseline calibration
Running Segment Description
Sampling interval: 1.0 sec/pt
Equilibrate at -90.00 °C
Ramp 20.000 °C/min to 300.00 °C
Delta T (uV)
Temperature (°C)



Traceable Calibration Materials

- NIST DSC calibration materials:
  - SRM 2232 **Indium** T_m = 156.5985°C
  - SRM 2220 **Tin** T_m = 231.95°C
  - SRM 2222 **Biphenyl** T_m = 69.41°C
  - SRM 2225 **Mercury** T_m = -38.70°C
- NIST: Gaithersburg, MD 20899-0001
  - Phone: 301-975-6776
  - Fax: 301-948-3730
  - Email: SRMINFO@nist.gov
  - Website: http://ts.nist.gov/srm

Traceable Calibration Materials

- LGC DSC Calibration Materials:
  - LGC2601: **Indium** (TA p/n: 915060-901)
  - LGC2608: **Lead**
  - LGC2609: **Tin**
  - LGC2611: **Zinc**
- Laboratory of the Government Chemist, UK
  - Phone: 44 (0) 181 943 7565
  - Fax: 44 (0) 181 943 7554
  - Email: orm@lgc.co.uk

Traceable Calibration Materials

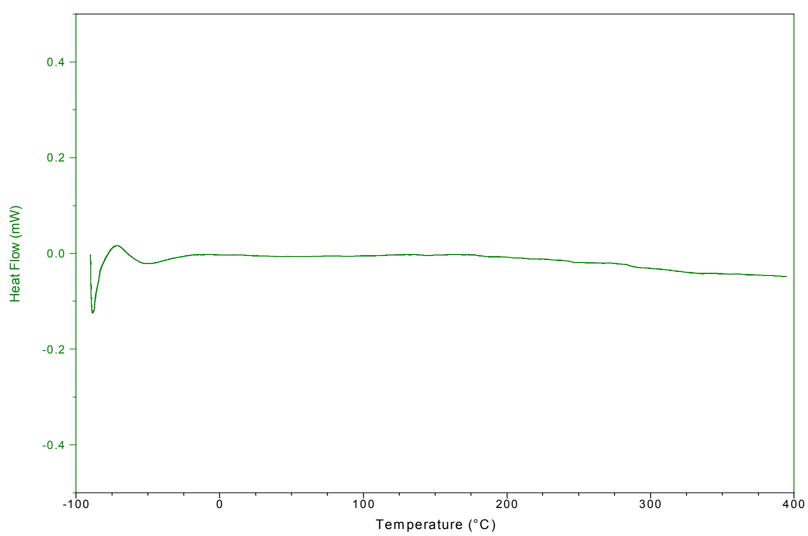
- Certified materials used to establish traceability of instrument calibration
- ISO/GLP certification often requires third party calibration of instruments:
  - Service provided by TA Instruments service representative using certified materials
  - Certificate of Calibration issued showing traceability of calibration to a national laboratory

Verifying Baseline

- After completion of calibration routine, run baseline
  - Standard mode
  - Empty cell, -90°C-400°C (w/ RCS)
  - Plot mW vs. temperature on a 1mW scale
    - Should look fairly flat on this scale
  - Measure bow,drift & zero
    - Bow <50 µW
    - Drift <50 µW
    - Should be around zero
- To verify performance in the future re-run

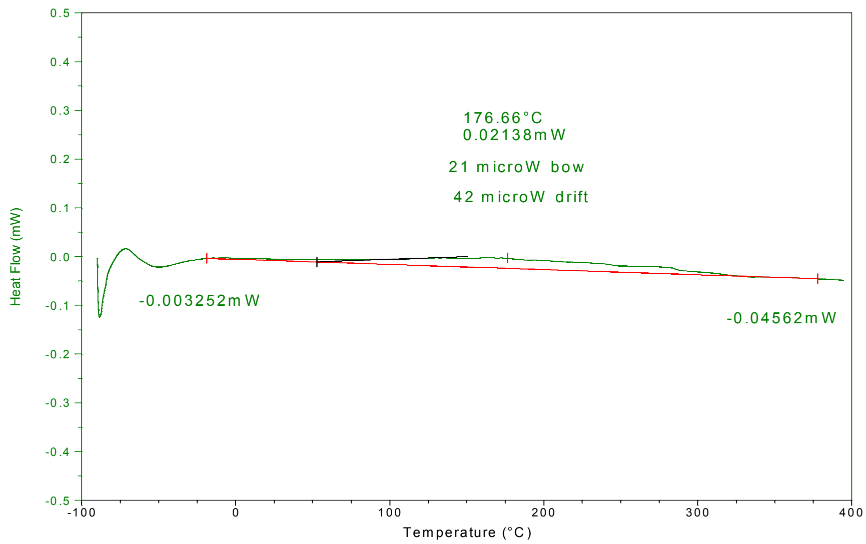
DSC Training Course

Verifying Baseline

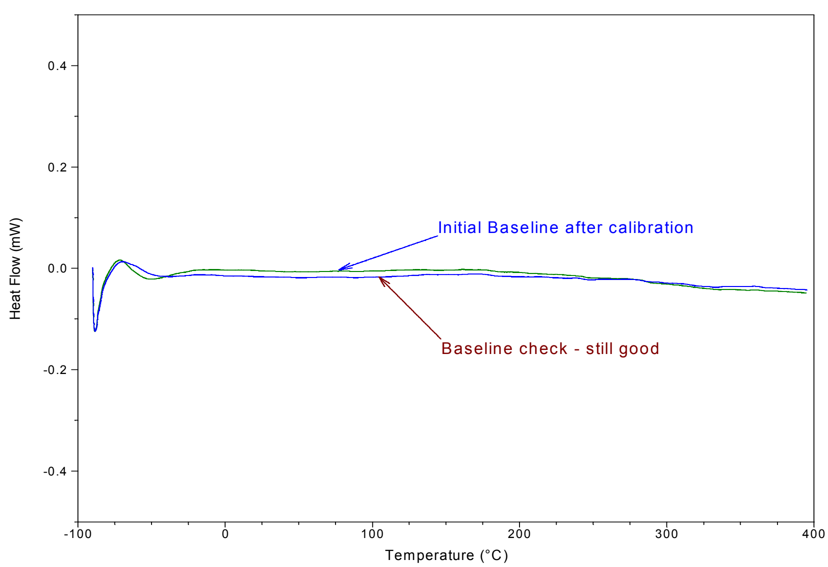


DSC Training Course

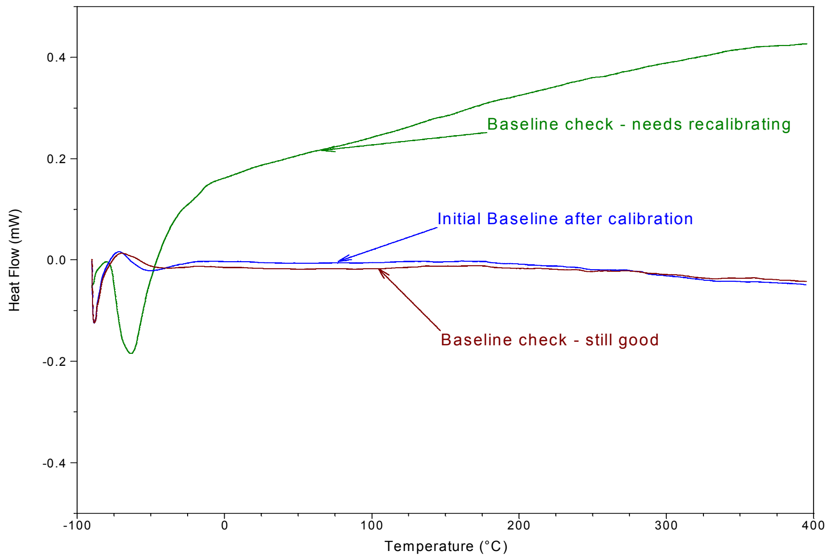
Verifying Baseline



Verifying Baseline



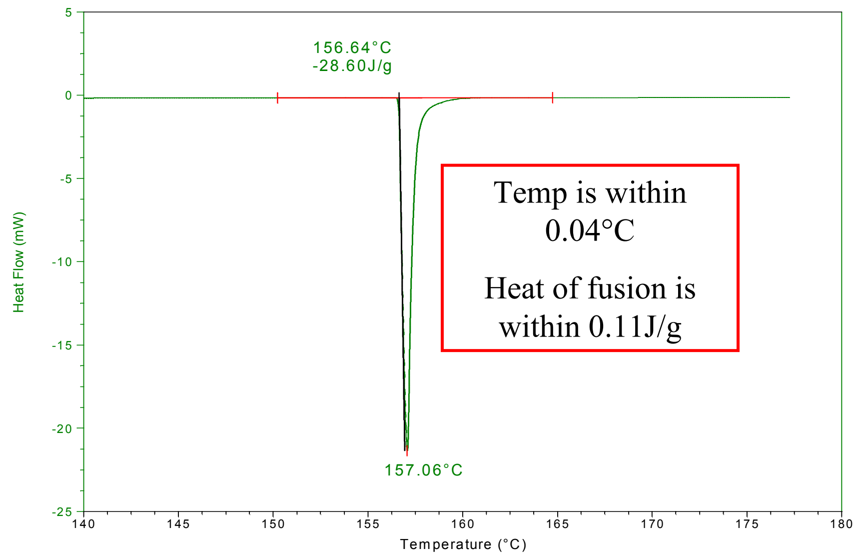
Verifying Baseline



Verifying Heat Flow & Temperature

- Run Indium as a sample (i.e. in std mode not cal mode)
- Analyze melt and record melt onset & heat of fusion
- Compare to known values
  - Melting of In 156.6°C
  - Heat of Fusion 28.71J/g

Verifying Heat Flow & Temperature

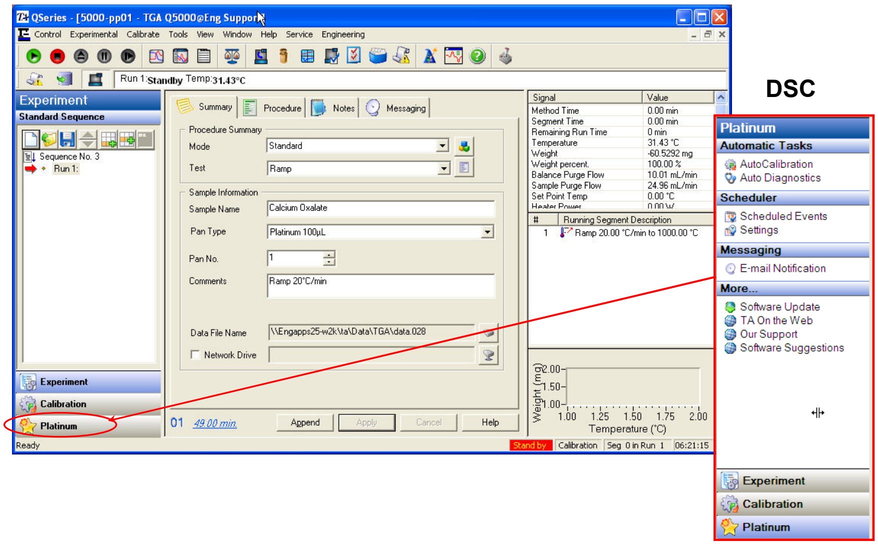


Q-Series Platinum Software

- Platinum features are designed to assist you in ensuring that your instrument is in proper working condition, calibrated, and has the latest software available.
  - Automatic Calibration Routines
  - Auto Diagnostics
  - Event Scheduler
  - Email/Messaging Notification
  - Live Software Updates

DSC Training Course

Platinum Software

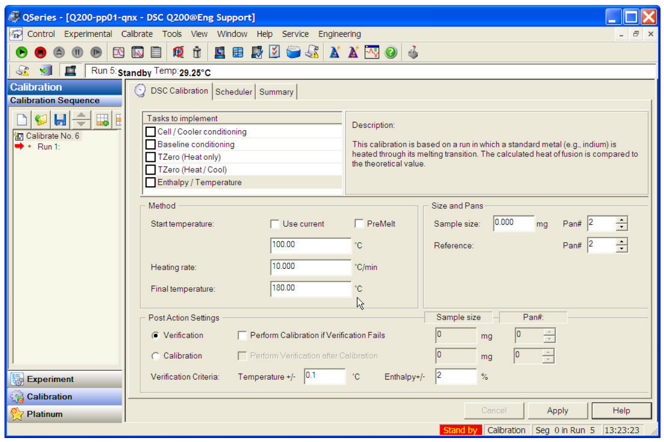


Automatic Calibration Routines

- DSC Automatic Calibration Routines
  - Baseline Calibration (T1)
  - Cell/Cooler Conditioning (T4 or T4P)
  - Baseline Conditioning (T4 or T4P)
  - Tzero Calibration (T4 or T4P)
  - Cell Constant/Temperature Calibration
  - Cell Constant/Temperature Verification

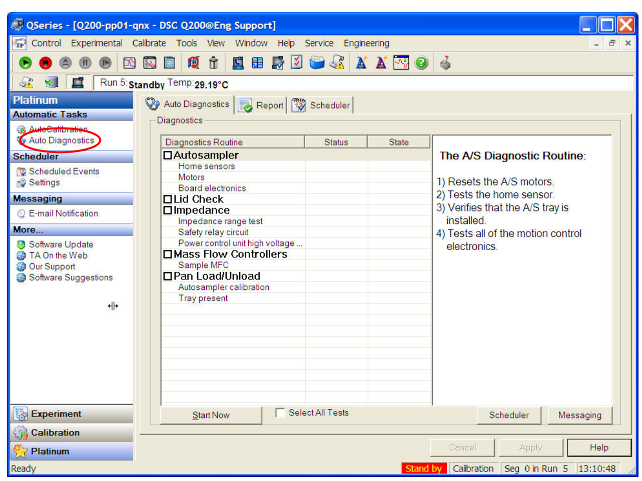
Calibration Sequence Generator

- Select Auto Calibration through Platinum options to initiate the Calibration Sequence Generator. Creates a calibration sequence based on your selections.



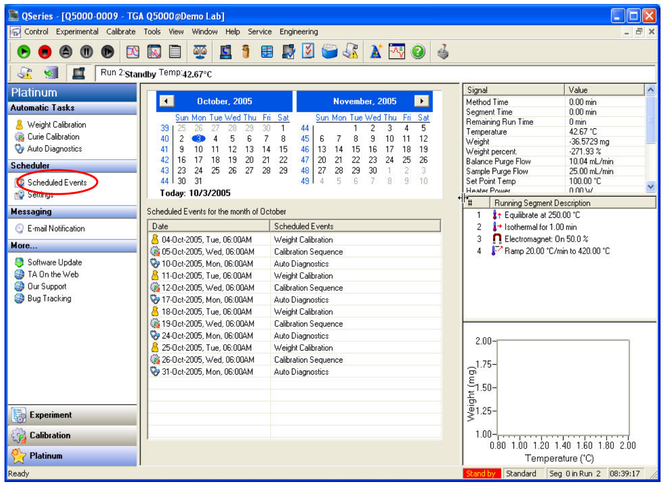
DSC Diagnostics Routine

- Perform a diagnostic check of the instrument
- List based on options (e.g., Autosampler, MFC, Cooler Type)



Event Scheduler

- Sequences, Auto-calibration, Auto-Verification and Diagnostics Events can be Scheduled via Platinum Software



SDT Q600 (2960) Calibration

- DTA Baseline & TGA Weight Calibration
  - 2 runs – empty beams & then calibration weights
- Temperature Calibration
  - Up to 5 temperature standards
- DSC Heat Flow Calibration
  - 2 runs – empty pans then sapphire

SDT Q600 (2960) DSC Heat Flow Calibration

- Two scans from ambient to 1500°C at 20 °C/min
  - empty alumina pans
  - sapphire in alumina sample pan
- Use Software to analyze
- E-curve will be calculated and transferred to the module when the user accepts the results

Instrument Preparation

- **Purge Gas**
  - Type of purge gas and flow rate affect calibration and therefore should be controlled
  - Nitrogen is preferred because it is inert and calibration is least affected by changes in flow rate
- **Cooling Accessories**
  - If used, they should be operating and equilibrated prior to calibration or sample runs
- **Warm-up Time/Environment**
  - Electronics should be given at least one hour to stabilize for important samples if the instrument has been turned OFF
  - Electronics are effected by ambient temperature. Avoid areas such as hoods or near an air conditioner

Recommended Purge Gas Flow Rates

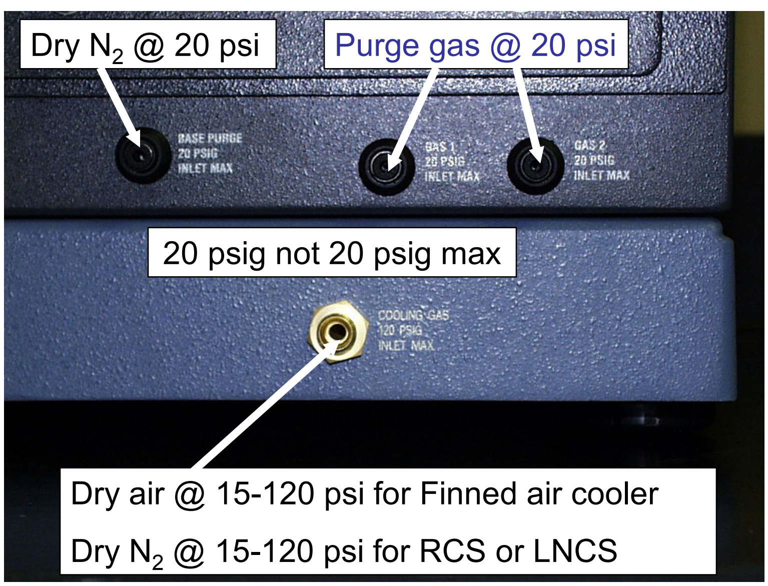
Module	**Purge Port**
All TA DSC's	50(N_2) or 25(He)
	(Purge in ml/min)

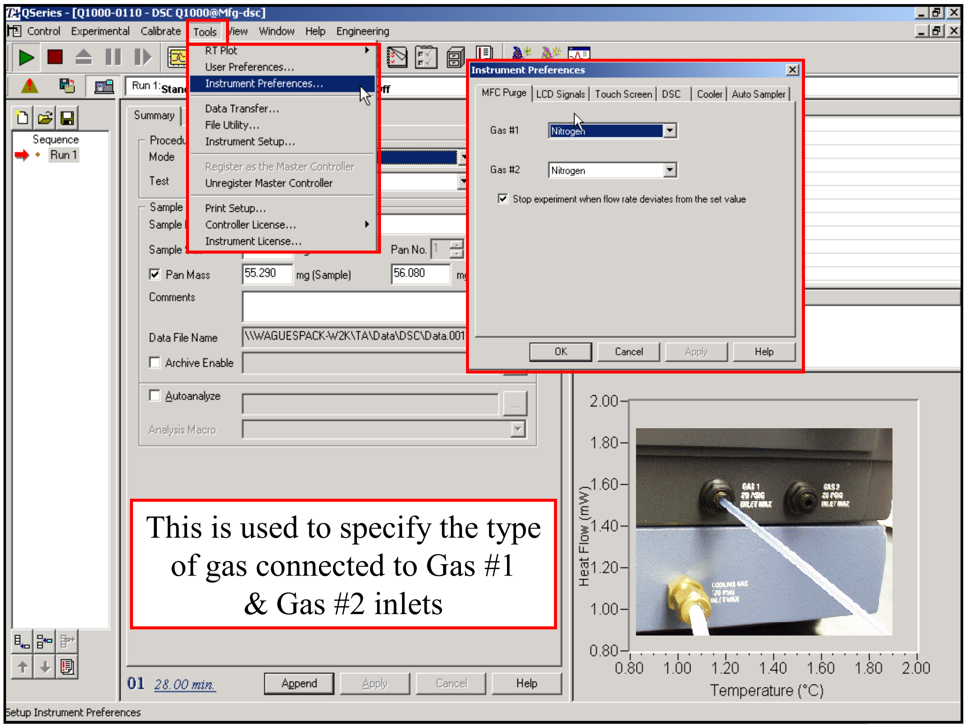
If you have a 2900s DSC, purge the vacuum port with 50ml/min if using a RCS or LNCA.

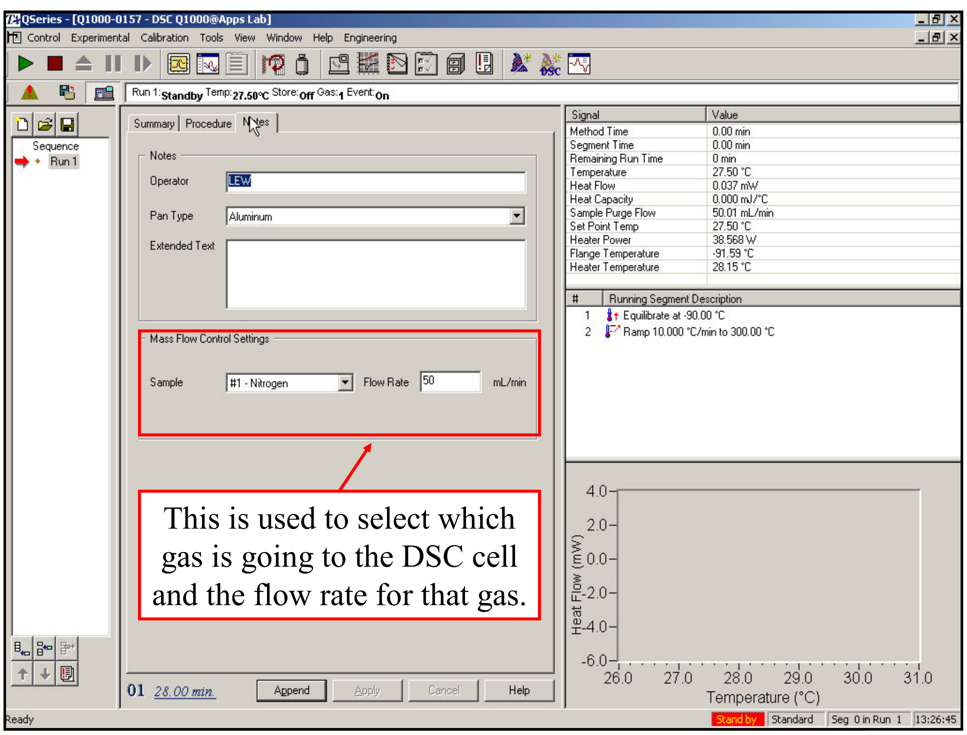
If purge gas is too slow - possible moisture accumulation & early aging of the cell

If purge gas is too fast – excessive noise

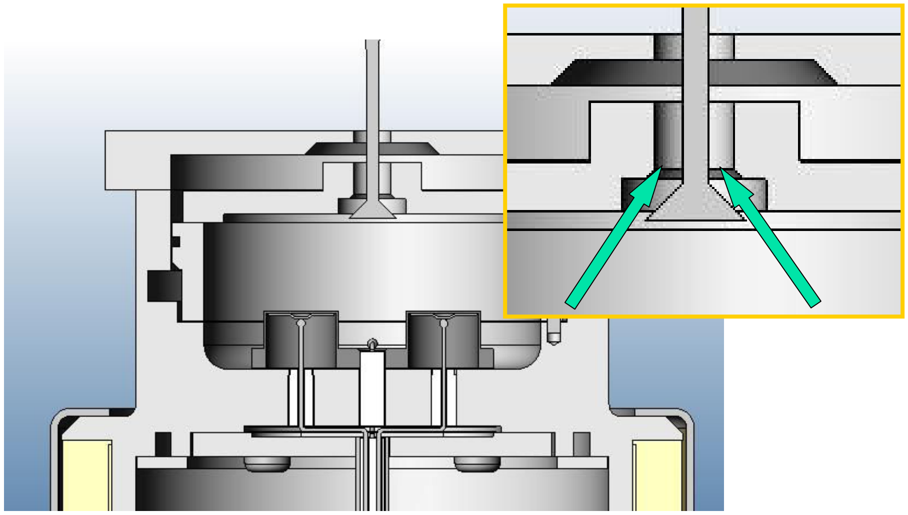
Purge gas ports on Q-Series DSC




QSeries - [Q1000-0110 - DSC Q1000@Mfg-dsc]
Control Experimental Calibrate Tools View Window Help Engineering
RT Plot
User Preferences...
Instrument Preferences...
Data Transfer...
File Utility...
Instrument Setup...
Register as the Master Controller
Unregister Master Controller
Print Setup...
Controller License...
Instrument License...
Instrument Preferences
MFC Purge LCD Signals Touch Screen DSC Cooler Auto Sampler
Gas #1 Nitrogen
Gas #2 Nitrogen
Stop experiment when flow rate deviates from the set value
OK Cancel Apply Help
This is used to specify the type of gas connected to Gas #1 & Gas #2 inlets
Heat Flow (mW)
Temperature (°C)
Setup Instrument Preferences


QSeries - [Q1000-0157 - DSC Q1000@Apps Lab]
Control Experimental Calibration Tools View Window Help Engineering
Summary Procedure Notes
Operator LEW
Pan Type Aluminum
Extended Text
Mass Flow Control Settings
Sample #1 - Nitrogen Flow Rate 50 mL/min
This is used to select which gas is going to the DSC cell and the flow rate for that gas.
Signal Value
Method Time 0.00 min
Segment Time 0.00 min
Remaining Run Time 0 min
Temperature 27.50 °C
Heat Flow 0.037 mW
Heat Capacity 0.000 mJ/°C
Sample Purge Flow 50.01 mL/min
Set Point Temp 27.50 °C
Heater Power 38.568 W
Flange Temperature -91.59 °C
Heater Temperature 28.15 °C
1 Equilibrate at -90.00 °C
2 Ramp 10.000 °C/min to 300.00 °C
Heat Flow (mW)
Temperature (°C)
Ready

Autolid II: Improved Purge Gas Exhaust



DSC Training Course

Selecting Optimum Experimental Conditions

- "Always" run a TGA experiment before beginning DSC tests on new materials
- Heat approximately 10mg sample in the TGA at 10°C/min to determine:
  - Volatile content
    - Unbound water or solvent is usually lost over a broader temperature range and a lower temperature than a hydrate/solvate
  - Decomposition temperature
    - DSC results are of little value once the sample has lost 5% weight due to decomposition (not desolvation)
    - Decomposition is a kinetic process (time + temperature dependent). The measured decomposition temperature will shift to lower temperatures at lower heat rates

DSC Training Course

Selecting Optimum Experimental Conditions

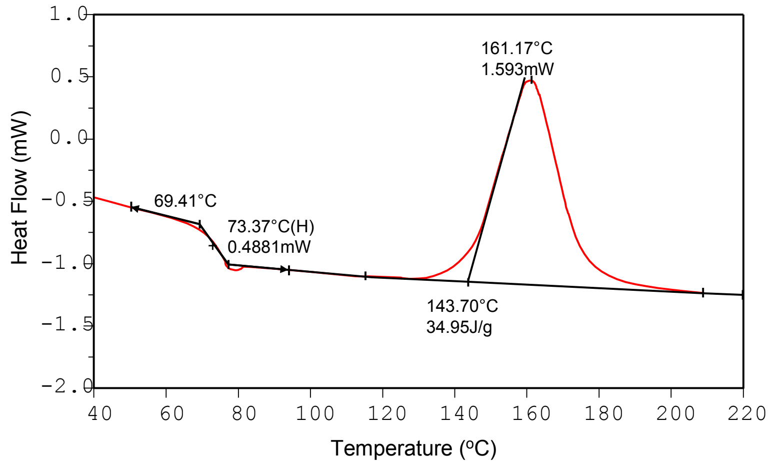
- Use TGA data to help select DSC experimental conditions
  - Crimped vs. Hermetic (sealed) Pan
    - Use hermetic pan if sample loses approximately 0.5% or more
  - Maximum Temperature
    - Excessive decomposition will contaminate DSC cell between runs
  - When comparing samples, always use the same experimental conditions

Optimization of DSC Conditions

- **Sample Preparation**
  - Keep thin; cut rather than crush
  - Weight of 10-15mg for polymers; 3-5mg for metal or chemical melting
  - Goal is to achieve a change of 0.1-10mW heat flow in going through the transition (see Figure #1)
  - If sample contains volatiles, put 5-10 pinholes in the lid of the pan before crimping in order to permit a continuous evaporation process

Heat Flow Change During a Transition

Figure #1



Selecting Optimum Experimental Conditions

- Sample Pan: Crimped vs. Hermetically Sealed
  - **Crimped pans** are lighter (» 23mg) and provide better sensitivity and resolution
  - **Hermetic aluminum pans** are heavier (» 55mg) but can be sealed to prevent loss of volatiles
  - **Hermetic stainless steel pans** (» 250mg) permit use of large samples (100mg) and higher temperatures/pressures (2000 psig = 1.4 MPa)
  - Care should be taken to keep the bottom of all pans flat to improve heat transfer/resolution

Optimization of DSC Conditions

Experimental Conditions (cont.)

- Select an end-temperature which does not cause decomposition of the sample to occur in the DSC.
- Decomposition products can condense in the cell and cause either corrosion of the cell or baseline problems
  - Use sealed glass ampoules or stainless steel pans, which can take high pressure (>1000psi), in order to study decomposition by DSC

Sample Pans

- Type of pan depends on:
  - Sample form
  - Volatilization
  - Temperature range
- Use lightest, flattest pan possible
- Always use reference pan of the same type as sample pan

Standard DSC Pans (Crimped)

- Pan & lid weighs ~23mg, bottom of pan is flat
- Used for solid non-volatile samples
- Always use lid (see exceptions)
  - Lid improves thermal contact
  - Keeps sample from moving
- Exceptions to using a lid
  - Running oxidative experiment
  - Running PCA experiment

Standard DSC Pans (Crimped)

- Crimped pans are available in:
  - **Aluminum:** up to 600°C
  - **Copper:** up to 725°C (in N_2)
  - **Gold:** up to 725°C
- Standard Pans without lids
  - **Graphite:** up to 725°C (in N_2)
  - **Platinum:** up to 725°C

Hermetic Pans (Sealed)

- Pan & Lid weigh ~55mg, bottom of pan is not as flat as std pans
- Used for liquid samples and samples with volatiles
- Always use lid (same exceptions as before)
- After sealing pans, the lid should form a dome

Hermetic Pans (Sealed)

- Hermetic Pans are available in:
  - Aluminum: <600°C; <3 atm (300 kPa gage)
  - Alodined Aluminum: <600°C; <3 atm (300 kPa gage)
    - (For aqueous samples)
  - Gold: <725°C; <6 atm (600 kPa gage)
- Specialized Sealed Pans
  - High Volume: 100µL; <250°C; 600 psig(4.1 MPa)
  - High Pressure: 35µL; <300°C; 1450 psig(10 MPa)

Note: 3 atm is approximately 44 psig

New Tzero Sample Press & Pans

- Completely Redesigned Press
- Two New Sample Pans
- Compatible with existing sample pans
- No tooling required
- Color-coordination between pan boxes and dies
- Improved hermetic sealing
- Improved DSC Performance

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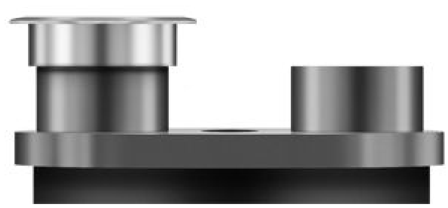
Factors Affecting Sensitivity/Resolution

Sensitivity

- Thermocouple Output
- Magnitude of ΔT
- Signal/Noise
- Baseline Quality



Resolution

- Time Constant of Transducer
- Pan Contact Resistance

The flatness of the bottom of the DSC pan in critical to optimizing resolution

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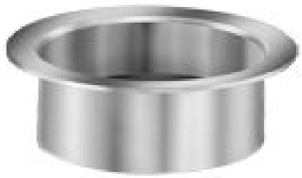
New TA Instruments Tzero Pans

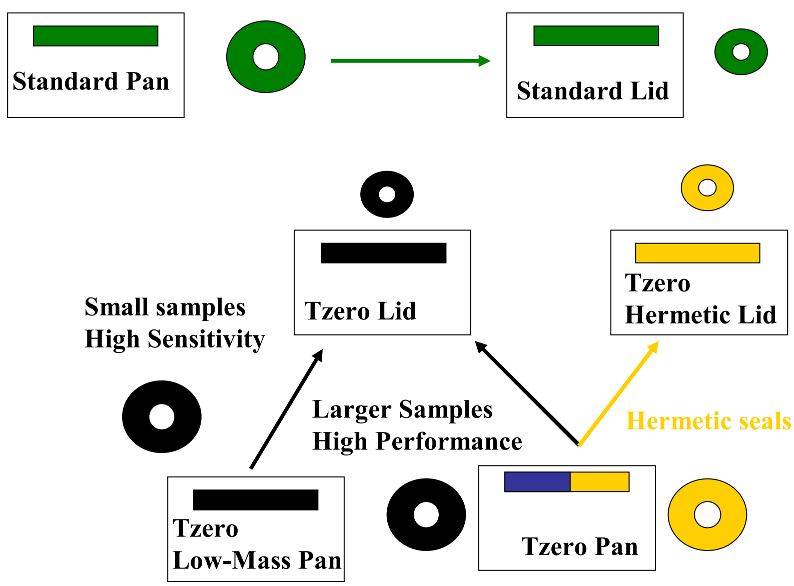
Tzero Pan



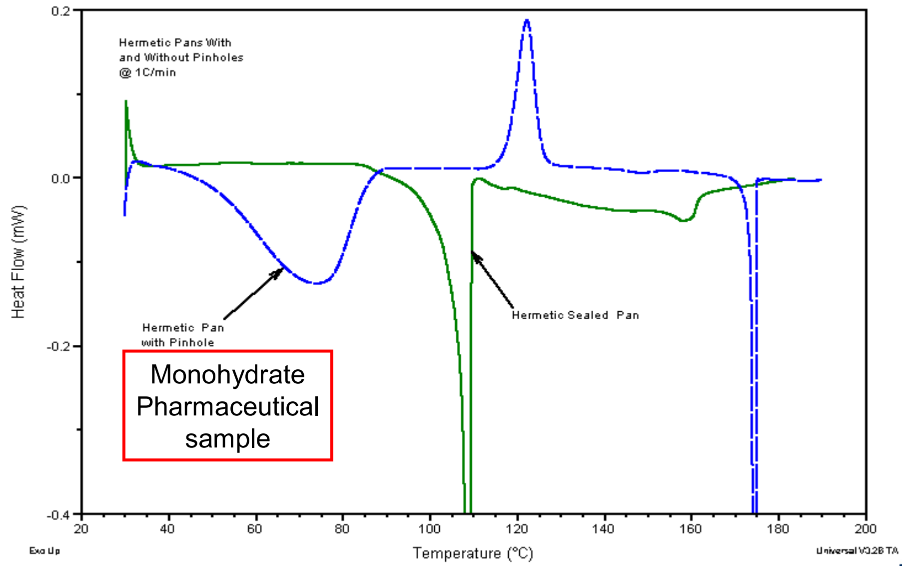
Tzero Low-Mass Pan

- The Tzero pan has been engineered to have a perfectly flat bottom and not to deform during crimping. This ensures the optimal contact between pan and sensor, minimizing the contact resistance and improving resolution.
- The Tzero Pan can be configured for crimped or hermetic use.
- The Tzero Low-Mass Pan is designed for the highest sensitivity when sample mass is limited.

Tzero Press Kit Configurations



It Does Matter What Pan You Use



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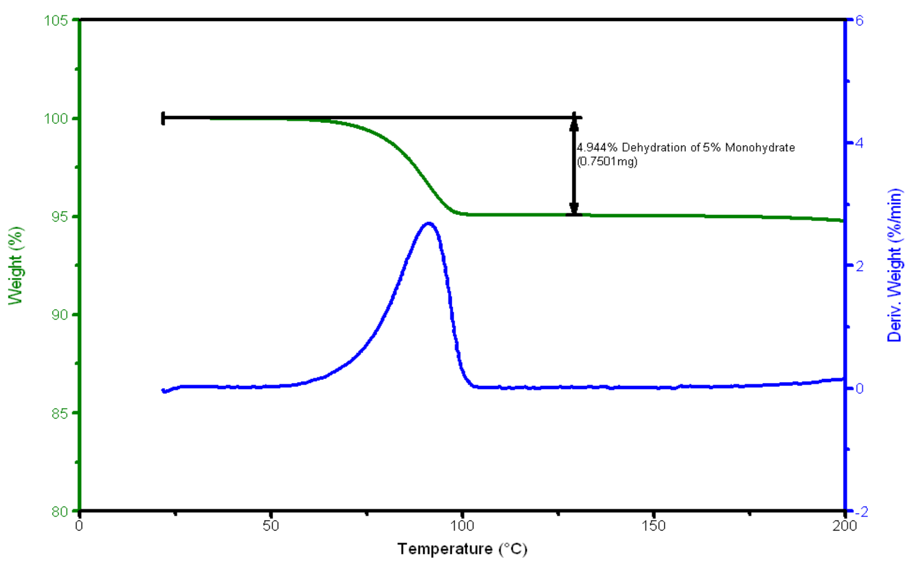
TGA of Monohydrate Pharmaceutical Drug



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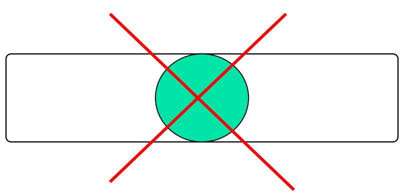
Sample Shape

- Keep sample thin
- Cover as much as the bottom of pan as possible

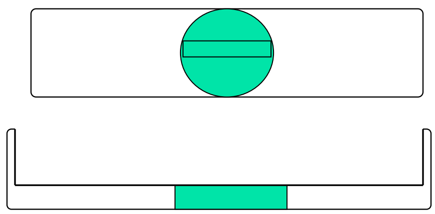
Sample Shape

- Cut sample to make thin, don't crush
- If pellet, cut cross section

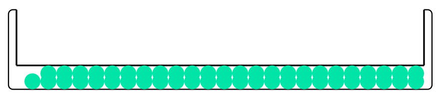


Sample Shape

- Cut sample to make thin, don't crush
- If pellet, cut cross section



- If powder, spread evenly over the bottom of the pan



Keeping the DSC Cell Clean

- One of the first steps to ensuring good data is to keep the DSC cell clean
- How do DSC cells get dirty?
  - Decomposing samples during DSC runs
  - Samples spilling out of the pan
  - Transfer from bottom of pan to sensor

How do we keep DSC cells clean?

- **DO NOT DECOMPOSE SAMPLES IN THE DSC CELL!!!**
- Run TGA to determine the decomposition temperature
  - Stay below that temperature!
- Make sure bottom of pans stay clean
- Use lids
- Use hermetic pans if necessary

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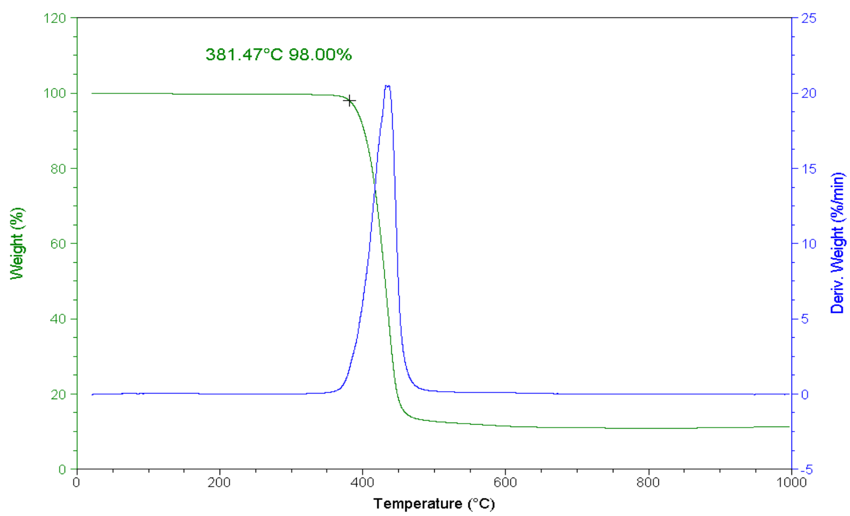
TGA Gives Decomposition Temperature



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Cleaning Cell (Q-Series Only)

- Use solvent – slightly damp swab with an appropriate solvent
    - Heat cell to 200°C for 10 min to drive off any remaining solvent
    - Solvents are Last Resort for 2900 Series
  - If the cell is still dirty………

Cleaning Cell (Q-Series and 2900 Series)

- If the cell is still dirty
  - Clean w/ brush

    - ssary
    - Be careful with the Tzero™ thermocouple
    - Blow out any remaining particles

Q-Series Cell Before Cleaning

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Brushing the Sample Sensor

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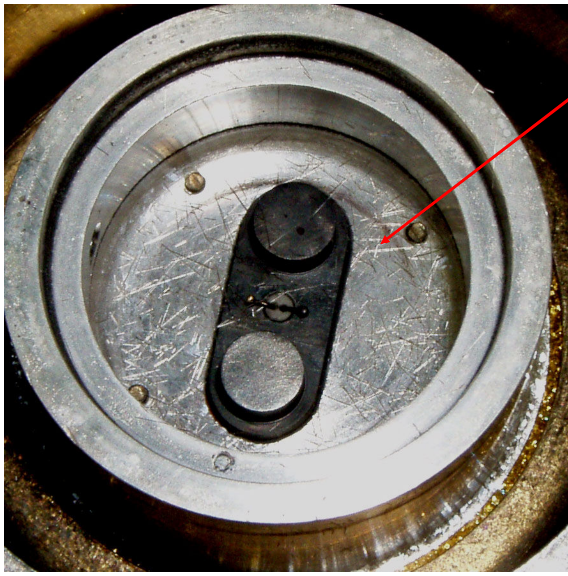
After Cleaning Sample Sensor



Fibers in cell from cleaning brush need to be removed

Cleaning Cell (Q-Series and 2900 Series)

- Bake out (Use as a last resort in Q-Series cell)
  - Air purge
  - Open lid
  - Heat @ 20°C/min to appropriate temp (max of 550°C) No Isothermal @ the upper temperature
  - Cool back to room temp & brush cell again
- Check for improved baseline performance

Cleaning Cell (2900 Series)

- **LAST RESORT for 2900 Series**
  - Use solvent – slightly damp swab with appropriate solvent
    - Keep solvent away from holes in base of cell
    - Heat cell to 200°C for 10 min to drive off any remaining solvent

What if I need help?

- On-site training & e-Training courses - see Website
- Call the TA Instruments Hotline
  - 302-427-4070 M-F 8-4:30 Eastern Time
  - mailto:thermalsupport@tainstruments.com
- Call the TA Instruments Service Hotline
  - 302-427-4050 M-F 8-4:30 Eastern Time
- Check out our Website
  - http://www.tainstruments.com/

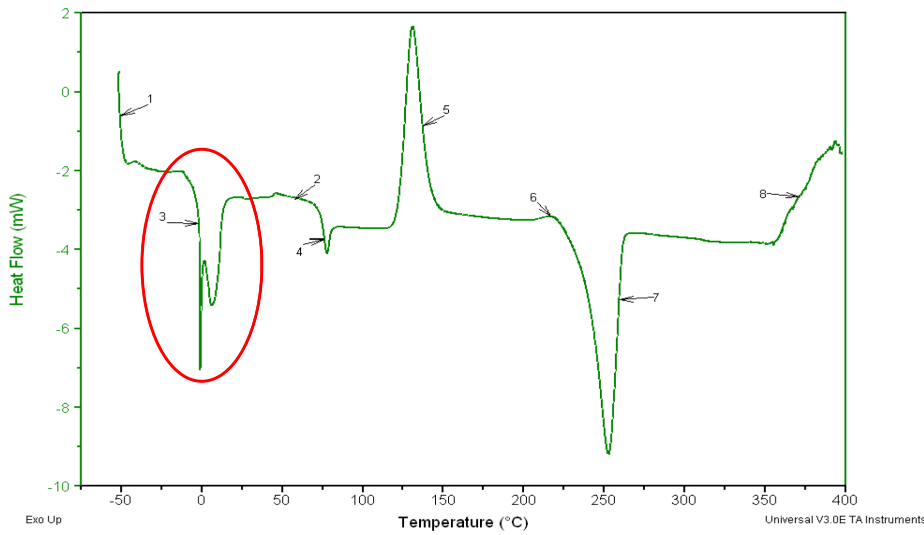
Interpretation of Undesirable Events in DSC Data

Topics

√	Event 1:	Large Endothermic Shift in the Baseline at the Beginning of the Experiment
√	Event 2:	Baseline Slope After Baseline Calibration
	Event 3:	Unexpected Transitions Near 0°C
	Event 4:	Shifts in the Baseline and Apparent Melting at the Glass Transition
	Events 5 and 6:	Exothermic Peaks in the Data Between the Glass Transition and Melting Temperature
	Event 7:	Changes in the Melting Transition Due to Thermal History
	Event 8:	Decomposition

[See Figure 5]

Figure 5



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Event 3: Unexpected Transitions Near 0°C

Event 3 in Figure 5 is caused by water. The transition is also much larger than normally seen in order to more easily illustrate it.

Water in the DSC Cell

- It is possible to get condensation of water within the DSC cell if the purge gas is not sufficiently dry or if the cell is opened to room atmosphere when its temperature is below the freezing point of water, 0°C.
- The transitions caused by water in the cell can cover a wide temperature range from –10°C to more than 50°C and are highly undesirable.

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Event 3 (cont.)

- When water condenses in the cell, it can condense on the sample pan, reference pan, sensors, and furnace. Water on the sample pan or inside it typically melts very sharply at 0°C as seen in the endothermic spike at 0°C in Figure 5.
- Water on the reference pan would look similar except that it would appear as an exothermic spike in the data. In this data, the melting peak is endothermic because most, if not all, of the water was on the sample. To get this undesirable transition for illustration purposes, the sample pan was removed from the DSC when its temperature was –50°C. Water from the room air condensed on the pan, plus some of it probably condensed in other parts of the cell.

Event 3 (cont.)

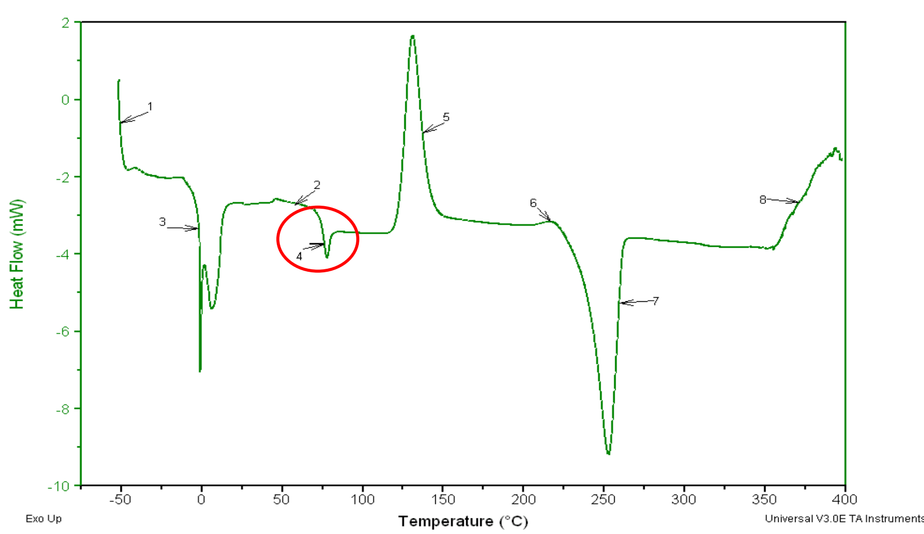
- The broader endothermic peak between 0°C and 25°C is due to the endothermic evaporation of the water on the DSC pan. As can be seen in the data, the baseline does not stabilize until almost 50°C when all of the water in contact with the pan and sensor has finally evaporated.
- To avoid artifacts in the data due to water, it is best to have a drying tube in the purge gas line between the source of the gas and the purge gas inlet on the DSC cell base. In addition, never open the cell to the atmosphere or load a sample when the cell temperature is below 0°C.

Event 3 (cont.)

Water in the Sample

- Many samples contain water and, therefore, can undergo a transition near 0°C due to this water.
- However, just because the sample contains water does not mean it will have a melting transition near 0°C.
- Water that is physically or chemically associated with sample material generally will not freeze and, therefore, cannot melt.
- Unassociated water or "free" water in the sample has the same properties as bulk water. However, the actual melting point is often lower than 0°C due to impurities dissolved in the water.

Figure 5



Event 4: Shifts in the Baseline

Shifts in the Baseline

- The most common baseline shift is due to the increase in heat capacity that occurs upon heating through the glass transition temperature. The size of the endothermic shift is a measure of the amount of amorphous material in the sample. The more amorphous the sample, the larger the baseline shift.
- Heat capacity is a measure of molecular mobility within the sample. Since there is a step-increase in molecular mobility within the sample as it is heated through its glass transition temperature, there is also a step-increase in the amount of heat required to continue heating the sample at the same rate above its Tg.

Event 4 (cont.)

- An exothermic shift (less endothermic) in the baseline while heating results in the baseline moving back closer to zero (0 mW) heat flow. This type of shift is much less common and in order for this to occur while heating, there must either be a reduction in molecular mobility or a reduction in sample mass. Most of the time, this type of positive shift is due to evaporation of some component within the sample.

Apparent Melting in the Glass Transition

- The endothermic shift in the baseline at the transition in Figure 5 is due to the glass transition of the amorphous PET polymer.

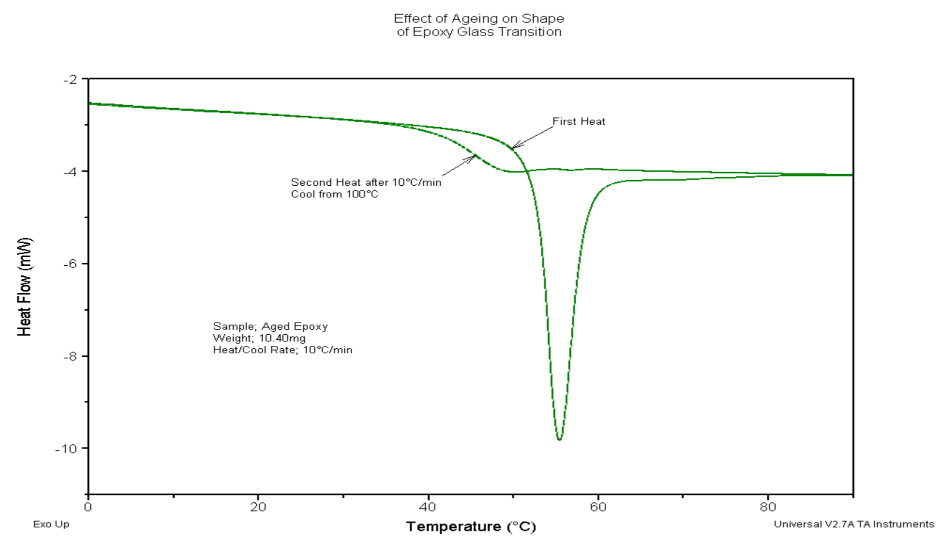
Event 4 (cont.)

- Depending on the thermal history of amorphous (glassy) polymers, the glass transition can appear as a simple step in the baseline or one that has a substantial endothermic peak that can be misinterpreted as a melting peak.
- Figure 6 shows the results from two experiments on the same sample; the only difference is the thermal history. The sample with the endothermic peak was stored for over ten years at a temperature just below its glass transition temperature. As it aged, the enthalpy of the sample decreased towards equilibrium, and it became denser and more brittle.

Event 4 (cont.)

- By heating a sample above the glass transition temperature and then cooling it back to room temperature, the previous thermal history is erased. This is the data marked as the "Second Heat" in Figure 6.
- The term for the endothermic peak that develops in the glass transition with aging at temperatures below the glass transition temperature is "enthalpic relaxation." It is due to the fact that amorphous materials are not in thermodynamic equilibrium but, with time, do relax and move towards equilibrium.

Figure 6



Aging of Amorphous Structure (Storage Stability)

Background Information

- At temperatures above Tg, there is high molecular mobility and the sample is in thermal equilibrium
- At temperatures well below Tg (Tg-40°C), molecular mobility is low and the existing amorphous structure is relatively stable
- At temperatures just below Tg (Tg-10°C), there is enough molecular mobility that the existing amorphous structure is not stable and will change with time as the amorphous material seeks a lower energy state (amorphous equilibrium or crystalline)

Aging of Amorphous Structure (Storage Stability)

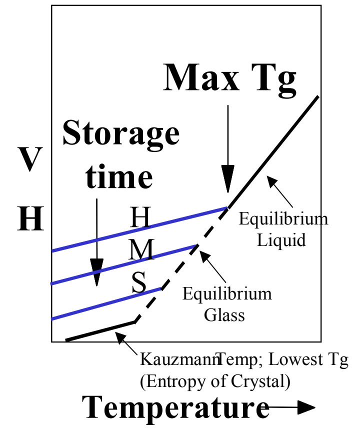
- Cooling at relatively high rates from temperatures above Tg to temperatures below Tg creates a meta-stable glass which ages towards equilibrium over time. The rate of change is a function of the storage temperature and molecular structure
- DSC/MDSC can be used to evaluate the stability of the meta-stable glass and compare the structural state of the amorphous phase

Some Definitions

- ***Enthalpic Relaxation***
  - The process of a meta-stable glass relaxing towards equilibrium at a temperature below Tg
  - Occurs as the sample is being cooled to temperatures below Tg
  - Occurs as the sample is being stored at temperatures below Tg
- ***Enthalpic Recovery***
  - The recovery of energy (J/g) lost during Enthalpic Relaxation. It (peak in DSC data @ Tg) occurs as the sample is heated to a temperature above Tg

Effect of Aging on Amorphous Materials

Physical Property	Response on Storage Below Tg
Specific Volume	Decreases
Modulus	Increases
Coefficient of Expansion	Decreases
Heat Capacity	Decreases
Enthalpy	Decreases
Entropy	Decreases



Where H = High relative cooling rate
M = Medium relative cooling rate
S = Slow relative cooling rate

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Effect of Cooling Rate on Shape of Tg

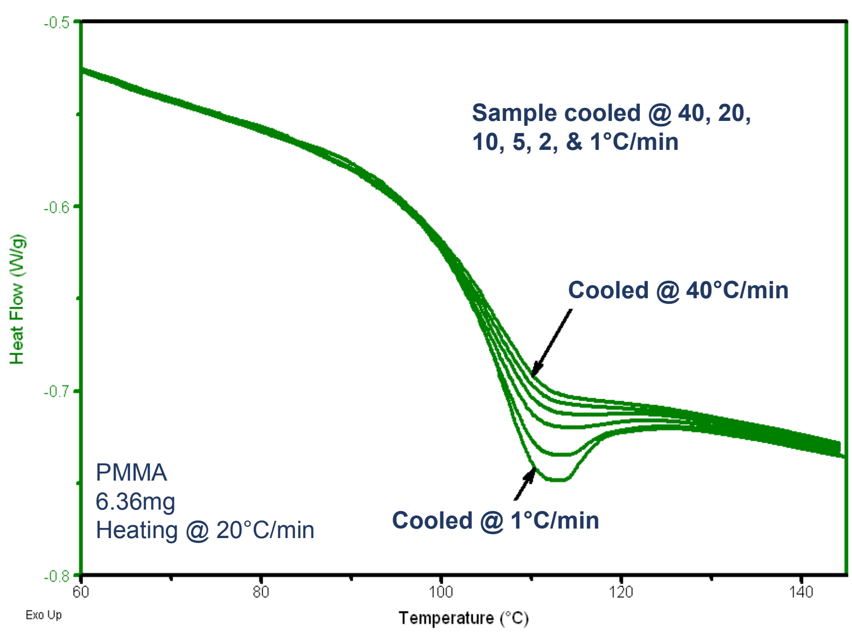
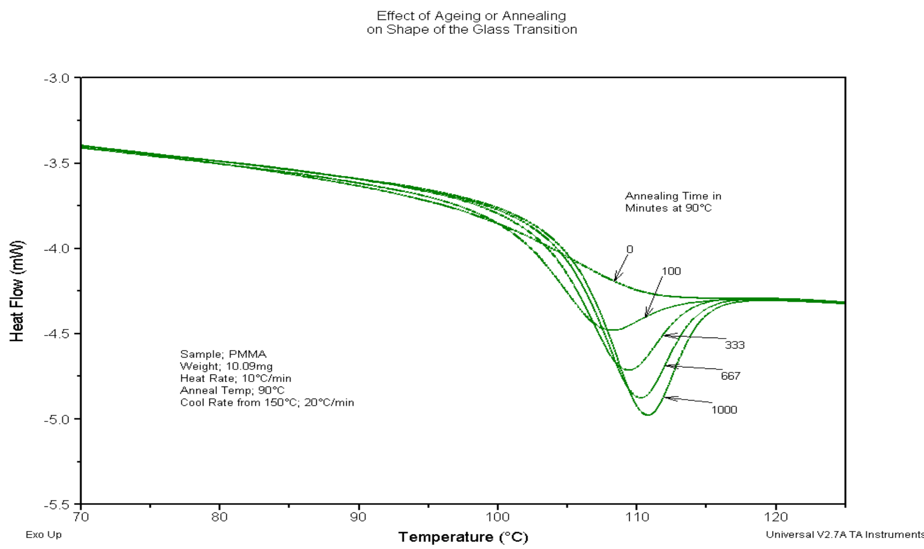


Figure 7



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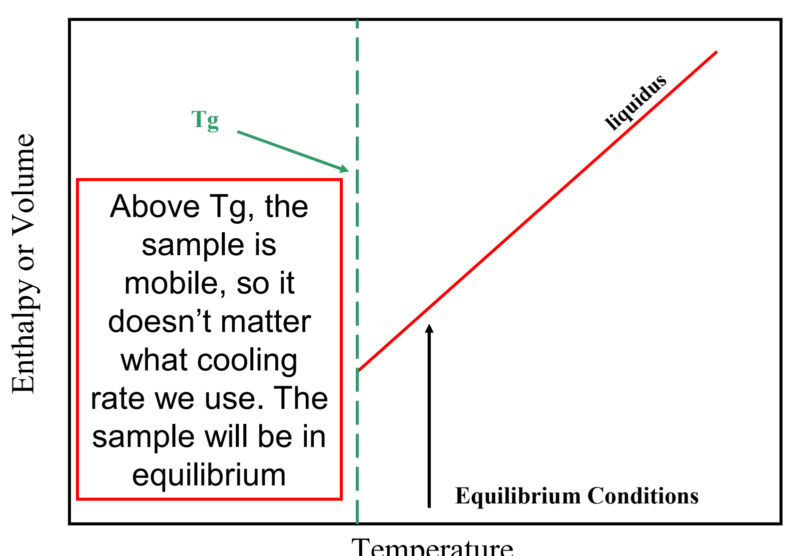
Enthalpy/Volume Diagrams



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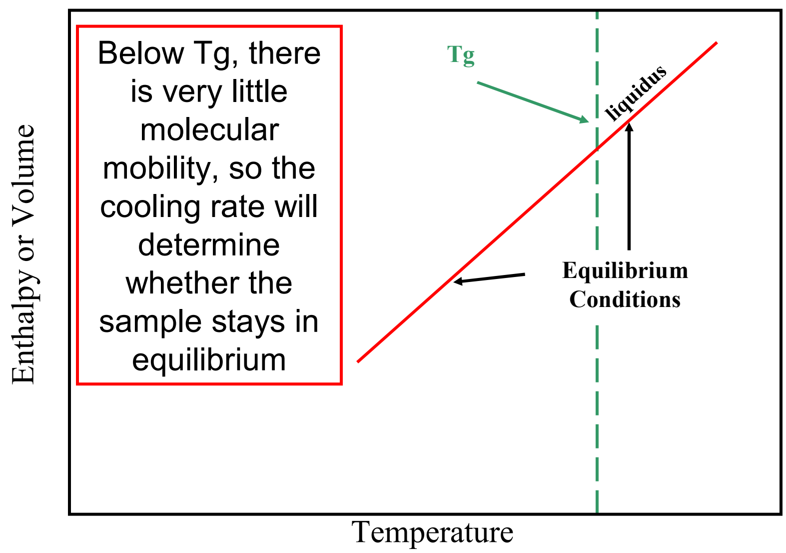
Enthalpy/Volume Diagrams



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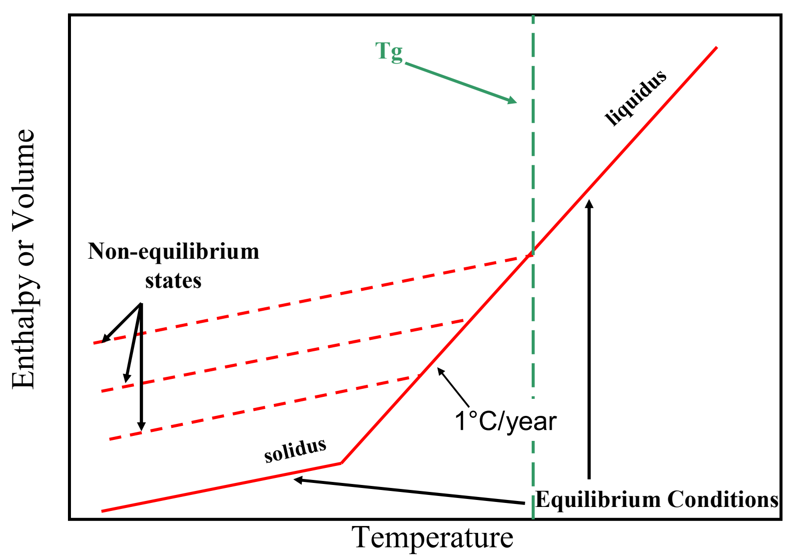
For Example



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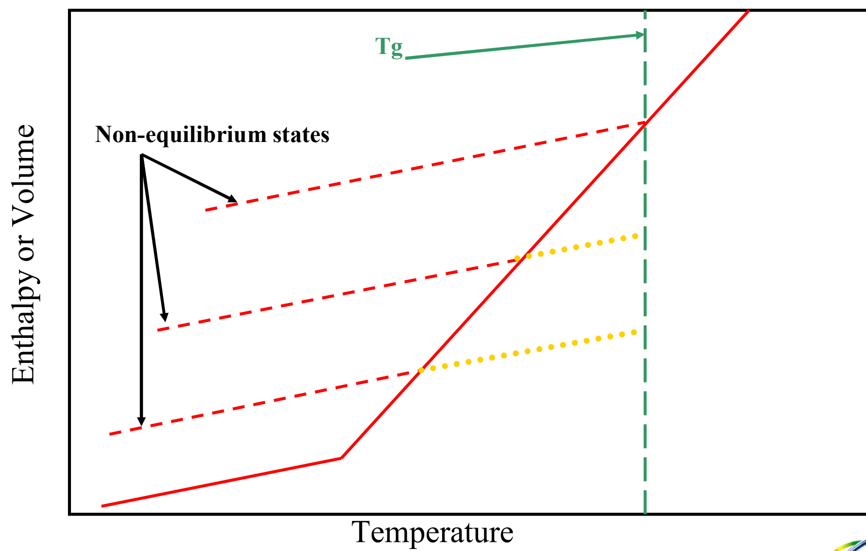
Enthalpy/Volume Diagrams

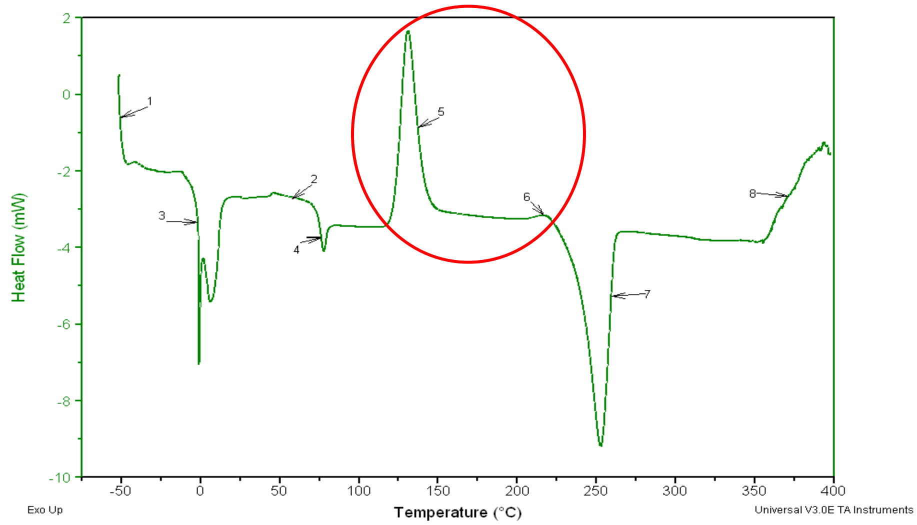


Importance of Enthalpic Relaxation

Is enthalpic recovery at the glass transition important?
…Sometimes

- Glass transition temperature, shape and size provide useful information about the structure of the amorphous component of the sample.
- This structure, and how it changes with time, is often important to the processing, storage and end-use of a material.
- Enthalpic recovery data can be used to measure and predict changes in structure and other physical properties with time.

Figure 5



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Events 5 and 6

Exothermic Peaks in the Data between the Tg and Melting Temperatures

- Events 5 and 6 in Figure 1 are the result of crystallization and crystal perfection processes that occur as the sample is heated.
- To understand what might be happening, so that the data is interpreted correctly, there are three factors that need to be considered:

  1. What is the thermal history of the sample?
  2. Does the material crystallize and, if so, how fast or slow (kinetics) does it crystallize as a function of time and temperature?
  3. How fast was the sample heated or cooled in the DSC experiment?

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Events 5 and 6 (cont.)

Thermal History

- When referring to "Thermal History," we are identifying the temperature versus time profile that the sample has been subjected to in the past.

Events 5 and 6 (cont.)

- As temperature is increased above Tg, molecular mobility increases rapidly. This permits the molecules to align with their neighbors and crystallize as seen in the exothermic peak centered near 130°C for the "First Heat."
- Although the baseline appears to stabilize between 150 and 225°C, there is an ongoing process of crystallization and crystal perfection over that temperature range as will be discussed later.
- The term "crystal perfection" is used to describe the process where small, less perfect crystals melt and then recrystallize into larger, more perfect crystals that will melt again at a higher temperature.

Events 5 and 6 (cont.)

Crystallization Kinetics

- Crystallization is a kinetic process, which means that the rate of crystallization is a function of both time and temperature. The fact that the peak of the crystallization process occurs near 130°C in Figure 8 is the result of the selected experimental conditions.
- Figure 9 shows how the cold crystallization peak broadens and shifts to a higher temperature as the heating rate is increased from 2 to 16°C/min. This shift is much larger than seen in the glass transition and melting processes, which have relatively minor kinetic contributions.

Figure 8

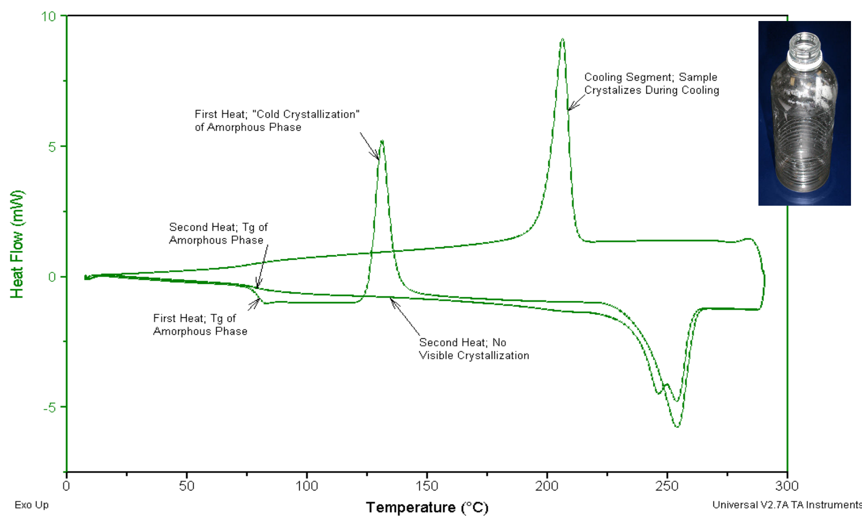

Figure 9

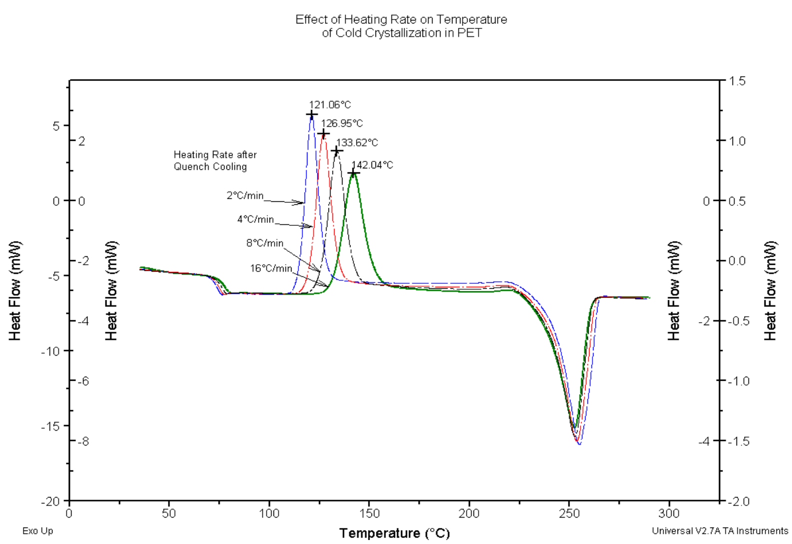

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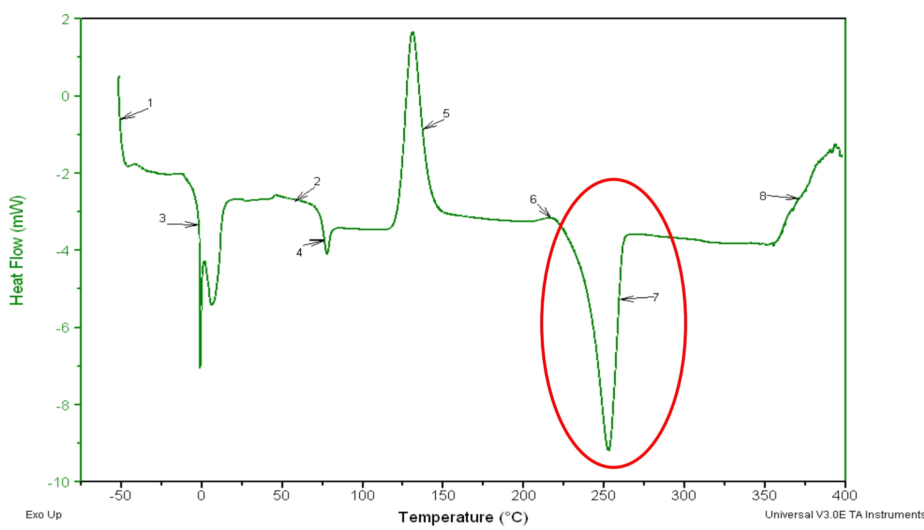
Figure 5



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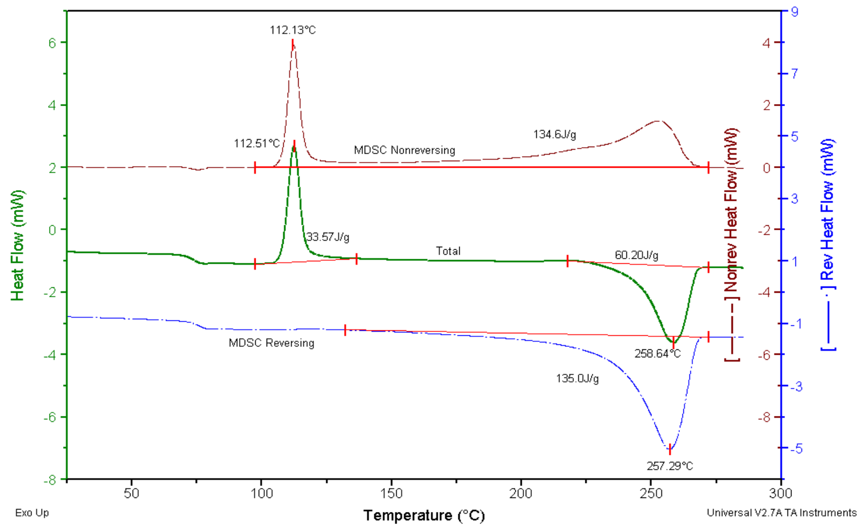
Event 7: The Melting Transition

- The melting transition can be the least complicated transition measured by DSC. However, it can also be the most complicated transition for some materials, especially semi-crystalline polymers.
- When measuring the melting transition, it is normal to measure the temperature range over which it occurs as well as the enthalpy of melting (ΔH_m) which is proportional to the crystalline content of the sample.

Event 7 (cont.)

- The complication occurs with semi-crystalline materials because of the fact that the sample can increase in crystallinity as it is being heated in the DSC. If this occurs and is not considered in calculating the crystallinity of the sample, an artificially large value will result.
- Figure 10 shows the data from an MDSC® experiment. The Total signal is qualitatively and quantitatively equivalent to traditional DSC. From just the Total signal, it is possible and quite common to calculate a crystallinity value which has an error in excess of 100%.

Figure 10



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Event 7 (cont.)

- The question is: "How can DSC provide such a wrong answer?" The answer is that it does not.
- The error is due to the integration limits selected by the operator.
- Total signal of DSC is often misleading because it measures only the sum of all exothermic and endothermic processes.
- Figure 11 shows that slower heating rates provide more exothermic (crystal perfection) activity in the temperature region between 150 and 220°C.
- The increased crystal perfection that occurs at slower heating rates causes the melting point to increase to higher temperatures.

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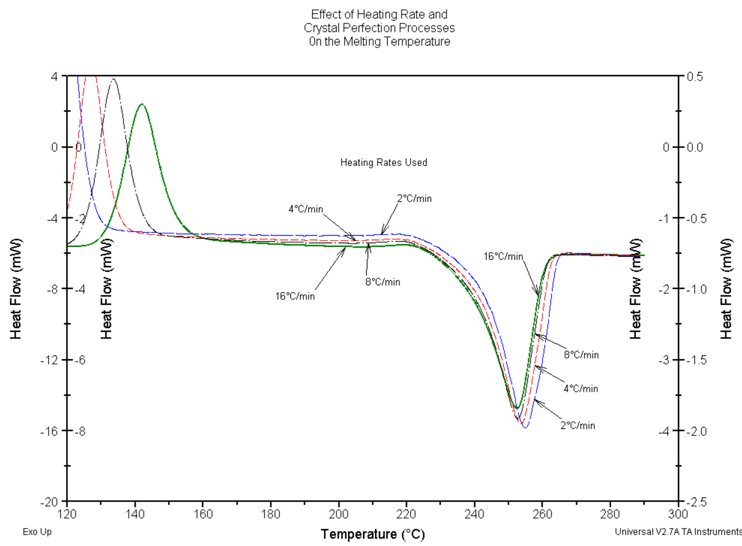
Figure 11



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Event 7 (cont.)

- The shape of the melting peak is also affected by crystal perfection processes that occur over the same temperature range as bulk melting. This often gives the appearance of two melting peaks rather than what actually is an exothermic crystallization peak superimposed on an endothermic melting peak.

- Figure 12 compares the shape of the melting process on the same sample of PET after it had been cooled at different rates from above its melting point. This is different from Figure 11 where all samples had the same thermal history (quench cooled) but were heated at different rates.

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Figure 12

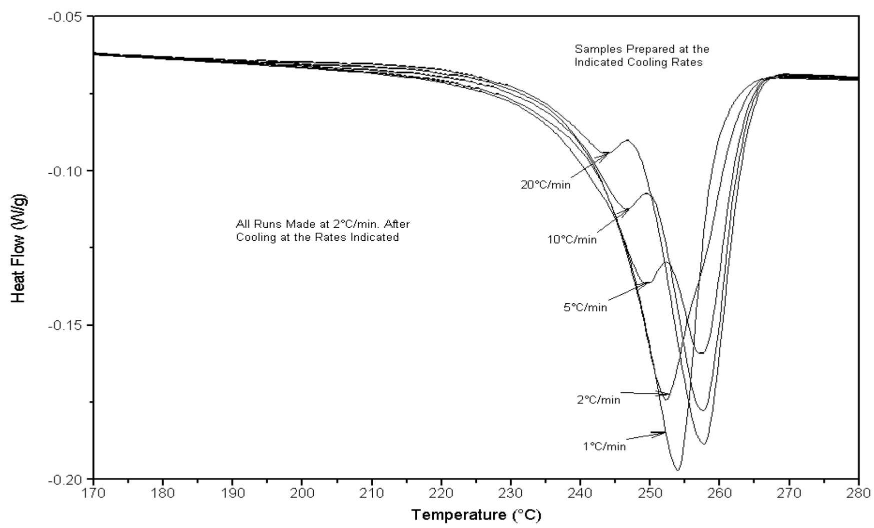

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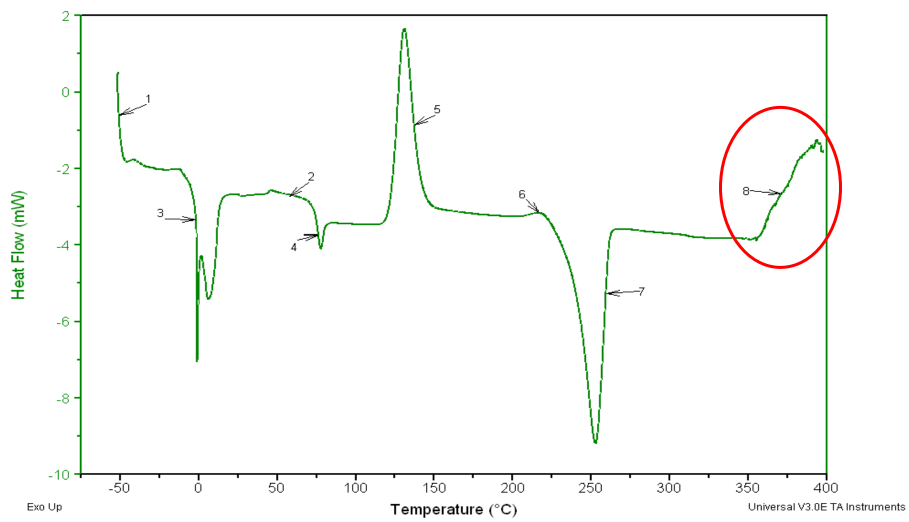
Figure 5



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Event 8: Decomposition

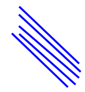
- Beginning at about 310°C in Figure 1, the sample of PET begins to decompose.
- Depending on the chemistry of the sample and type of sample pan used, decomposition can either be endothermic or exothermic.
- Decomposition usually involves a release of some volatiles. The process of off-gasing is usually erratic, and the data can become noisy and nonreproducible.
- Decomposing samples in a DSC will adversely affect the baseline and may corrode the DSC cell.

Applications

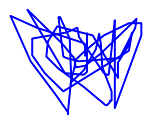
- Thermoplastics
- Thermosets
- Pharmaceuticals
- Heat Capacity
- Glass Transition
- Melting and Crystallization
- Additional Applications Examples

Thermoplastic Polymers

Semi-Crystalline or Amorphous



Crystalline Phase
melting temperature Tm
(endothermic peak)



Amorphous Phase
glass transition temperature (Tg)
(causing ΔCp)

Tg < Tm

Crystallizable polymer can crystallize on cooling from the melt at Tc
(Tg < Tc < Tm)

DSC of Thermoplastic Polymers

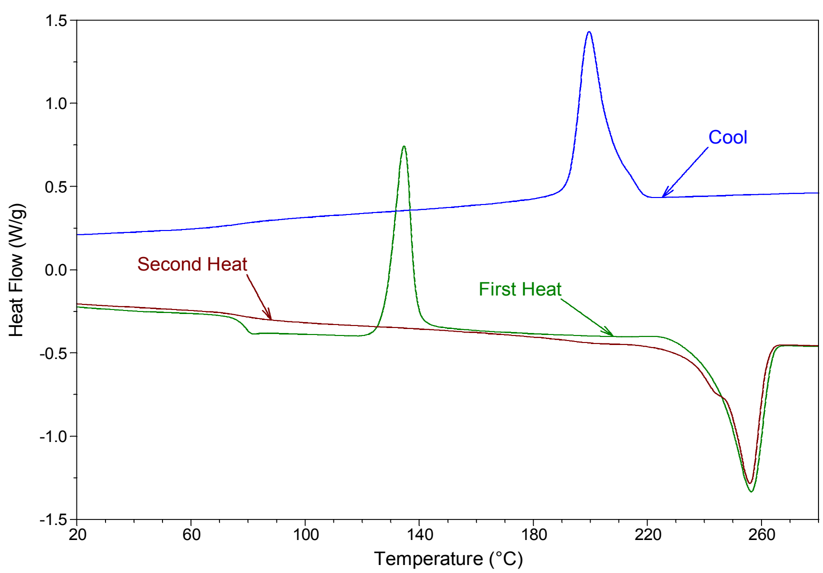
- Tg
- Melting
- Crystallization
- Oxidative Induction Time (OIT)

- General Recommendations
  - 10-15mg in crimped pan
  - H-C-H @ 10°C/min

Selecting Experimental Conditions

- Thermoplastic Polymers
  - Perform a Heat-Cool-Heat Experiment at 10°C/min.
  - First heat data is a function of the material and an unknown thermal history
  - Cooling segment data provides information on the crystallization properties of the polymer and gives the sample a known thermal history
  - Second heat data is a function of the material with a known thermal history

Heat/Cool/Heat



Selecting Experimental Conditions

Thermoplastic Polymers (con't)

- Interpreting Heat-Cool-Heat Results:
- One of the primary benefits of doing Heat-Cool-Heat is for the comparison of two or more samples which can differ in material, thermal history or both
  - If the materials are different then there will be differences in the Cool and Second Heat results
  - If the materials are the same and they have had the same thermal history then all three (H-C-H) segments will be similar
  - If the materials are the same but they have had different thermal histories then the Cool and Second Heat segments are similar but the First Heats are different

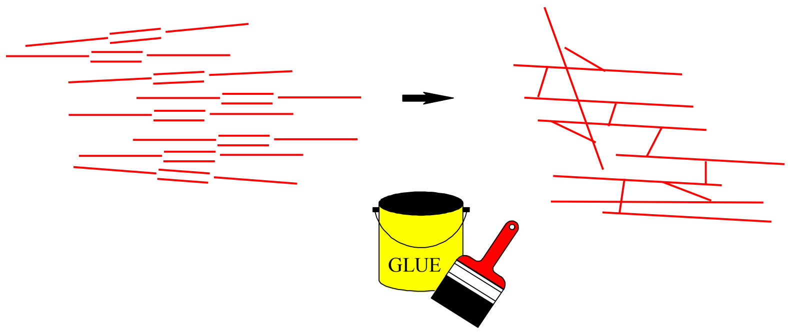
Selecting Experimental Conditions

- During first heat the maximum temperature must be higher than the melting peak end; eventually an isothermal period must be introduced
  - Too high temperature/time:
    - decomposition could occur
  - Too low temperature/time:
    - possibly subsequent memory effect because of the fact that crystalline order is not completely destroyed
- For non-crystallizable (amorphous) thermoplastics the maximum temperature should be slightly above Tg (removal of relaxation effects, avoid decomposition)

Thermosetting Polymers

A + B → C

Thermosetting polymers react (cross-link) irreversibly. A+B will give out heat (exothermic) when they cross-link (cure). After cooling and reheating C will have only a glass transition Tg.



DSC of Thermosetting Polymers

- Tg
- Curing
- Residual Cure

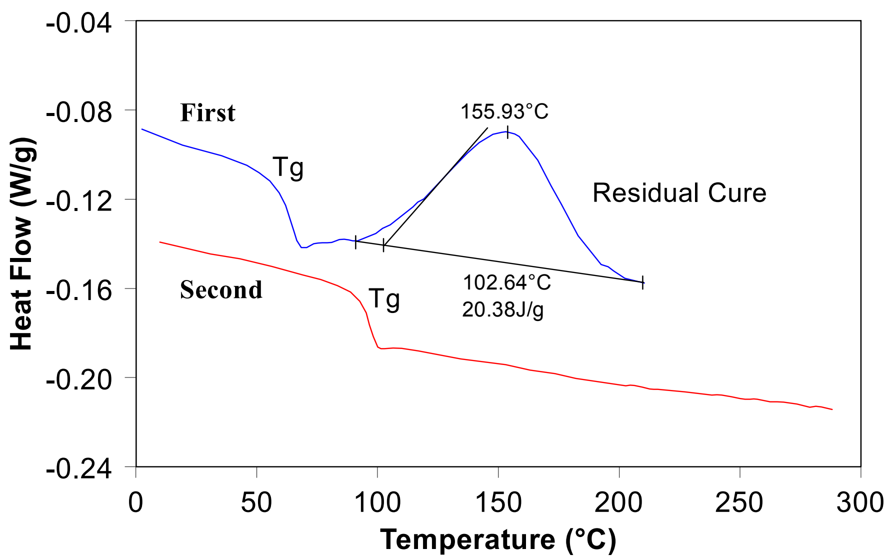
- General Recommendations
  - 10-15 mg in crimped pan if solid; hermetic pan if liquid
  - H-C-H @ 10°C/min

Selecting Experimental Conditions

Thermosetting Polymers

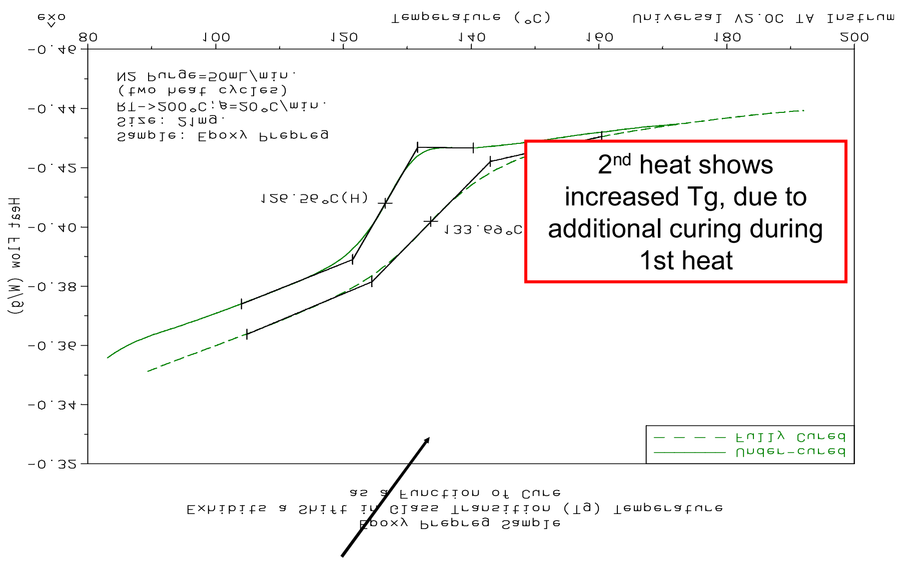
- Anneal the sample(if needed), then Heat-Cool-Heat at 10°C/min.
  - Anneal approximately 25°C above Tg onset for 1 minute to eliminate enthalpic relaxation from Tg (if needed)
  - **First Heat** is used to measure Tg and residual cure (unreacted resin). Stop at a temperature below the onset of decomposition
  - Cooling segment gives the sample a known thermal history
  - **Second Heat** is used to measure the Tg of the fully cured sample.
    - The greater the temperature difference between the Tg of the First and Second Heats the lower the degree of cure of the sample as received

Comparison of First and Second Heating Runs



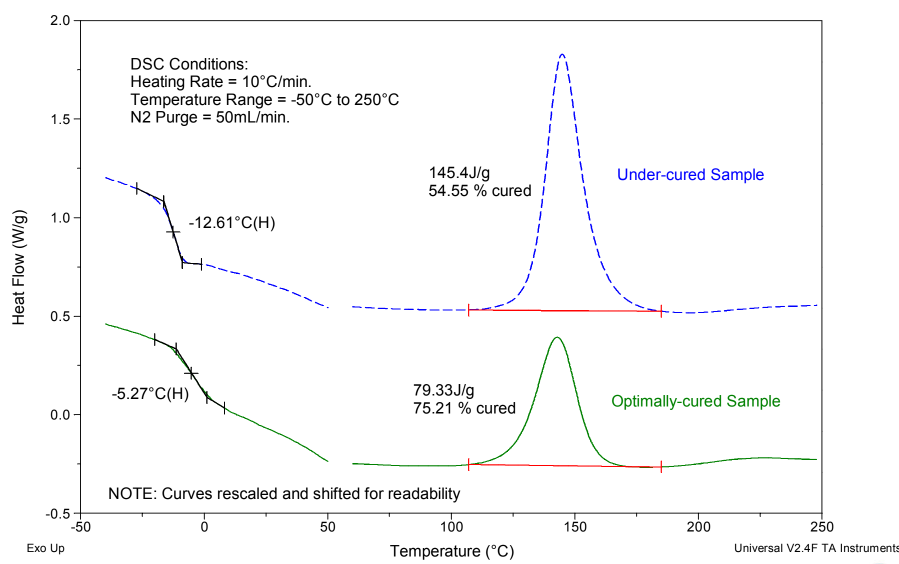
DSC Training Course

Characterization of Epoxy Prepreg



Note: Small exotherm due to residual cure

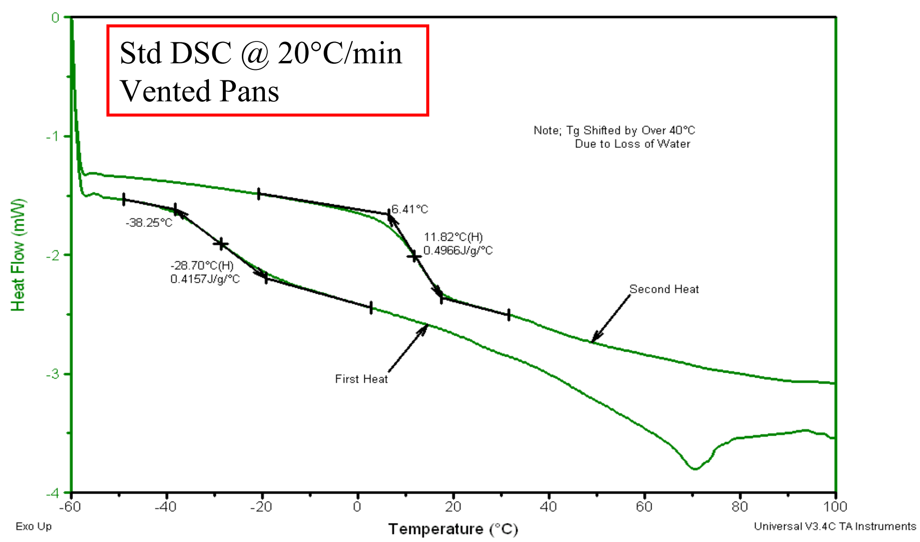
Determination of % Cure



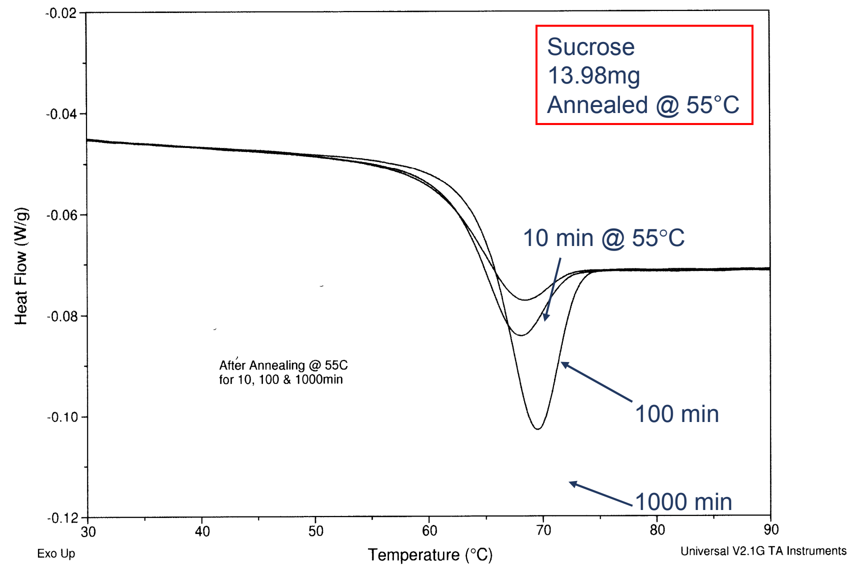
Pharmaceuticals

- Tg
- Melting
  - Purity
- Polymorphs
- General Recommendations
  - Use TGA to determine pan type
  - Use 1-5 mg samples (use 1mg for purity)
  - Initial H-C-H @ 10°C/min (1°C/min for purity)
  - If polymorphs present heat faster to inhibit polymorphic transformations

Tg of Sucrose Varies with Moisture Content



Structure Changes With Time



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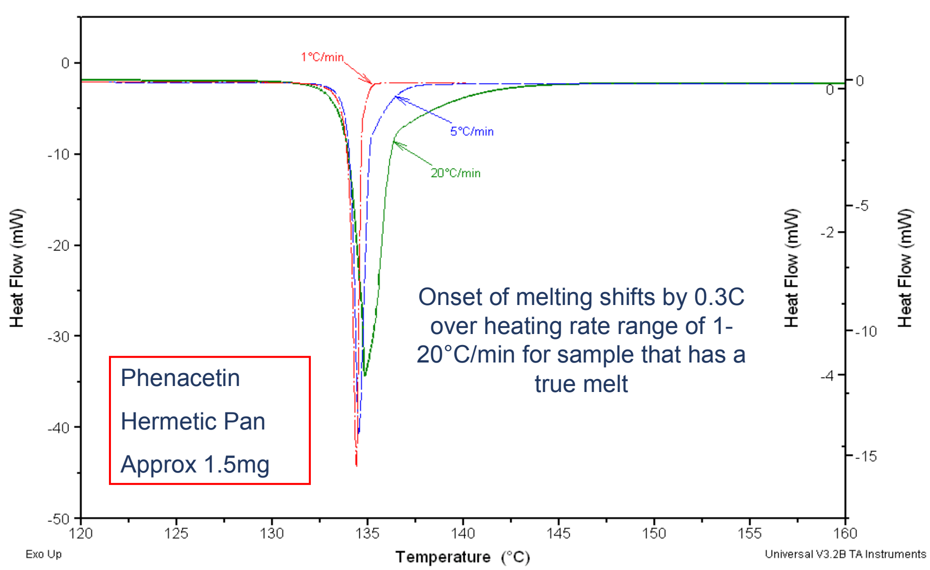
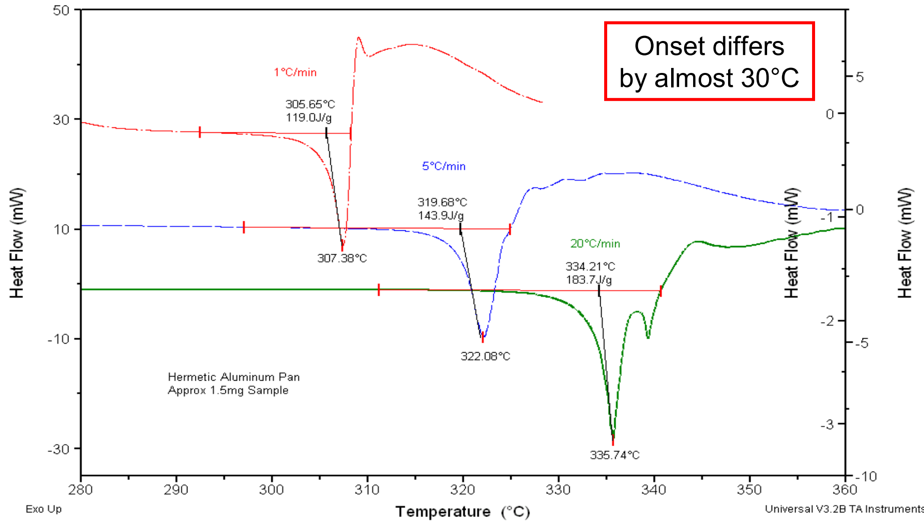
Melting is Not Heating Rate Dependent



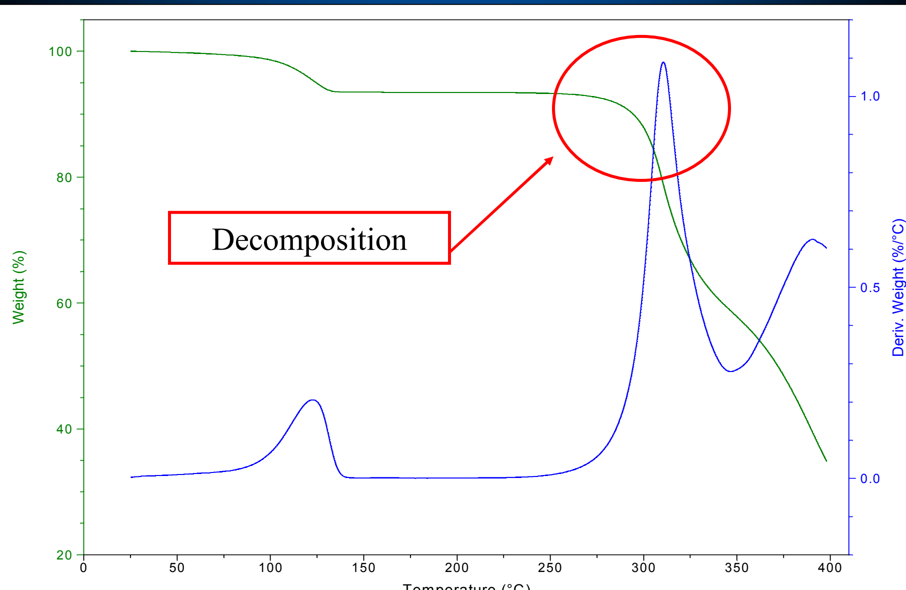
DSC Training Course

Ciprofloxacin Hydrochloride Decomposes

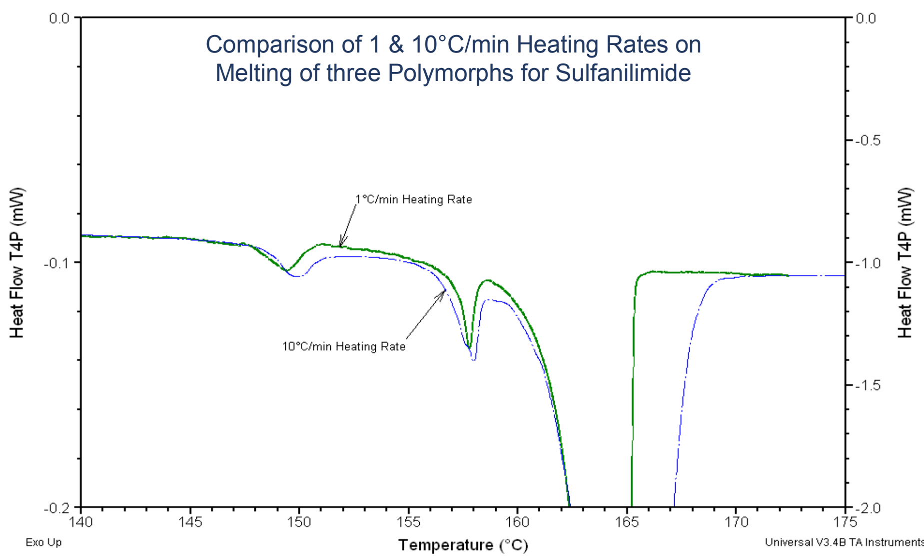
Decomposition is kinetic (heating rate dependent)



TGA of Ciprofloxacin Hydrochloride



Sulfanilimide



DSC Training Course

Specific Heat Capacity

- What is it?
- How is it observed and measured?
- Methods for calculating specific heat capacity
- What affects the specific heat capacity of a polymer?

DSC Training Course

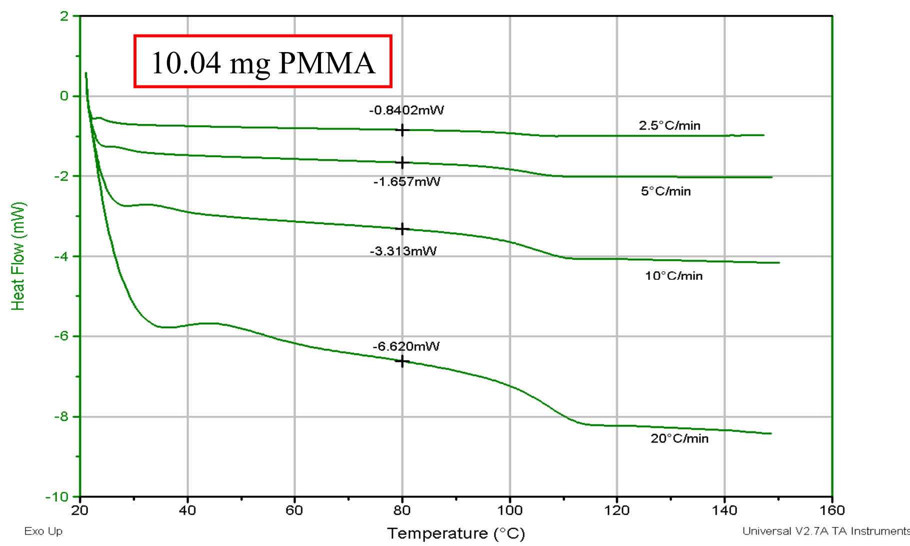
What is Heat Capacity?

- Heat capacity is the amount of heat required to raise or lower the temperature of a material.
- Specific heat capacity refers to a specific mass and temperature change for the material (J/g°C)

Why is Heat Capacity Important?

- Thermodynamic property of material (vs. heat flow)
- Measure of molecular mobility
- Provides useful information about physical properties of the material as a function of temperature

Heat Flow Due to Heat Capacity



Measuring Heat Capacity

- In a DSC experiment, heat capacity is measured as the absolute value of the heat flow, divided by the heating rate, and multiplied by a calibration constant.

$$dH/dt = Cp\,(dT/dt)$$

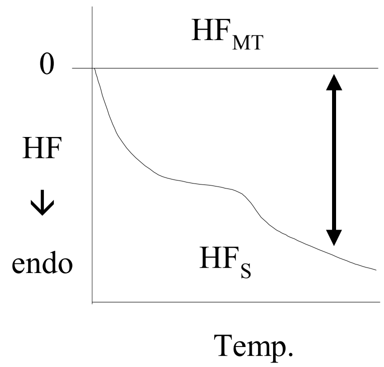
or

$$Cp = [(dH/dt)/(dT/dt)] \times K$$

K = calibration constant

Conventional DSC Cp Measurement

$$Cp = K \times \frac{HF_S - HF_{MT}}{\text{Heat Rate} \times wt}$$



Where:

K = Calibration constant

HF_S = Differential heat flow with sample

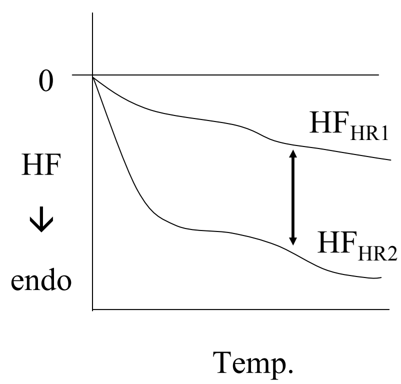
HF_{MT} = Differential heat flow with empty pans

wt = weight of sample

DSC Training Course

Alternative DSC Cp Measurement

$$Cp = K \times \frac{HF_{HR2} - HF_{HR1}}{(HR_2 - HR_1)\, wt}$$



Where:

K = Calibration constant

HF_{HR1} = Differential heat flow of sample at HR_1

HF_{HR2} = Differential heat flow of sample at HR_2

HR_2 = Heating rate 2

HR_1 = Heating rate 1

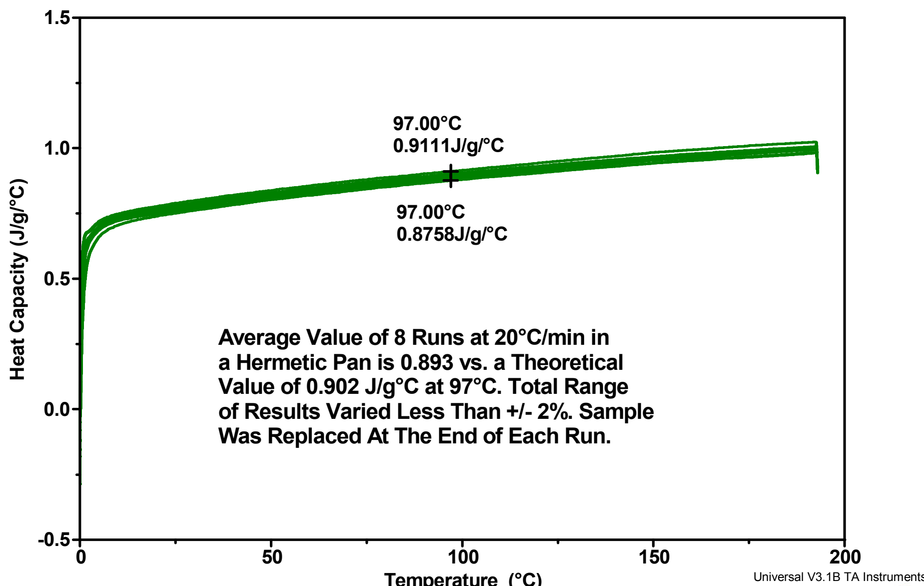
wt = weight of sample

DSC Training Course

Direct CP Measurement on Q2000/1000

- Unlike any other DSC, the heat flow signal of the Q2000/1000 is an absolute signal:
  - Baseline is flat
  - Absolute zero heat flow value established as part of method
- By knowing absolute values of the heat flow and heating rate, heat capacity is calculated in real time and stored in data file
- Accuracy and precision is generally ± 1-2% with just single run measurements

Q1000 Direct Heat Capacity



What Affects the Specific Heat Capacity?

- Amorphous Content
- Aging
- Side Chains
- Polymer Backbone
- Copolymer Composition

- Anything that effects the mobility of the molecules, affects the Heat Capacity

Effect of Amorphous Content on Cp

- Amorphous Cp is greater than Crystalline Cp

- Amorphous Content increases Specific Heat Capacity

- Crystalline polymers contain more order and thus fewer degrees of molecular motion. Less molecular motion results in lower specific heat capacity.

Heat Capacity Summary

- Anything that effects the mobility of the molecules, affects the Heat Capacity
- The Q2000/1000 provides direct Cp measurement with one run(pan weights required)

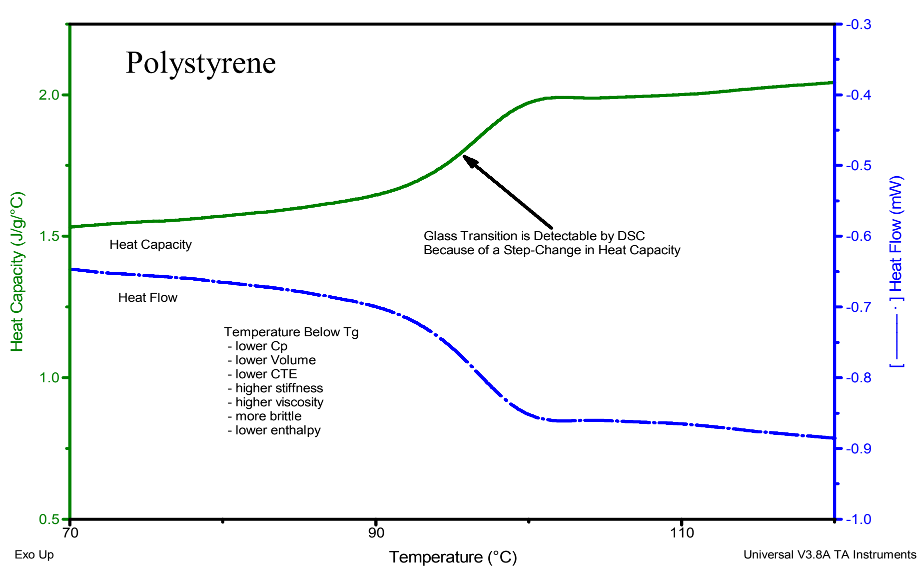
Glass Transitions (Tg)

- The glass transition is a step change in molecular mobility (in the amorphous phase of a sample) that results in a step change in heat capacity
- The material is rigid below the glass transition temperature and rubbery above it.
  - Amorphous materials flow, they do not melt (no DSC melt peak)

Glass Transitions

- The change in heat capacity at the glass transition is a measure of the amount of amorphous phase in the sample
- Enthalpic recovery at the glass transition is a measure of order in the amorphous phase. Annealing or storage at temperatures just below Tg permit development of order as the sample moves towards equilibrium

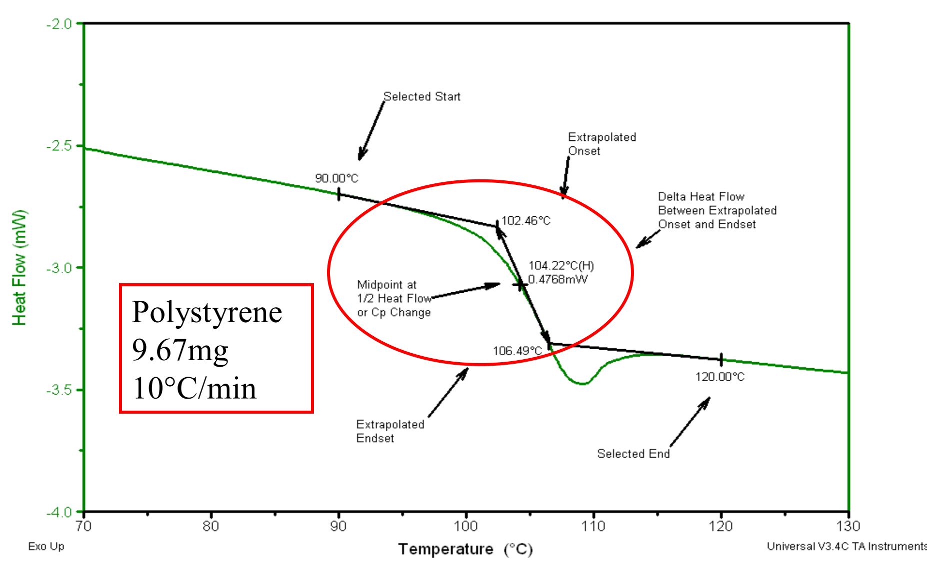
Heat Flow & Heat Capacity at the Tg



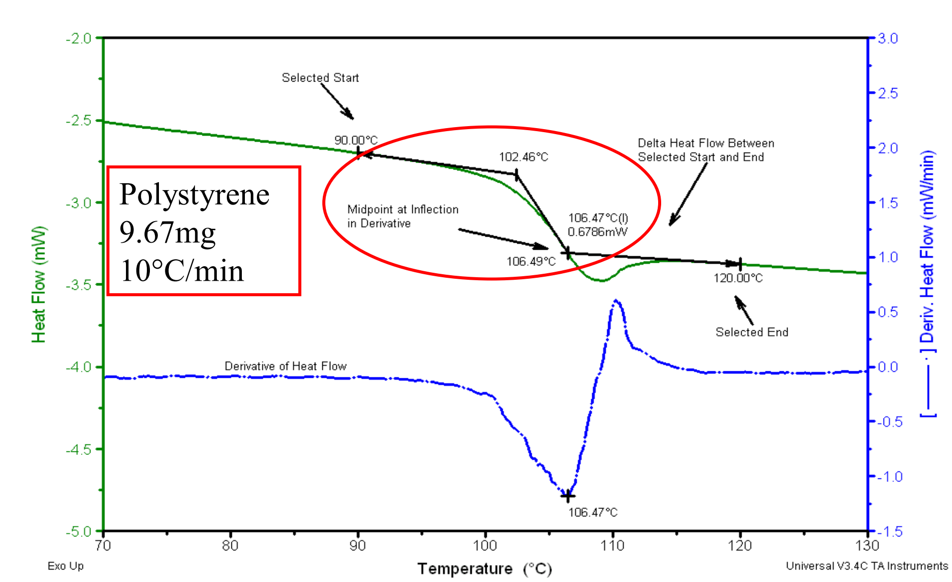
Measuring/Reporting Glass Transitions

- The glass transition is always a temperature range
- The molecular motion associated with the glass transition is time dependent. Therefore, Tg increases when heating rate increases or test frequency (MDSC®, DMA, DEA, etc.) increases.
- When reporting Tg, it is necessary to state the test method (DSC, DMA, etc.), experimental conditions (heating rate, sample size, etc.) and how Tg was determined
  - Midpoint based on ½ Cp or inflection (peak in derivative)

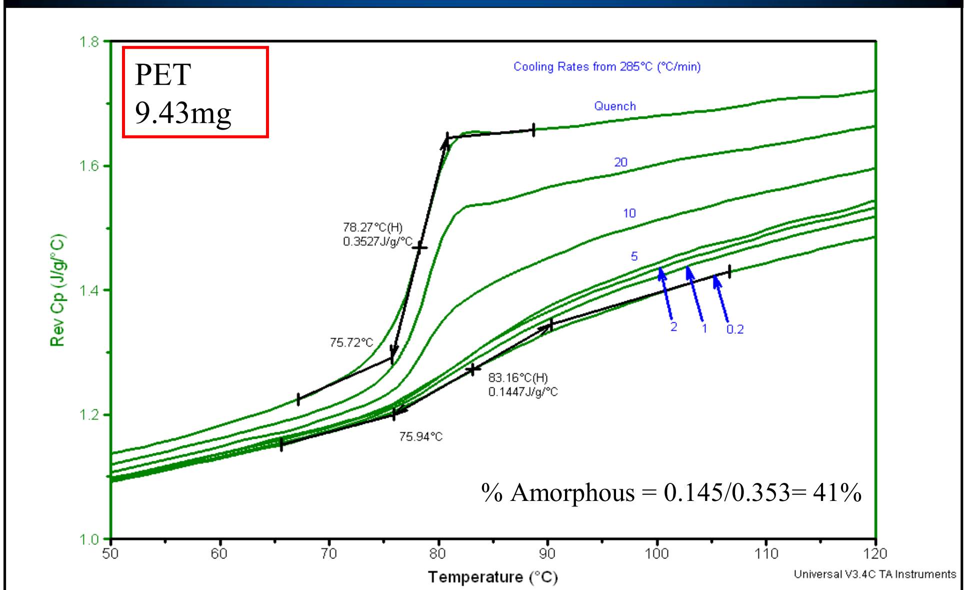
Glass Transition Analysis



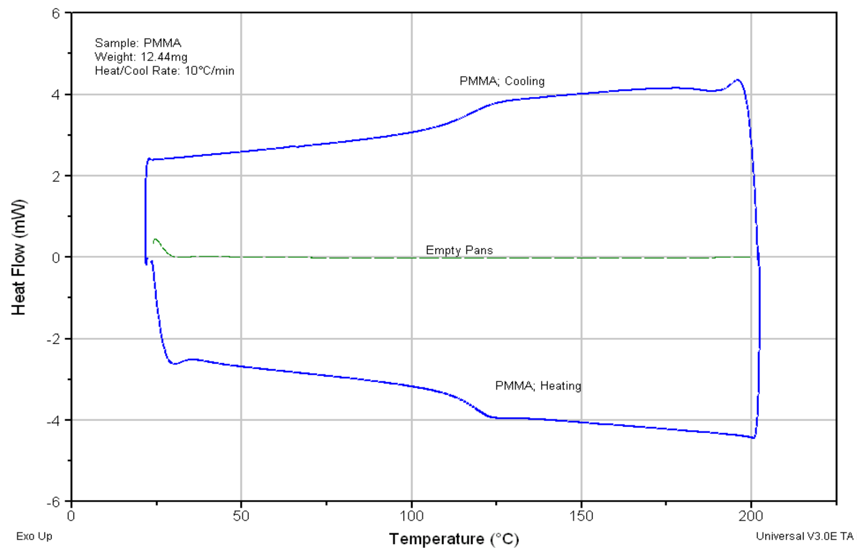
Glass Transition Analysis



Step Change in Cp at the Glass Transition



A Glass Transition is Reversible



What Affects the Glass Transition?

- Heating Rate
- Heating & Cooling
- Aging
- Molecular Weight
- Plasticizer
- Filler
- Crystalline Content
- Copolymers
- Side Chains
- Polymer Backbone
- Hydrogen Bonding

Anything that effects the mobility of the molecules, affects the Heat Capacity and, in turn, the Glass Transition

Suggestions for Finding Weak Tg's

- Know your empty-pan baseline
- Get as much material in the amorphous state
  - Cool rapidly to reduce or eliminate crystallization
- Use MDSC®
- Or use Quasi-Isothermal MDSC

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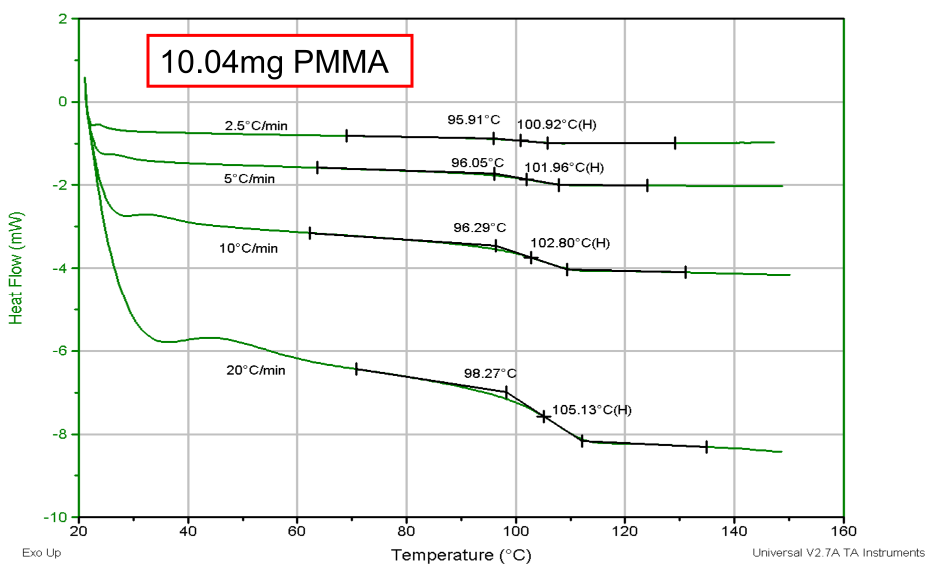
Effect of Heating Rate on the Tg



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Effect of Heating Rate on the Tg

Heating Rate (°C/min)	Heat Flow @ 80°C	Tg Onset (°C)	Tg Midpoint (°C)	½ Width of Tg (°C)
2.5	-0.84	95.9	100.9	5.0
5.0	-1.66	96.0	102.0	6.0
10.0	-3.31	96.3	102.8	6.5
20.0	-6.62	98.3	105.1	6.8

Glass Transition Summary

- The glass transition is due to Amorphous material
- The glass transition is the reversible change from a glassy to rubbery state & vice-versa
- DSC detects glass transitions by a step change in Cp

Melting

- In a DSC, a melt peak shows up as an endotherm during the conversion of Crystalline structure to Amorphous structure
- If a material is 100% Amorphous, we will not see a melting peak by DSC
- We integrate this endothermic peak, on a time basis to determine the Heat of Fusion

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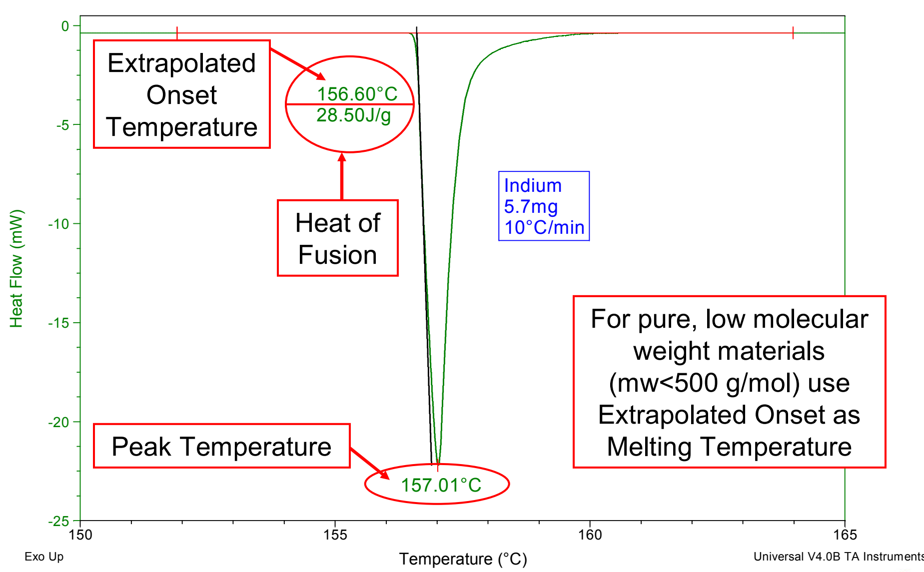
Melting of Indium



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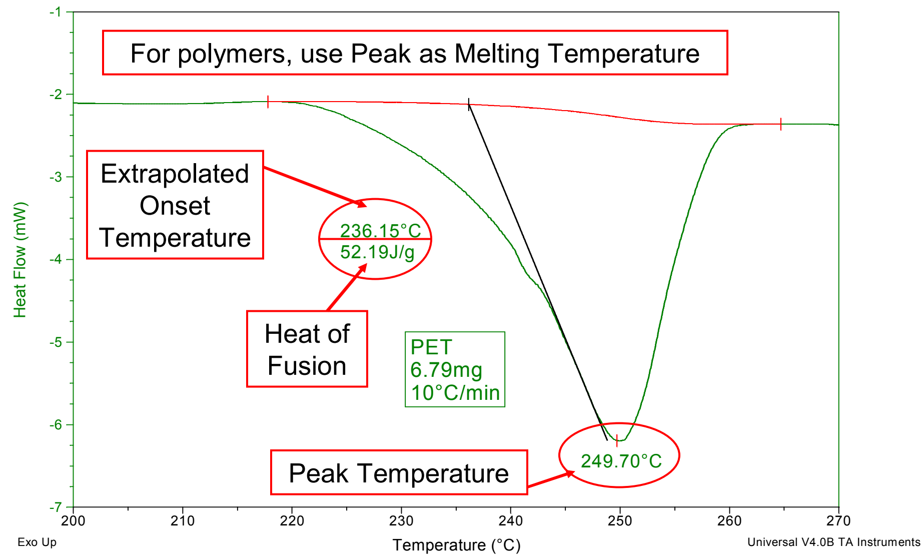
Melting of PET



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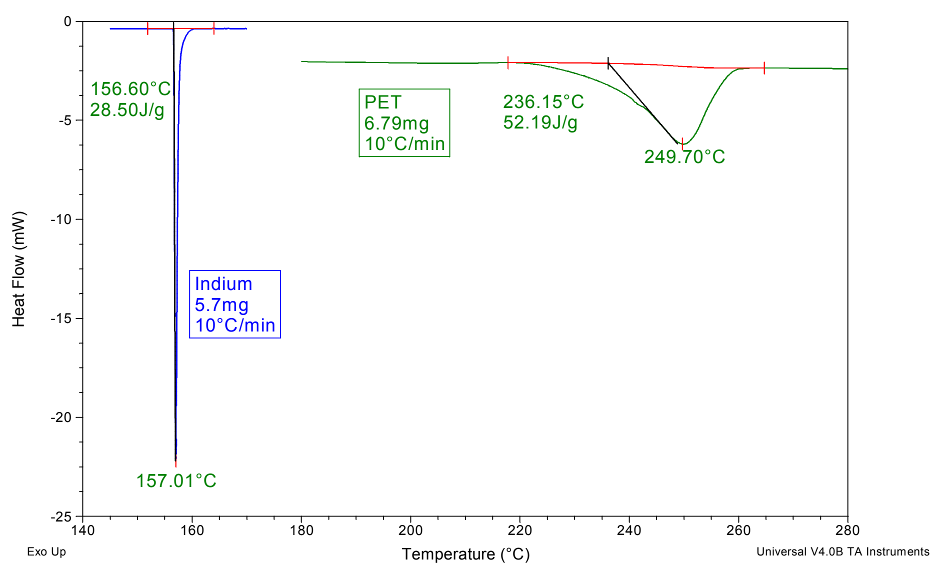
Comparison of Melting



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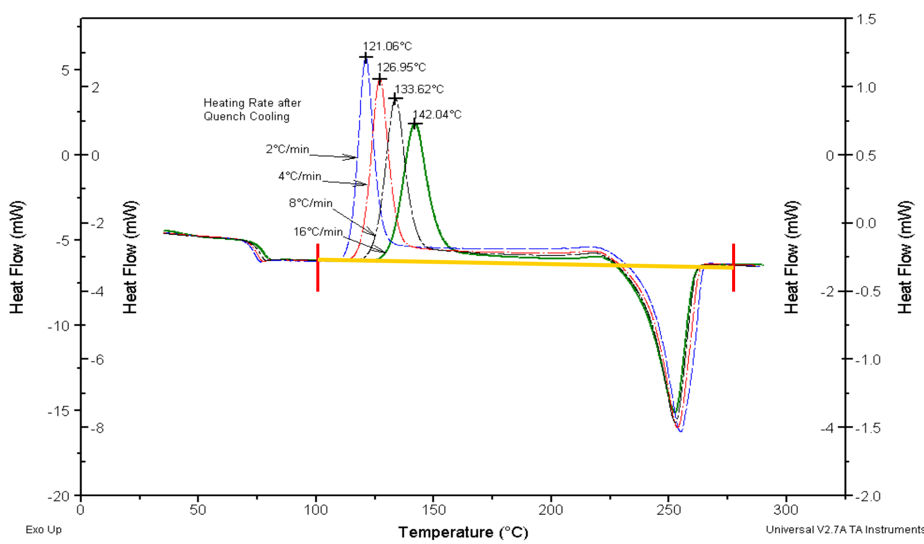
Analyzing/Interpreting Results

- It is often difficult to select limits for integrating melting peaks
  - Integration should occur between two points on the heat capacity baseline
  - Heat capacity baselines for difficult samples can usually be determined by MDSC® or by comparing experiments performed at different heating rates
  - Sharp melting peaks that have a large shift in the heat capacity baseline can be integrated with a sigmoidal baseline

Baseline Due to Cp



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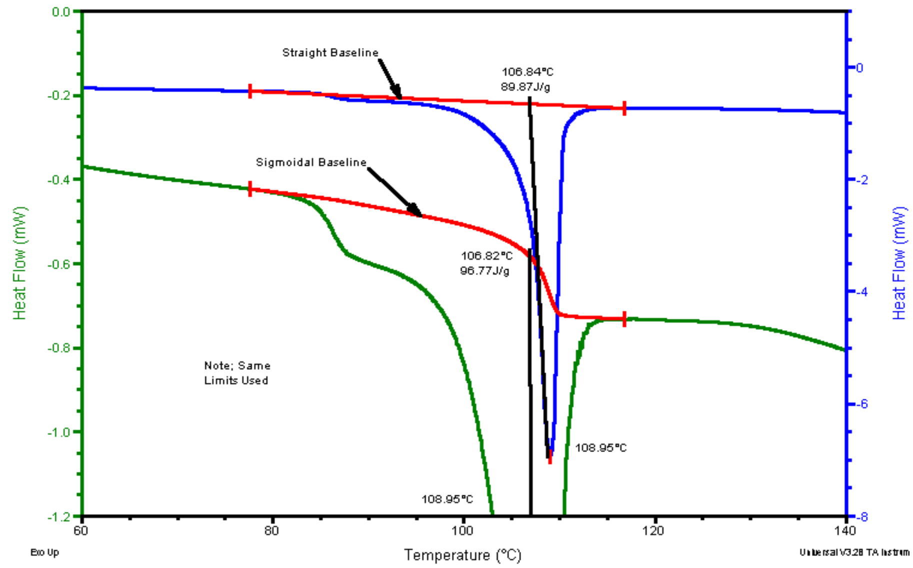
Baseline Type



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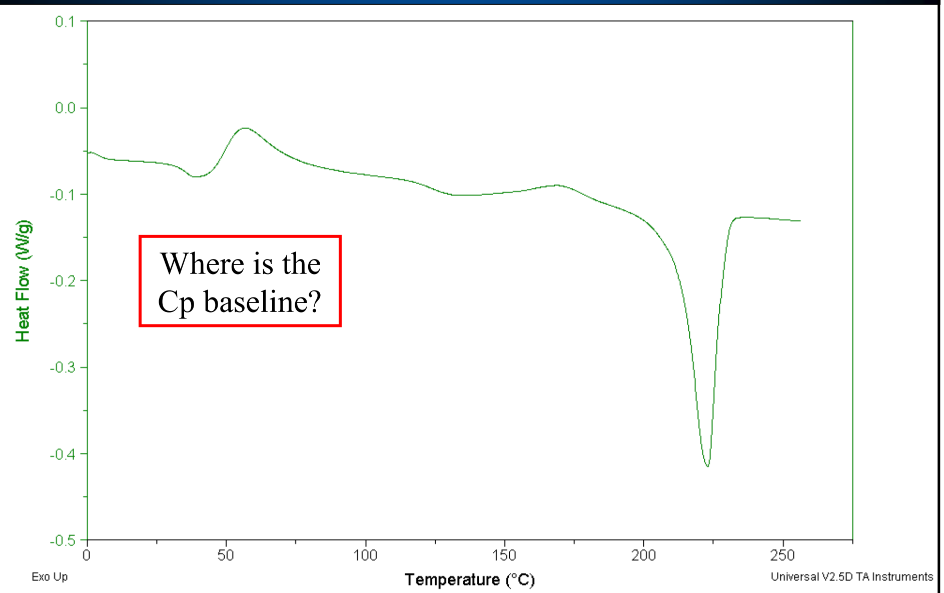
DSC of Polymer Blend



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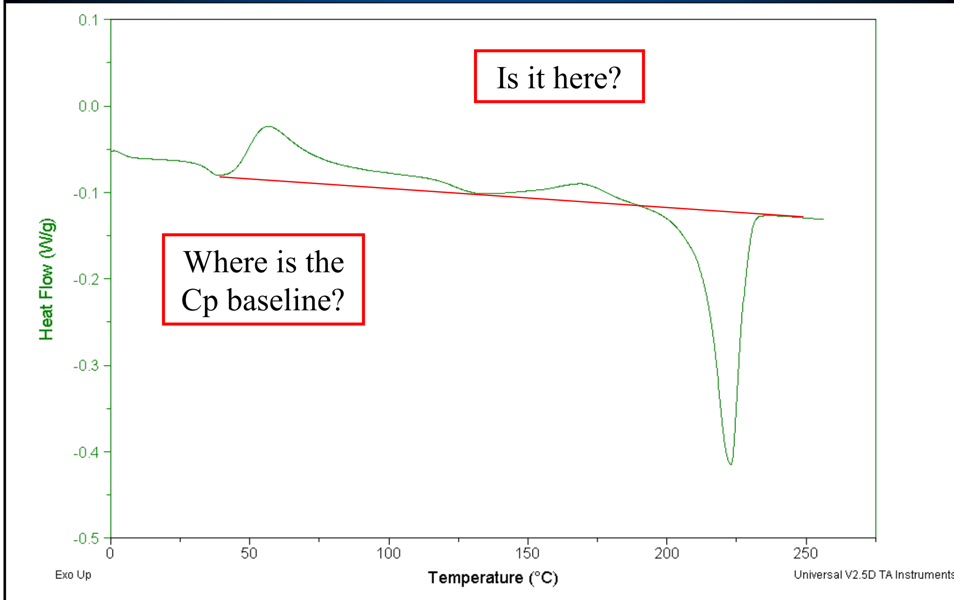
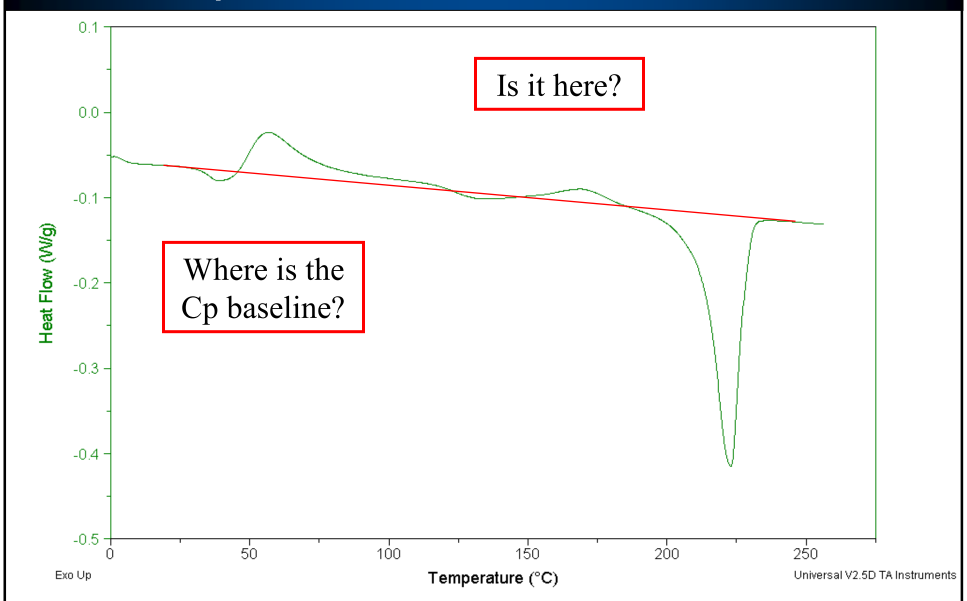
DSC of Polymer Blend



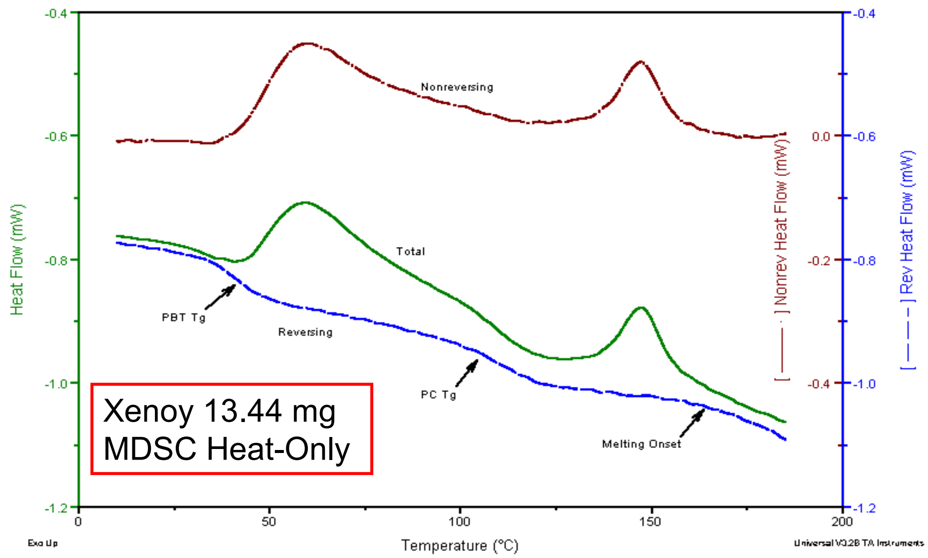
DSC Training Course

DSC of Polymer Blend



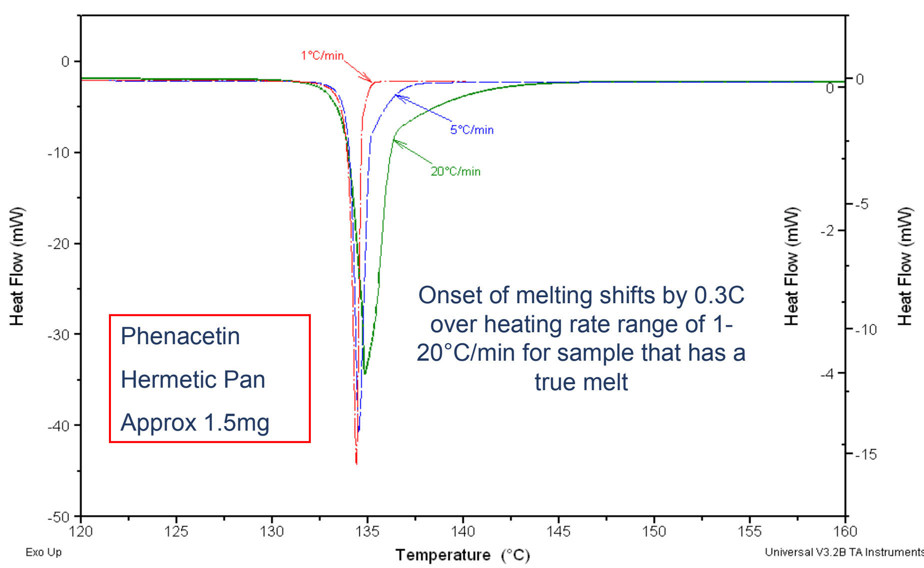
DSC Training Course

MDSC® Aids Interpretation



DSC Training Course

Is this Melting?



DSC Training Course

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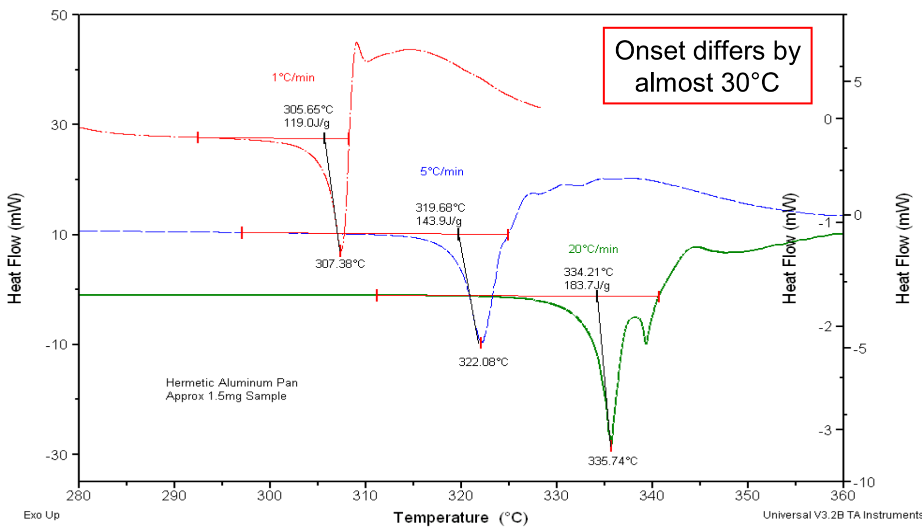

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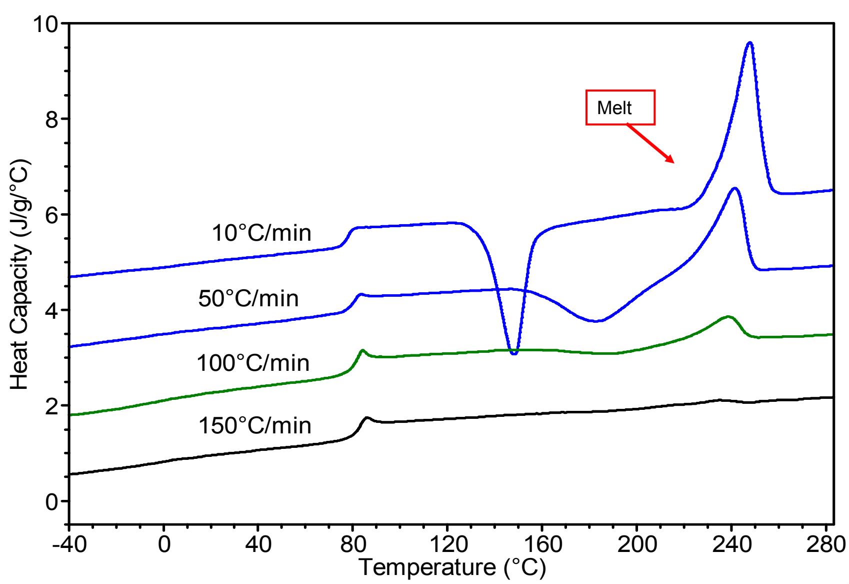
Effect of Heating Rate on Melting



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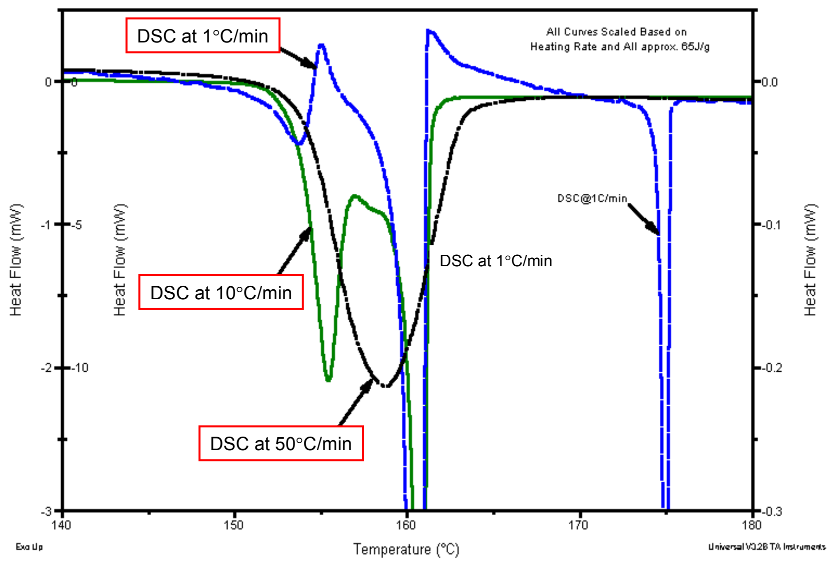
Effect of Heating Rate on Polymorph



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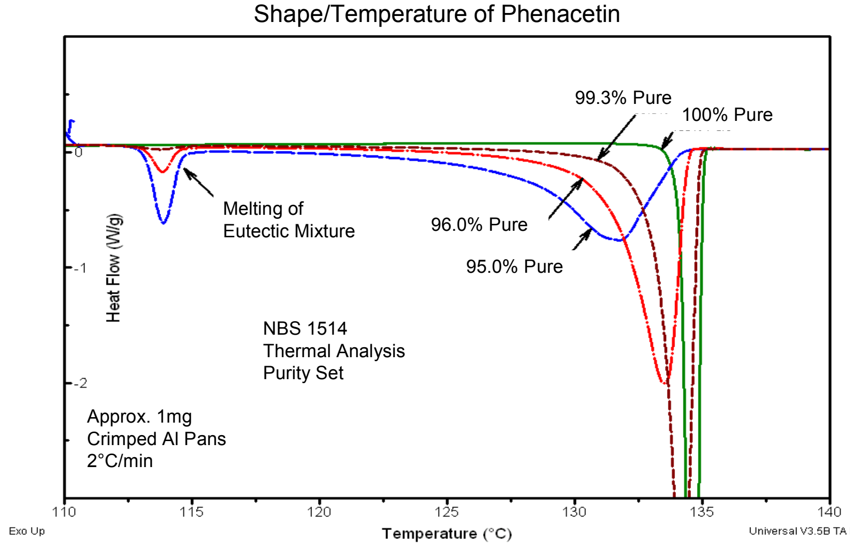
Effect of Impurities on Melting

Effect of p-Aminobenzoic Acid Impurity Concentration on the Melting Shape/Temperature of Phenacetin



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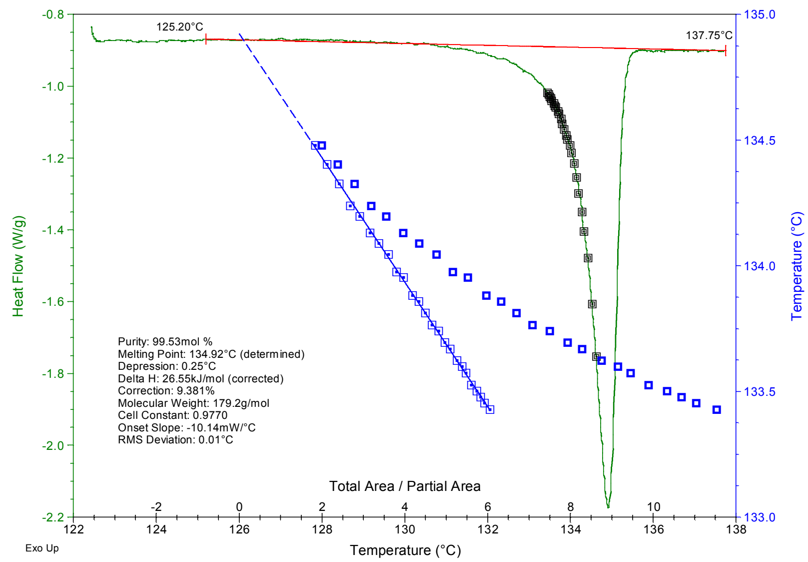
Van't Hoff Purity Calculation



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Calculation of % Crystallinity

- Sample must be pure material, not copolymer or filled
- Must know enthalpy of melting for 100% crystalline material (ΔH_{lit})
- You can use a standard ΔH_{lit} for relative crystallinity

For standard samples:

% crystallinity = 100* ΔH_m / ΔH_{lit}

For samples with cold crystallization:

% crystallinity = 100* (ΔH_m - ΔH_c)/ ΔH_{lit}

DSC Training Course

ATHAS Databank

The Advanced THermal Analysis System

- Home
- About Us
- Research
- Publications
- Teaching
- Sevices and Consulting
- ATHAS DataBank

The ATHAS Data Bank on thermal properties of macromolecules and related substances is maintained and continuously improved.

A Data Bank contains three major parts: (I) A Data Bank of the experimental and calculated heat capacities. (II) Recommended data of thermodynamic properties of macromolecules and related small molecules (C_p, approximate and exact vibrational spectra, *H*, *S*, and *G*). (III) A table of thermal properties (glass and melting temperatures, heats of fusion (if crystallization is possible), and other auxiliary data on molecular motion and phase structure.

The Data Bank is developed as an **integrated system**, available over the Internet from the special ATHAS website already created at Rzeszow University of Technology (http:// *athas.prz.rzeszow.pl/*).

Next

Designed by Mirosław Kaczmarski

The ATHAS Databank is a source for the ΔH_f for common polymers

ATHAS Summary Page for PET

Poly(ethylene terephthalate) (PET)

ΔH_f in kJ/mol

Summary

	Tg	dCp	Tm	dHf	SHG	So	Theta1	Theta3	Ns	Cp
(c)	-	-	553	26.9	X	0	586	54	15	1.0-10
(a)	342	77.8(4+1)	-		X	22	586	44	15	1.0-590
PET	8	8	10,43	10	8,57	33*	30	30	30	8,29

- Explanations

The data are separated into

- Cp Experimental and Calculated -Crystalline
- Cp Experimental and Calculated -Amorphous
- Cp, H,S,G -Crystalline
- Cp, H,S,G -Amorphous
- Cp Figure, H,S,G Figure These are picture files and may need some time to load.
- References

Last revision May 6, 1997 by Marek Pyda
URL : http://funnelweb.utcc.utk.edu/~athas/.../phenylen/pet/pet.html

PET Data from ATHAS

Poly(ethylene terephthalate) (PET)

Crystalline Calculated Data

```
*****************************************************************
*         Advanced   THermal   AnalysiS   Laboratory            *
*                1993  Recommended Data  of                     *
*        Thermodynamic   Properties   of   Macromolecules       *
*****************************************************************

Name :              Poly(ethylene terephthalate)

File Name :         PET

Structure :    O      O
               ||     ||
             (O-C-C6H4-C-O-CH2-CH2-)
```

Calculate g/mole from molecular structure which equals 192 g/mole for PET

< Crystalline >

T	index	Cp	H - H0[C]	S	H0[C] - G
(K)	*	(J/K.mol)	(J/mol)	(J/K.mol)	(J/mol)
0.10	4	0.000	0.00	0.000	0.00
0.20	4	0.000	0.00	0.000	0.00

ATHAS Summary Page for PET

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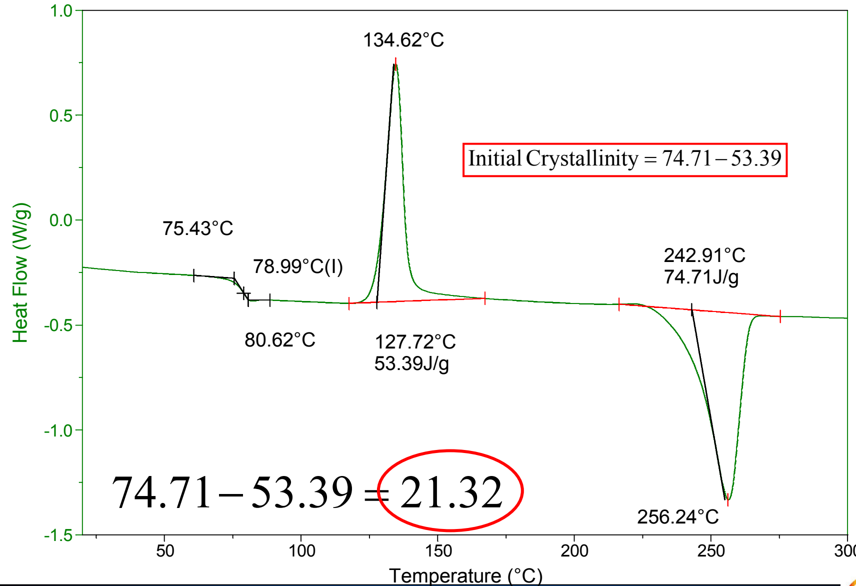
- References

$$\frac{26.9kJ/mol}{192g/mol} \times 1000 = 140J/g$$

PET – Initial Crystallinity



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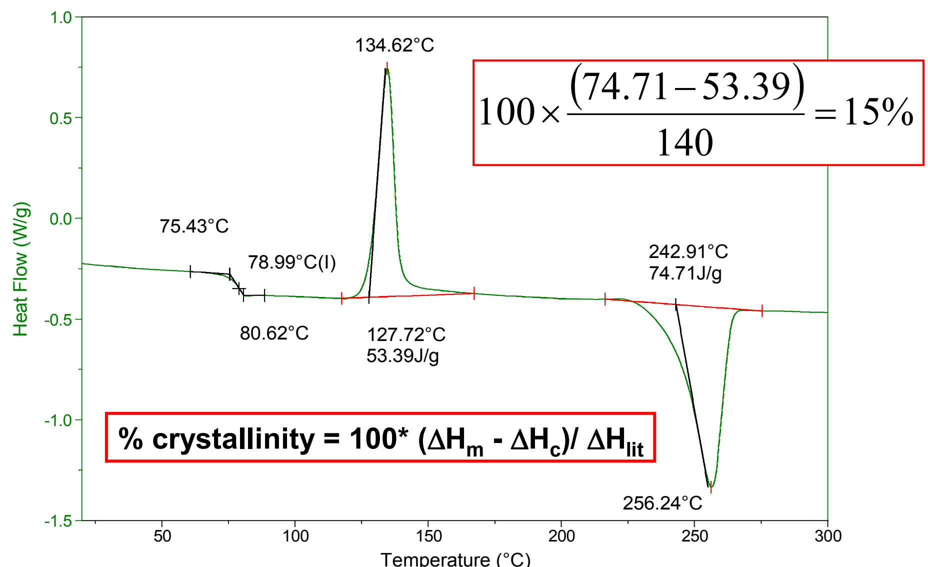
PET



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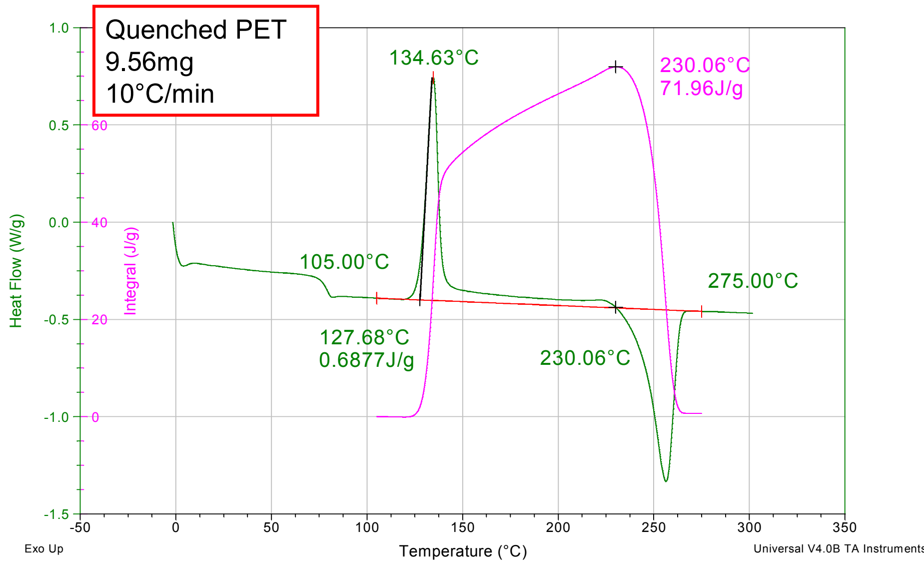
PET % Crystallinity

- 21J/g Initial Crystallinity or 15% Crystalline
  - Does that sound right?

PET % Crystallinity

- 21J/g Initial Crystallinity or 15% Crystalline
  - Does that sound right?
- The sample is quenched cooled PET
- We know that quenched cooled PET is 100% amorphous
- Why does DSC give us the wrong answer?

Change in Crystallinity While Heating



Crystallization

- Crystallization is a kinetic process which can be studied either while cooling or isothermally
- Differences in crystallization temperature or time (at a specific temperature) between samples can affect end-use properties as well as processing conditions
- Isothermal crystallization is the most sensitive way to identify differences in crystallization rates

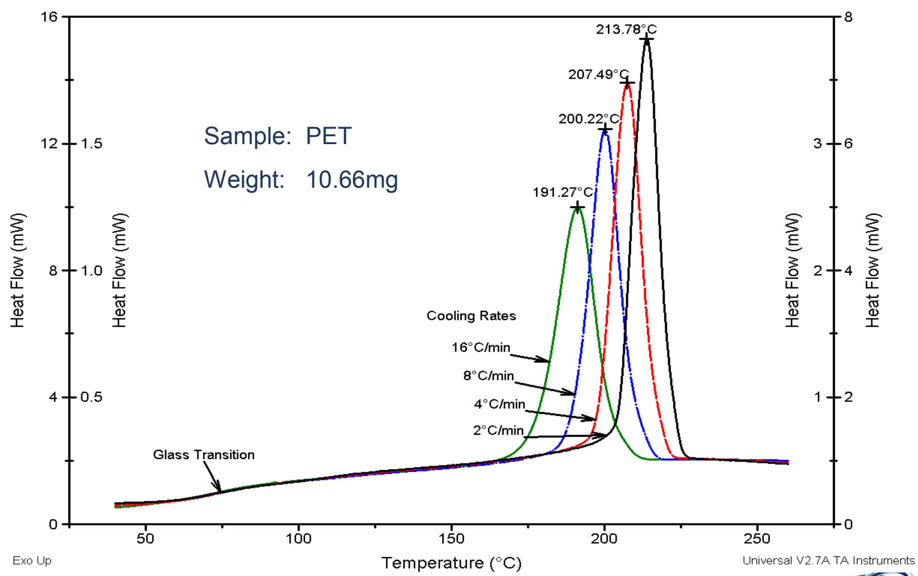
Crystallization

- Crystallization is a two step process:
  - Nucleation
  - Growth
- The onset temperature is the nucleation (T_n)
- The peak maximum is the crystallization temperature (T_c)

Crystallization

- A temperature shift is seen in the cooling data on the next slide. In this example, the samples were cooled from 285°C to room temperature at 2 to 16°C/min. The higher rates of temperature change broaden the crystallization process and shift it further in temperature from the starting point.

Effect of Cooling Rate on Crystallization



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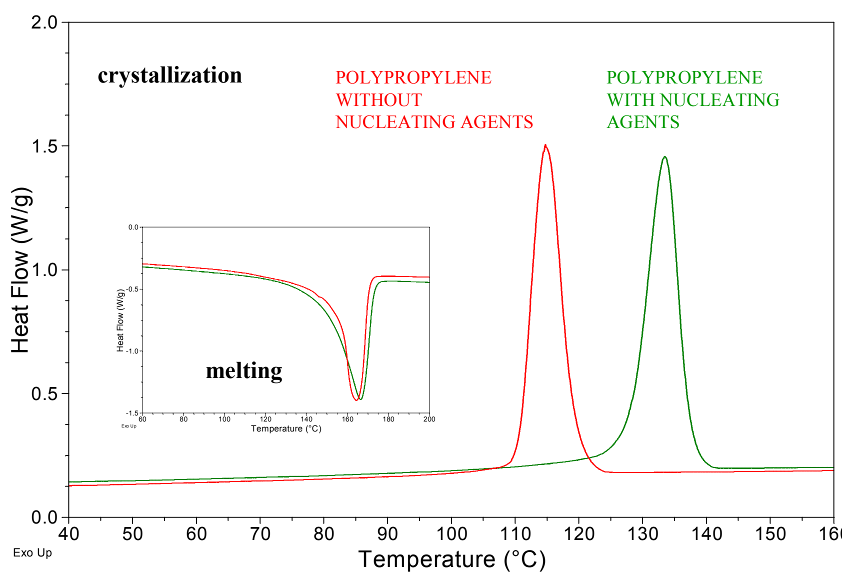
Effect of Nucleating Agents



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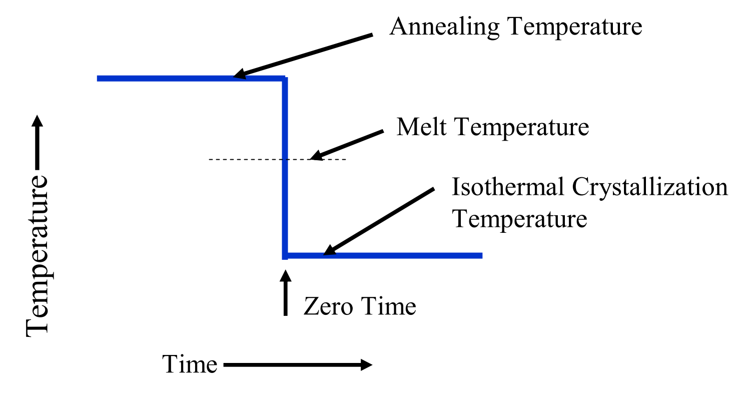
What is Isothermal Crystallization?

- A Time-To-Event Experiment



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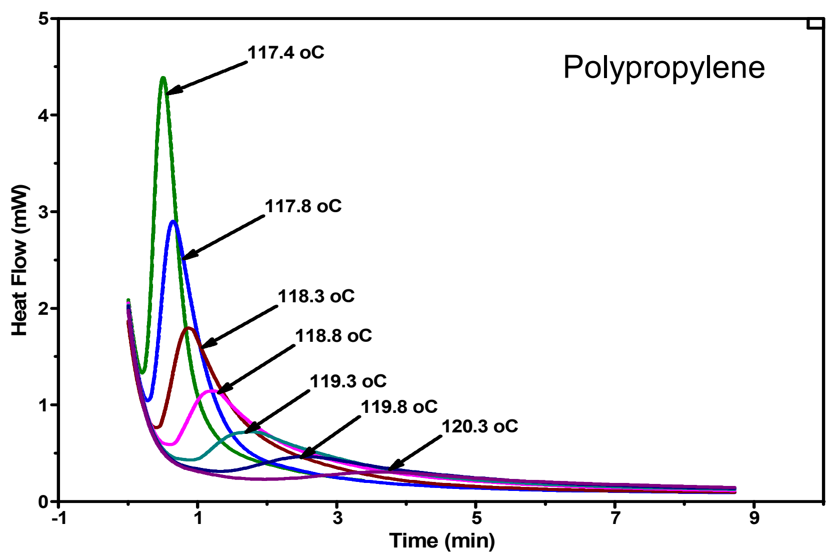
Isothermal Crystallization



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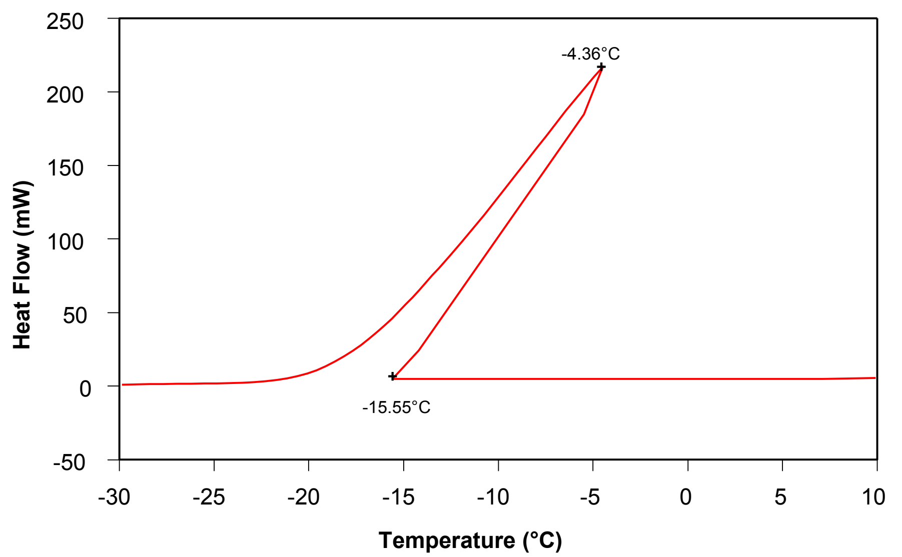
Supercooling of Water



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