DSC & Modulated DSC (MDSC®)
Theory and Applications Online Courses

Part 1: Theory & Instrumentation

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Differential Scanning Calorimetry
(DSC)

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Agenda

- Understanding DSC and MDSC techniques
  - How heat flow is measured on a DSC
  - When and why it is important to use MDSC
  - How MDSC heat flow signals are calculated
- Calibration & Verification
- Instrument & Method Considerations
  - Purge Gas
  - Cooling Accessories
  - Sample Pans & Sample Preparation
  - DSC Cell Cleaning
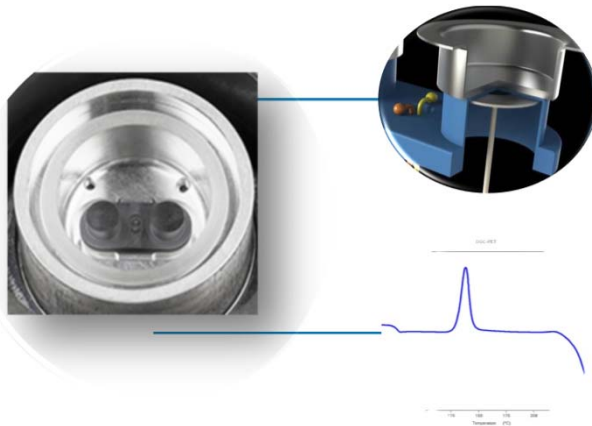 - Experimental Setup and Method Development

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What is a Differential Scanning Calorimetry

- A DSC measures the difference in Heat Flow Rate between a sample and inert reference as a function of time and temperature
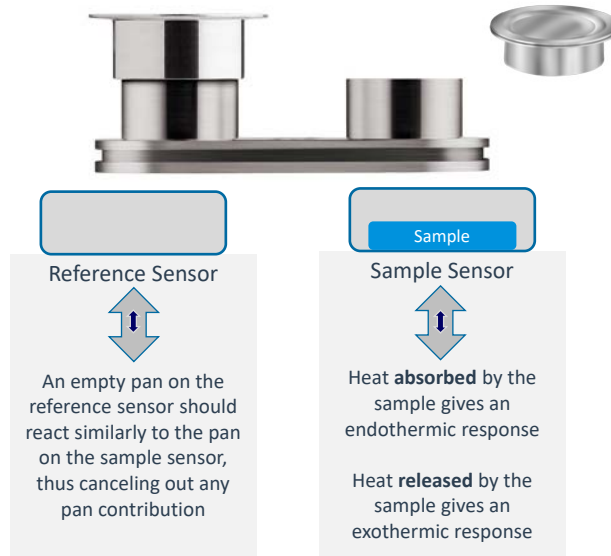
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Simple Heat Flux DSC Cell Schematic

Reference Sensor

Sample Sensor

Sample

An empty pan on the reference sensor should react similarly to the pan on the sample sensor, thus canceling out any pan contribution

Heat **absorbed** by the sample gives an endothermic response

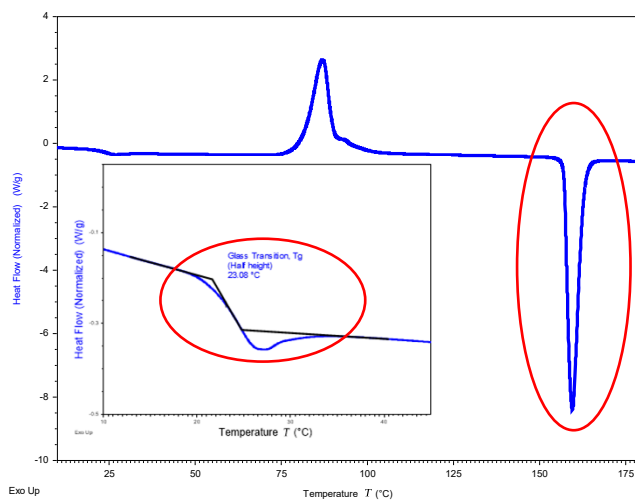Heat **released** by the sample gives an exothermic response

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Endothermic Heat Flow – Heat Absorbed by Sample
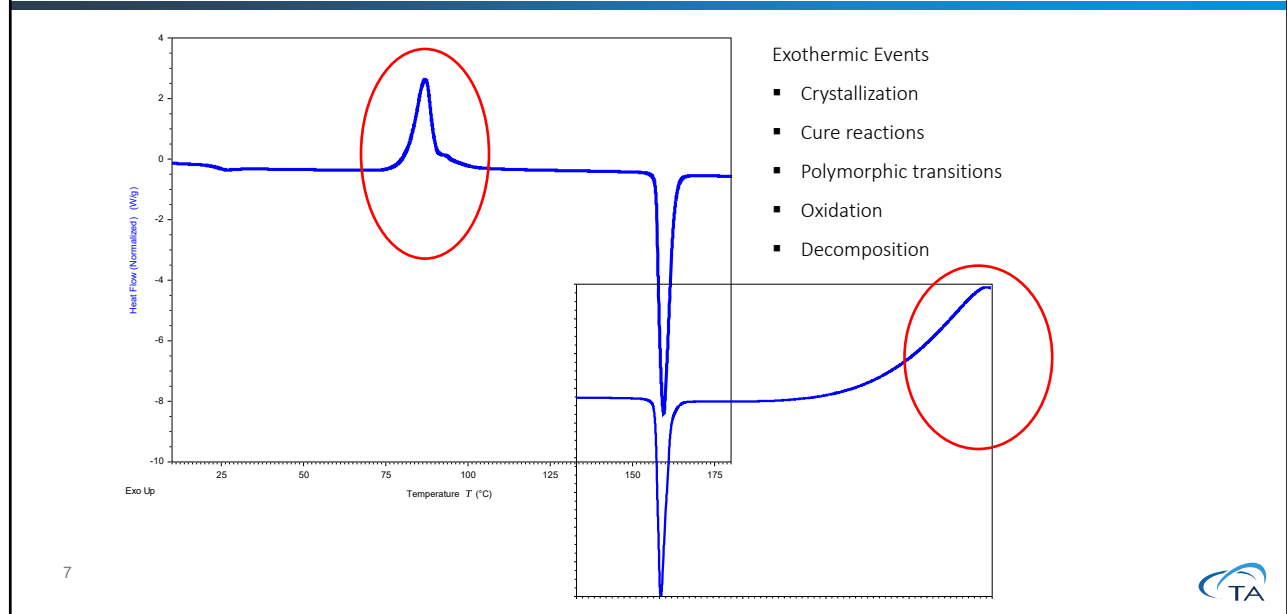

Endothermic Events

- Glass transition
- Melting
- Evaporation/ volatilization
- Enthalpic recovery
- Polymorphic transitions
- Some decompositions

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Exothermic Heat Flow – Heat Released by Sample

Exothermic Events

- Crystallization
- Cure reactions
- Polymorphic transitions
- Oxidation
- Decomposition

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DSC Heat Flow Equation

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

$$(\text{mW or } \frac{mJ}{s})$$

$$Cp = \text{Sample Heat Capacity}$$
$$= \text{Sample Specific Heat x Sample Weight}$$

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

$$\frac{dT}{dt} = \text{Heating Rate (°C/min)}$$

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

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DSC Heat Flow

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

Heat Capacity

Glass Transition
Some Melting

Kinetic

Crystallization
Some melting
Cure reactions
Volatilization
Decomposition
Denaturation

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TA

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What DSC Can Tell You

- Identification of amorphous & crystalline material
- Identification of phase transitions and changes of state
- Specific Heat Capacity – measure of molecular mobility
- Heats of fusion & reactions
- Oxidative/Thermal Stability
- Reaction Kinetics

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TA

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Modulated DSC® Theory
(MDSC®)

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What is MDSC?

- MDSC separates the Total heat flow of DSC into two parts based on the response of the system to a changing heating rate. The changing heating rate is effected by 'superimposing' a sinusoidal heating rate on a linear heating rate.

- In general, only heat capacity and melting respond to the changing heating rate resulting in an increase in signal. Kinetic events tend to occur at different temperatures as a function of heating rate. For example, increasing the heating rate can shift decomposition to a higher temperature.

- The Reversing and Nonreversing signals of MDSC are not necessarily a measure of reversible and nonreversible properties.

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MDSC® Theory: Heat Flow Signals

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

Total Heat Flow

Reversing Heat Flow

Non-Reversing Heat Flow

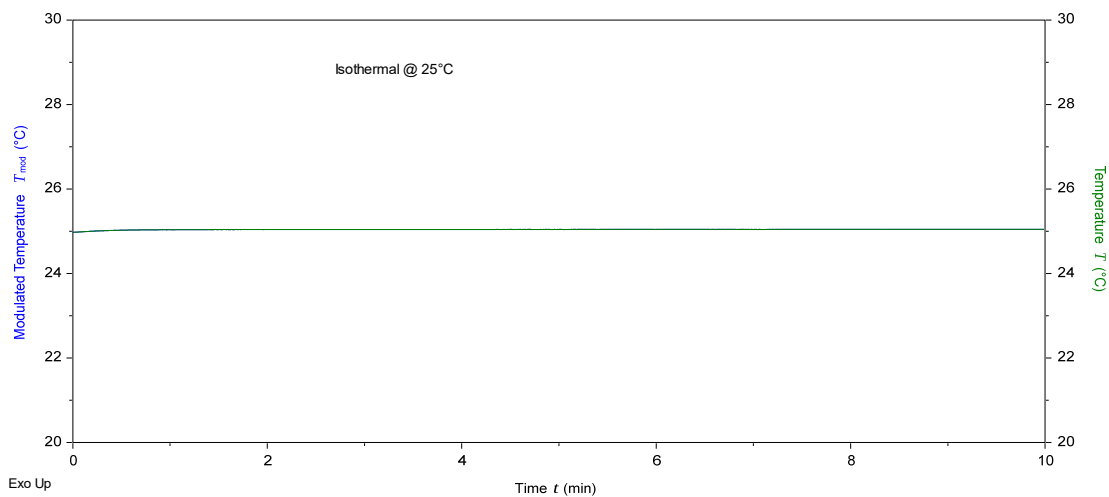•All Transitions

•Heat Capacity
•Glass Transition
•Melting

•Enthalpic Recovery
•Evaporation
•Crystallization
•Thermoset Cure
•Denaturation
•Decomposition
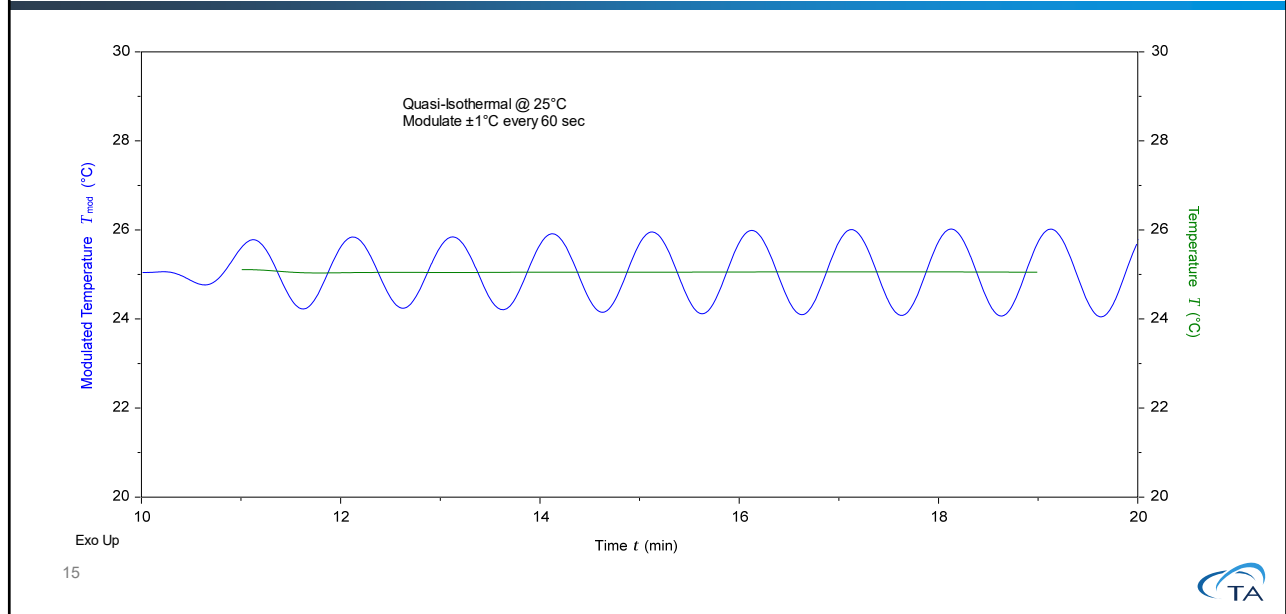•Some Melting
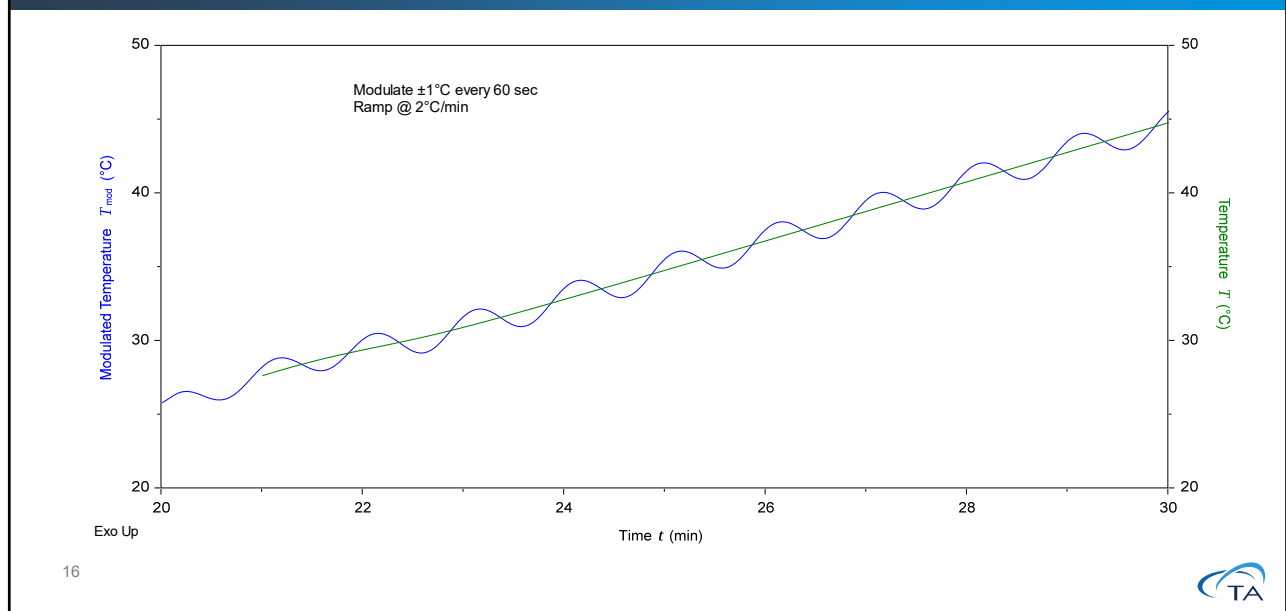•Chemical Reactions

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Isothermal @ 25°C

Isothermal @ 25°C

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MDSC - Quasi-Isothermal @ 25°C

Quasi-Isothermal @ 25°C
Modulate ±1°C every 60 sec

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MDSC – 1°C amplitude, every 60 sec, @ 2°C/min

Modulate ±1°C every 60 sec
Ramp @ 2°C/min

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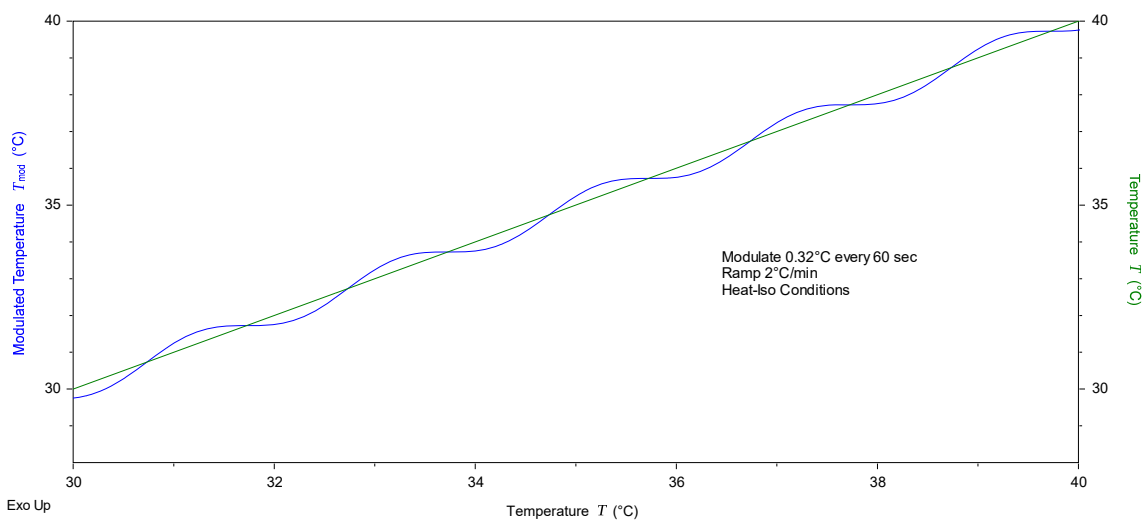# MDSC® Theory: Calculation of MDSC® Signals

- All MDSC signals are calculated from three measured signals.
  - Time
  - Modulated Temperature and by implication Modulated Heating Rate
  - Modulated Heat Flow
- During the setup of the MDSC experiment, the user enters the following parameters:
  - Average (or underlying) heating rate (°C/min)
  - Temperature modulation period (seconds)
  - Temperature modulation amplitude (°C)

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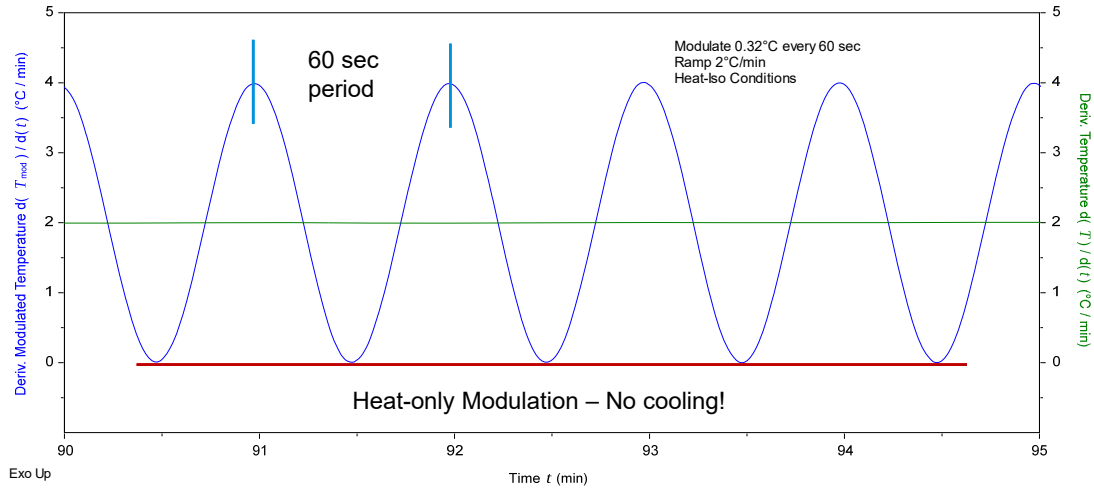# Average & Modulated Temperature

Modulate 0.32°C every 60 sec
Ramp 2°C/min
Heat-Iso Conditions

Exo Up

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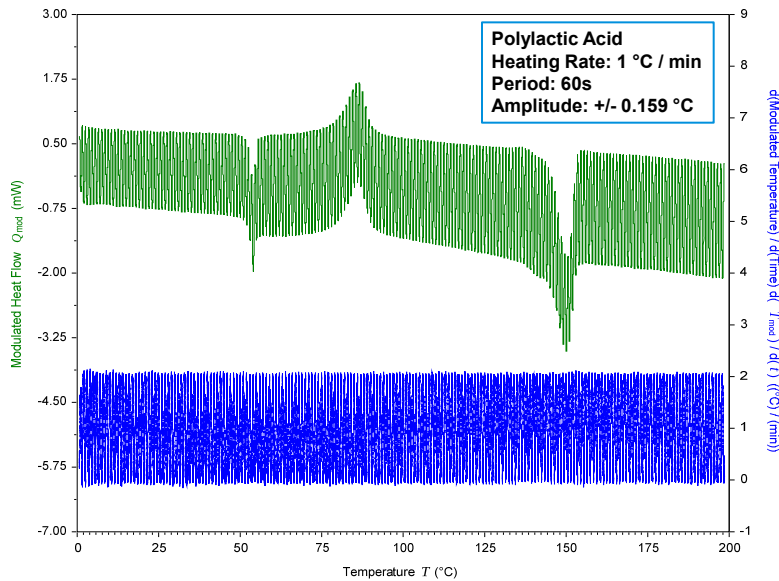## Average and Modulated Heating Rate

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MDSC® Raw Data Signals

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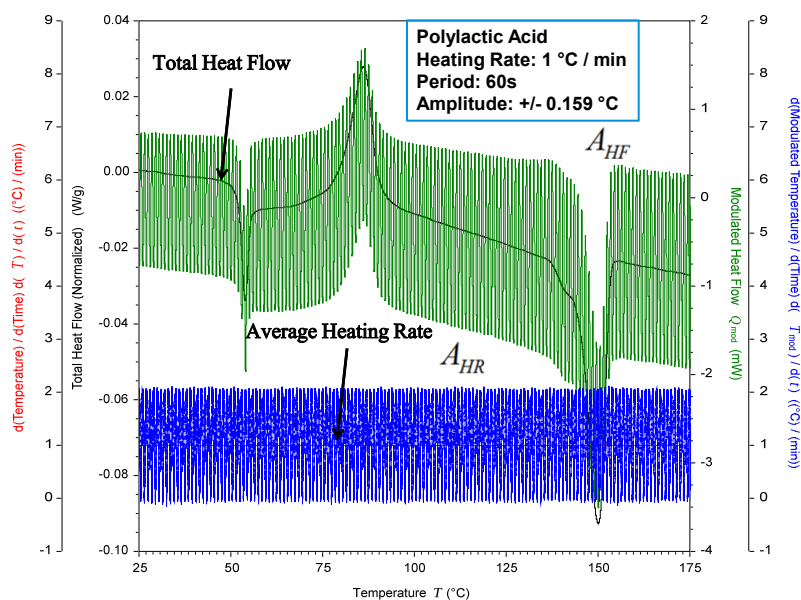## MDSC Theory: Calculation of MDSC® Signals – Simple Deconvolution

- Raw data is averaged over a period of 1 oscillation and the average is subtracted from the raw data.

- Modulation is analyzed using a Fourier Transform which yields the amplitude of the heat flow response at the modulation frequency.

- This results in the following:

    – *<dQ/dt>* = average heat flow; Q = heat

    – A_{HF}= Amplitude of heat flow modulation

    – A_{HR} = Amplitude of modulated heating rate

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MDSC® Raw Data Signals: Modulated Heat Flow and Modulated Heating Rate with Calculated Total (or Average) Heat Flow and Average Heating Rate
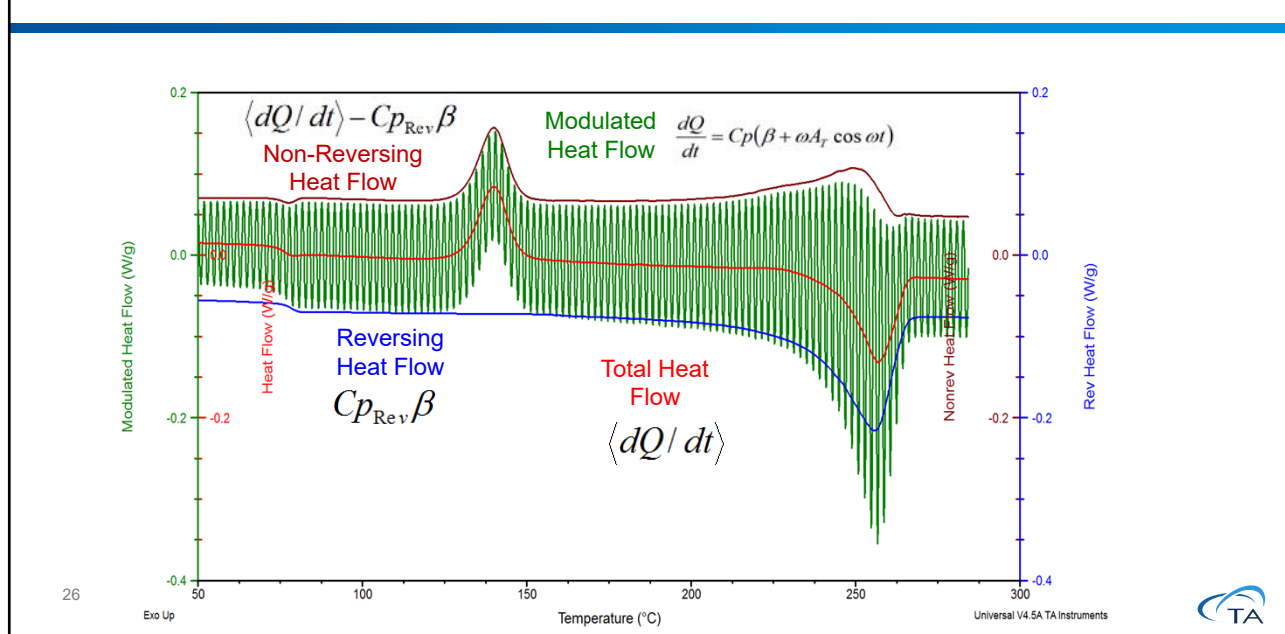

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MDSC® Theory: Calculation of MDSC® Reversing Heat Flow and Reversing *Cp*
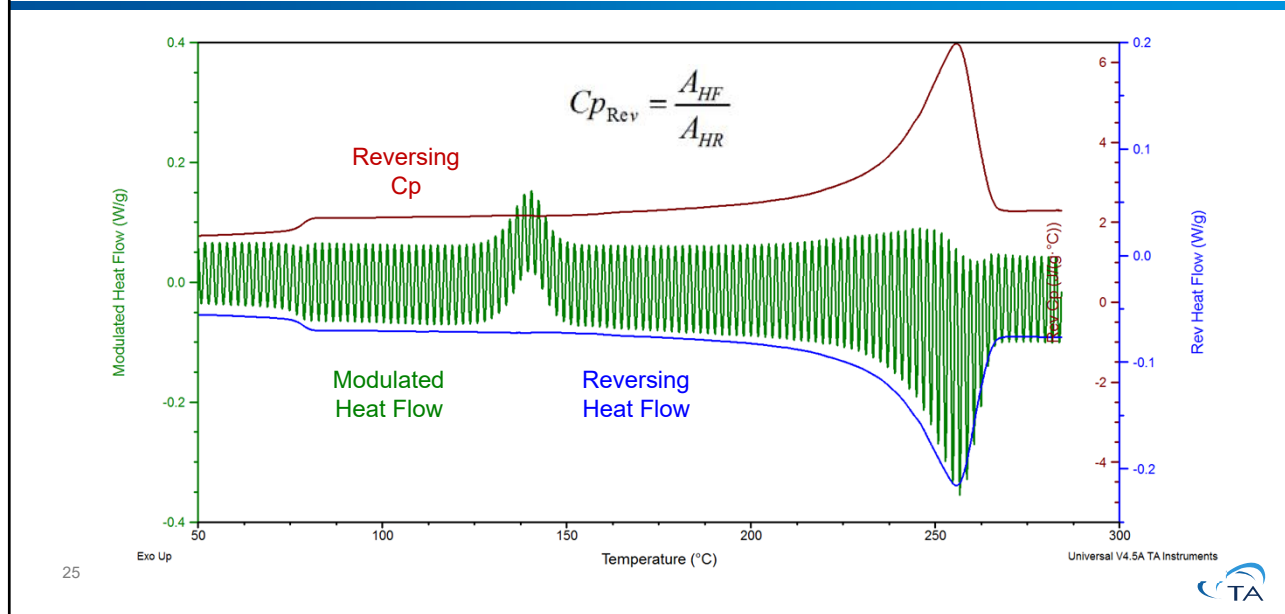
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MDSC® Theory: Calculated MDSC® Heat Flow Signals Summary

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Modulated DSC® (MDSC®)

When and Why to Use MDSC

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When & Why to Use MDSC?

- Run a conventional DSC experiment @ 10°C/min first
  - It may provide all the information you need
- Reasons to run MDSC:
  - Identify heat capacity and kinetic transitions
  - Separate overlapping thermal transitions
  - Detect weak glass transitions
  - Most accurate determination of polymer crystallinity
  - Accurate measurement of heat capacity in a single experiment
  - Gain insight into structural change
  - And many others…
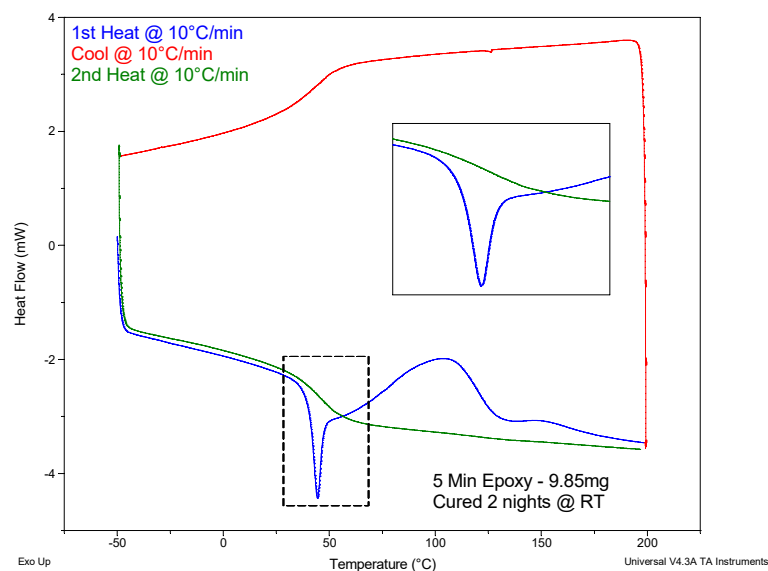
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When & Why to Run MDSC® – Amorphous Materials

- If you're looking for a Tg –
  - If the Tg is detectable and can be routinely analyzed, then you may not need to use MDSC
  - However, if the Tg is hard to detect, or has a large enthalpic recovery, then run MDSC

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Epoxy Cured 48 Hours: Heat Cool Heat

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Rev-Heat Flow Easily Shows Tg
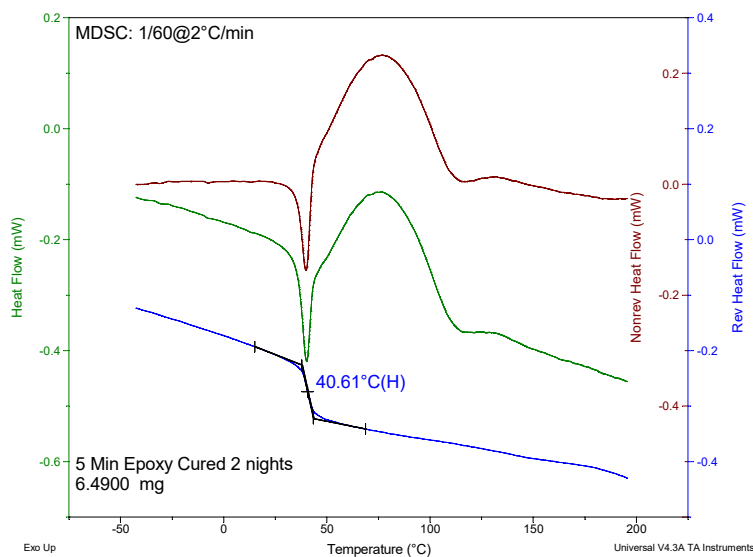
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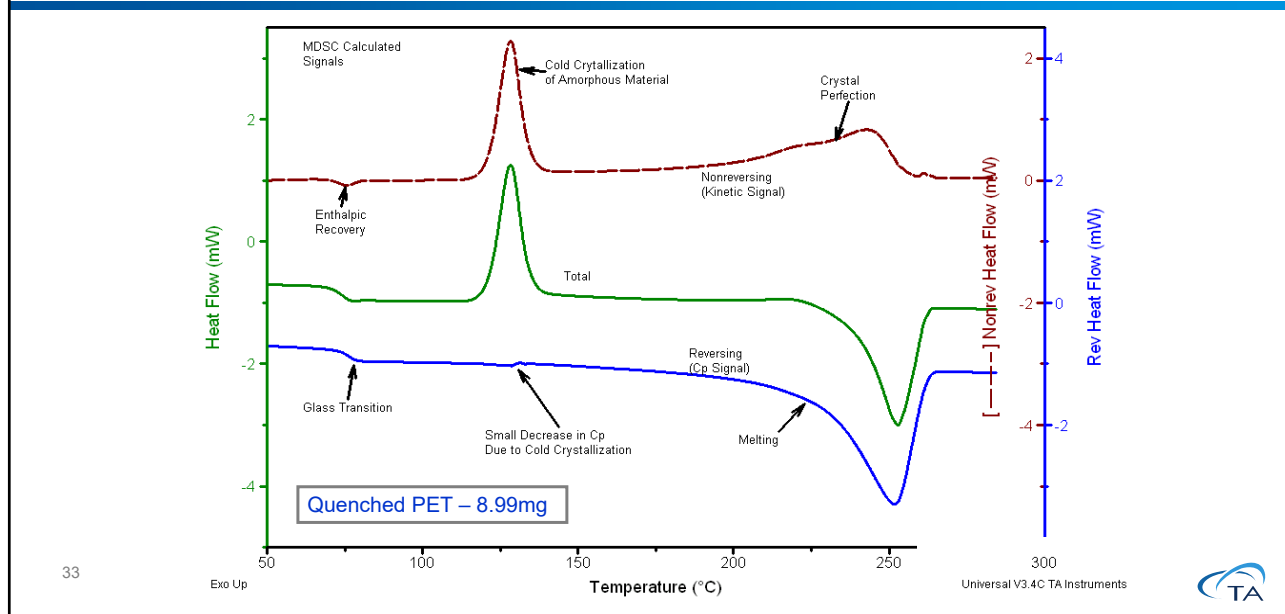## When & Why to Run MDSC®: Crystalline Materials

- If you are studying polymer melting and crystallization
  - If the melting process appears normal (single endothermic peak) and there is no *apparent* crystallization of the sample as it is heated, then there **may** be no need to use MDSC
  - However, if melt is not straightforward, or crystallization may be occurring as the sample is heated, use MDSC

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Calculated MDSC Heat Flow Signals

MDSC Calculated Signals

Cold Crytallization of Amorphous Material

Crystal Perfection

Nonreversing (Kinetic Signal)

Enthalpic Recovery

Total

Reversing (Cp Signal)

Glass Transition

Small Decrease in Cp Due to Cold Crystallization

Melting

Quenched PET – 8.99mg

Exo Up

Universal V3.4C TA Instruments

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DSC of Complex Polymer Blend

Xenoy is a blend of PBT & PC

DSC@10C/min; How Would You Interpret The Data?

**Quenched Xenoy
13.44mg
DSC @ 10°C/min**
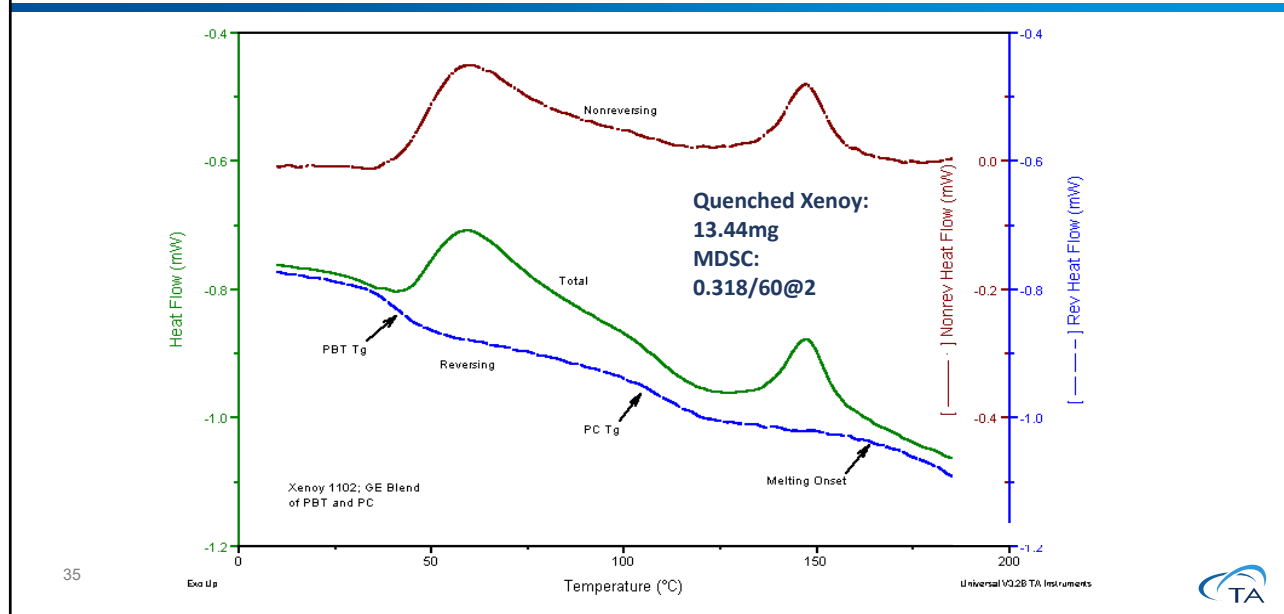
Exo Up
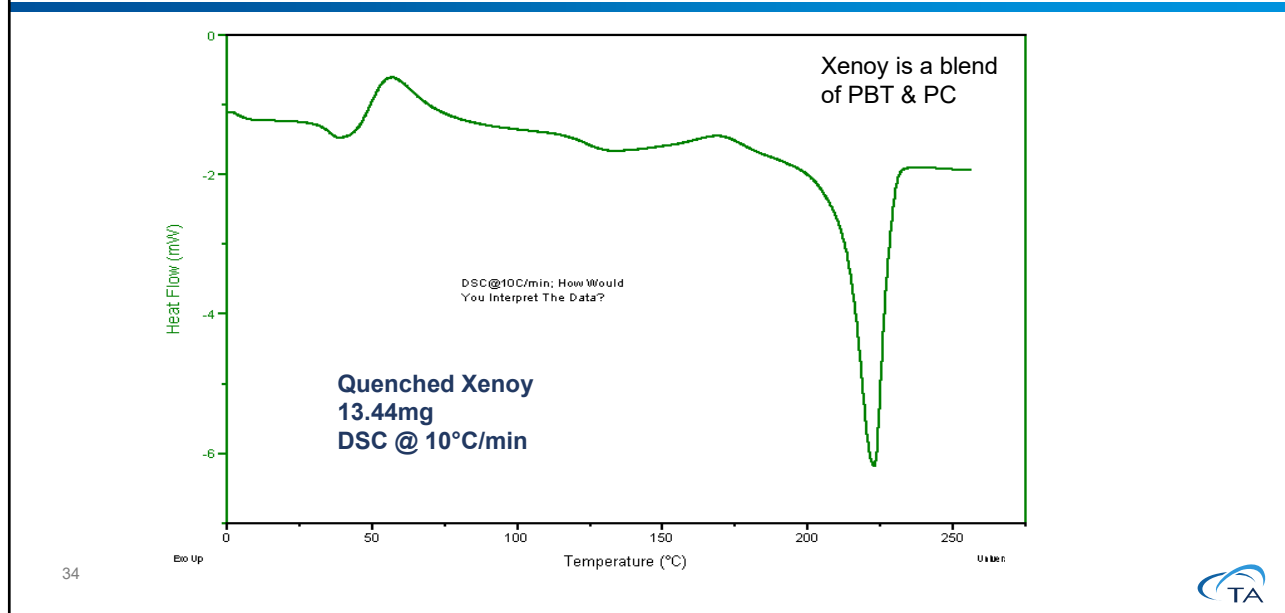
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MDSC® of Complex Polymer Blend

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When & Why to Run MDSC®: Heat Capacity measurements

- If you want to measure accurate heat capacity (Cp), or the change in Cp as a function of time at an isothermal temperature – run MDSC

- Modulated DSC offers two methods for obtaining heat capacity
  - Dynamic Ramp: Use the 'Reversing Heat Capacity' signal, after obtaining a KCp value.
  - Quasi Isothermal: Very simple and accurate means for measuring specific heat capacity. No calibration is needed, KCp is determined at each temperature so accuracy is excellent.

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Most Accurate Cp Determination
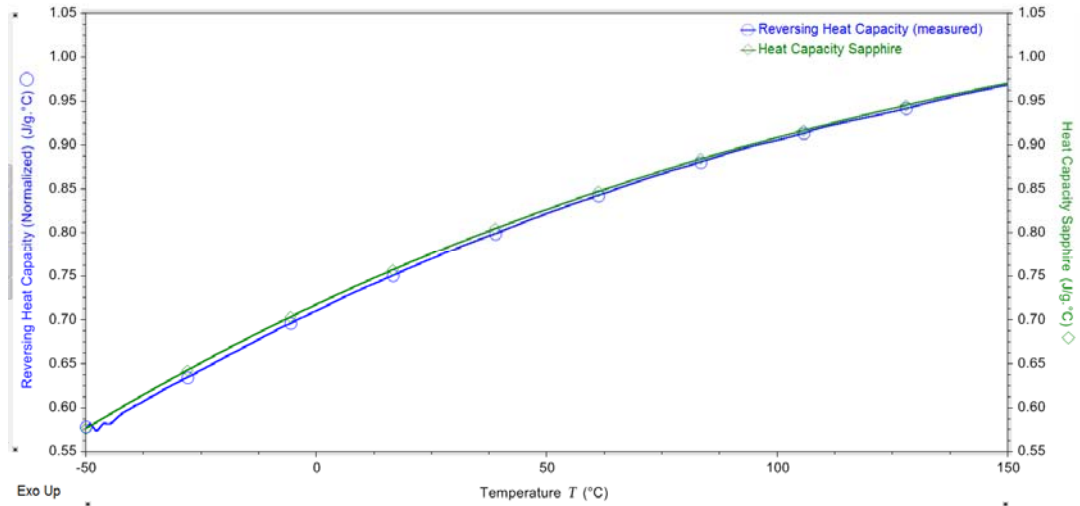
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Calibration & Verification

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Calibration of Specific Instrument Models

Tzero Measurement of Rs and Cs	**Baseline calibration** Measurement of slope and offset	**Cell constant and temperature**

DSC2500

DSC250

1st Generation Discovery

Q2000

Q200

DSC 25

Q20

All DSCs
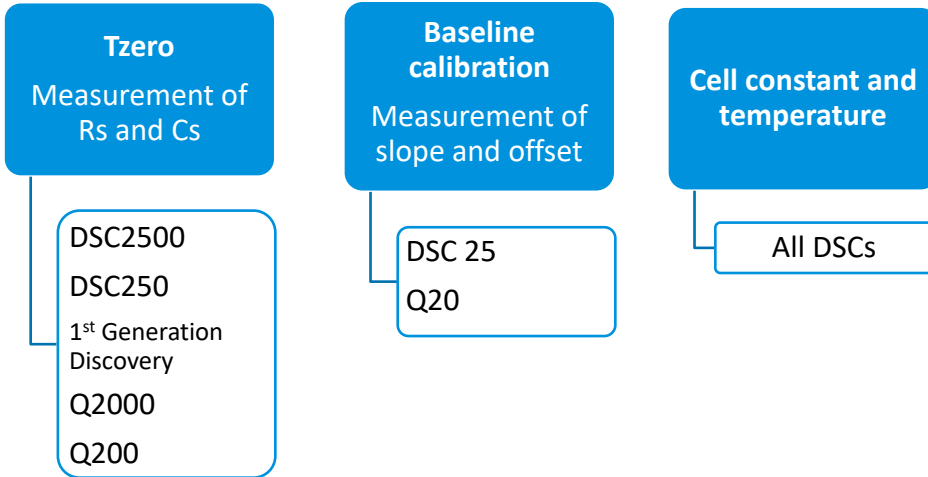
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Calibration Setup in Trios
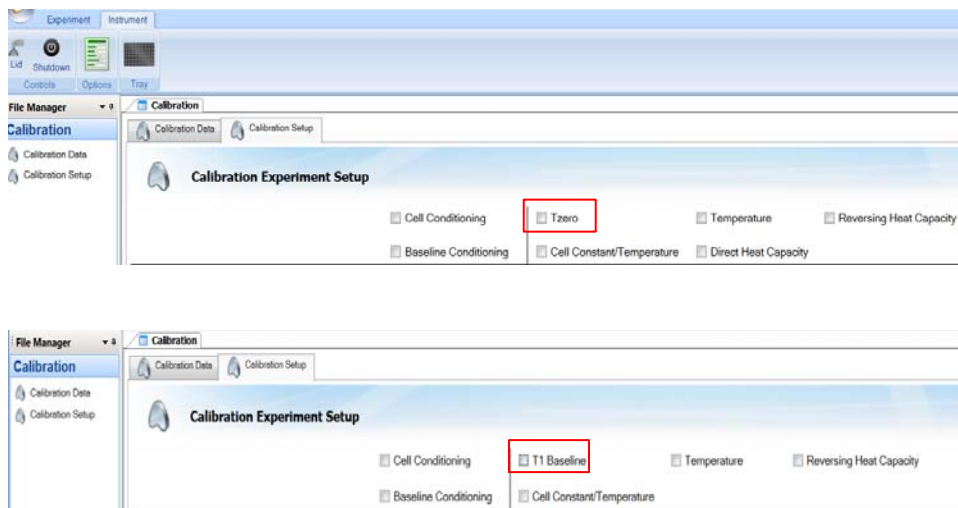
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General Calibration and Verification Guidelines

Calibration	Verification
• Use Calibration Mode • Calibrate upon installation • Re-calibrate if does not pass verification or if instrument setup is modified	• Determine how often to verify data • Run a reference material as a sample (in standard mode) • Compare results vs literature values • If results are within your tolerance – system checks out and does not need re-calibration • If results are out of tolerance, then re-calibrate

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Requirements Prior to Calibration

- DSC cell must be free of contaminants

- An inert purge gas, such as nitrogen, where the flow rate is controlled to 10-50 ml/min +/- 5 ml/min

- A balance to weigh specimens and containers to at least +/- 0.1 mg. The balance should have a capacity greater than 20 mg.

- High purity reference materials (>99.99%) for calibration

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Instrument Setup Factors Affecting Calibration

Purge Gas Type

- Re-calibrate baseline/Tzero, temperature and cell constant
- Thermal conductivity of helium ≠ Thermal conductivity of nitrogen/air/oxygen ≠ Thermal conductivity of argon

Cooling Accessories

- Re-calibrate baseline/Tzero, temperature and cell constant
- The position of the cooling head around the cell will affect the calibration of the instrument. Uninstallation and reinstallation of a cooling accessory or changing the cooling accessory warrants a complete re-calibration

Pan Selection

- Re-calibrate temperature and cell constant
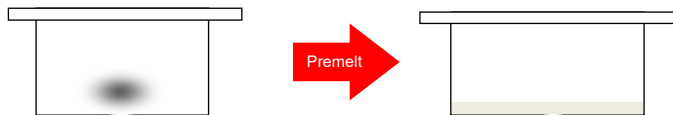- It will not impact the baseline/Tzero calibration

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Temperature and Cell Constant Calibration

- Prepare a 3-5 mg sample of indium and "pre-melt" prior to first use

Premelt

- Verify at least once a month

- Typical values for cell constant:
  - 0.9 to 1.2 (in N_2)
  - Helium will typically give higher values for the cell constant
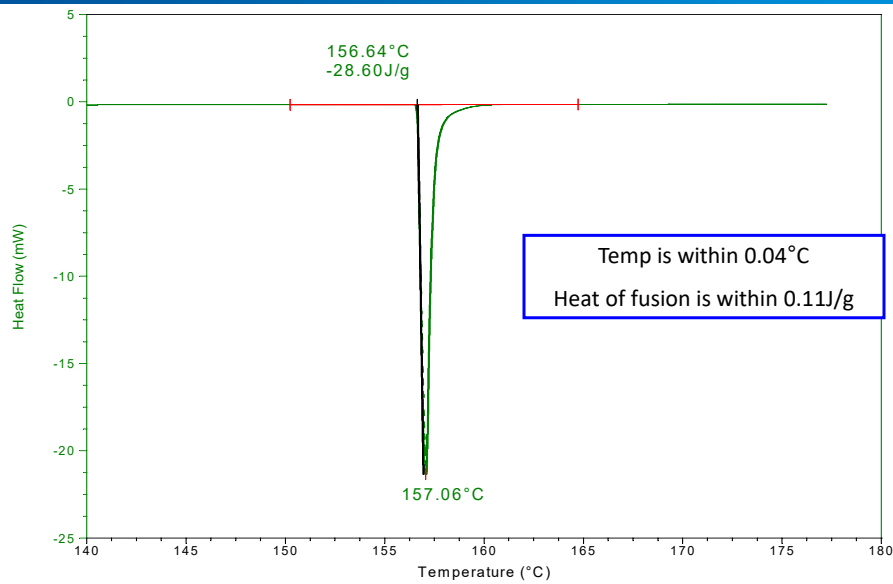
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Verifying Cell Constant & Temperature

- Run Indium as a sample (i.e. in standard mode not calibration 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

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Verifying Cell Constant & Temperature

156.64°C
-28.60J/g

Temp is within 0.04°C

Heat of fusion is within 0.11J/g

157.06°C

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Reference Standards for Calibration

- Enthalpy (cell constant)
  - Benzoic acid (147.3 J/g) Tm = 123°C
  - Urea (241.8 J/g)   Tm = 133°C
  - Indium (28.71 J/g)   Tm = 156.6°C
  - Anthracene (161.9 J/g) Tm = 216°C

  > * GEFTA recommended
  > *Thermochim. Acta*, 219 (**1993**) 333.
  >
  > \# ITS 90 Fixed Point
  >
  > E Zone refined organic compound (sublimes)

- Temperature
  - Cyclopentane* -150.77°C
  - Cyclopentane* -135.09°C
  - Cyclopentane* -93.43°C
  - Cyclohexane # -83°C
  - Gallium # 29.76°C
  - Phenyl Ether # 30°C
  - p-Nitrotoluene E 51.45°C
  - Naphthalene E 80.25°C
  - Indium # 156.60°C
  - Tin # 231.95°C
  - Lead* 327.46°C
  - Zinc # 419.53°C

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Verifying Baseline

- Run Empty cell (no pans), -90°C to 400°C (w/ RCS) at 20°C/min
  - Experiment is run in the standard mode
  - Plot mW vs. temperature on a 1mW scale
    - Should look fairly flat on this scale
    - Should be around zero heat flow
  - Measure drift and compare to instrument specifications.
  - Verify performance periodically
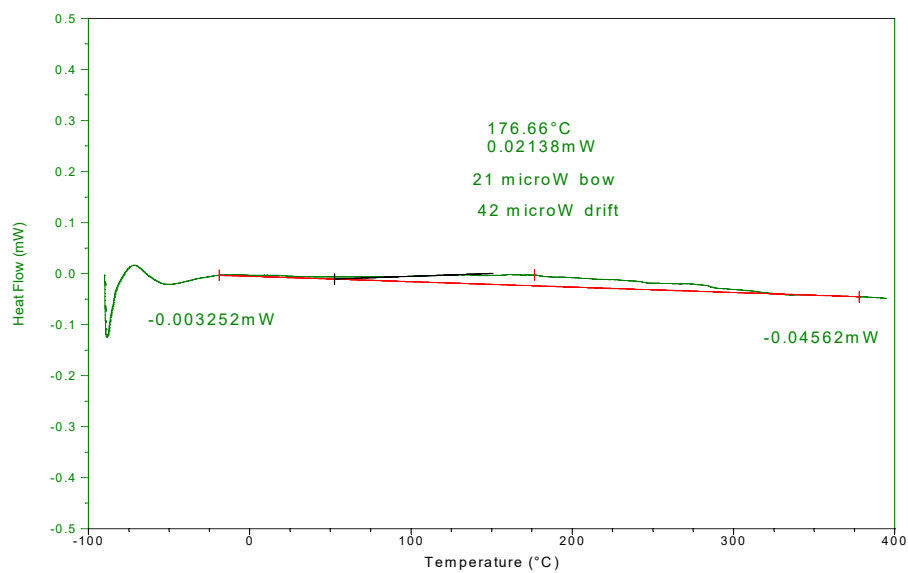
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Verifying Baseline

- Importance of a flat baseline:
  - Detecting very weak transitions
  - Accurate integration of enthalpy
    - Kinetics, partial area analysis, extent of reactions
    - Initial crystallinity
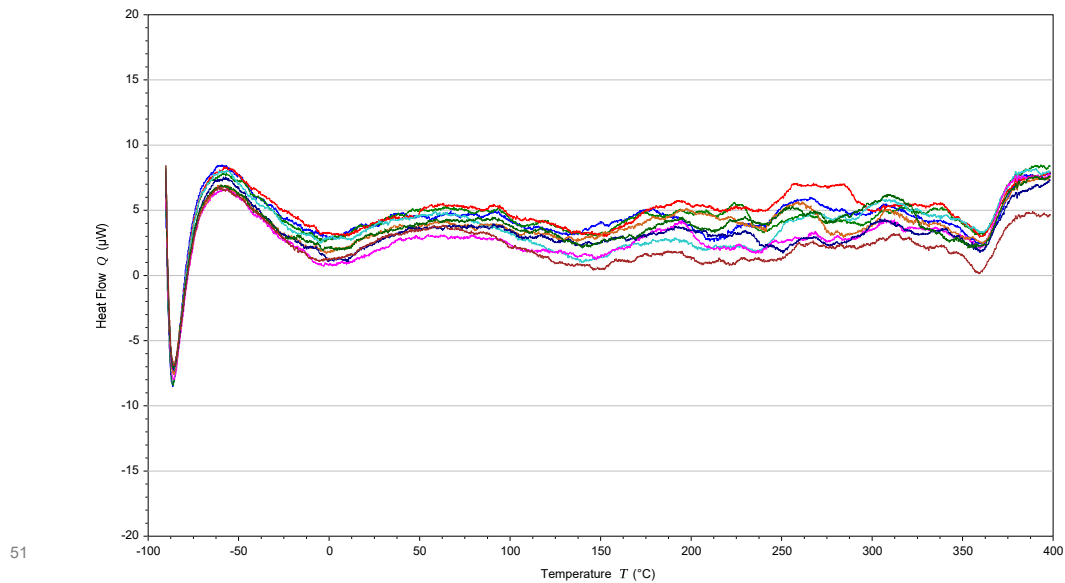
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Verifying Baseline

176.66°C
0.02138mW

21 microW bow

42 microW drift

-0.003252mW

-0.04562mW

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Empty Cell Baseline at 20 ºC/min – DSC2500
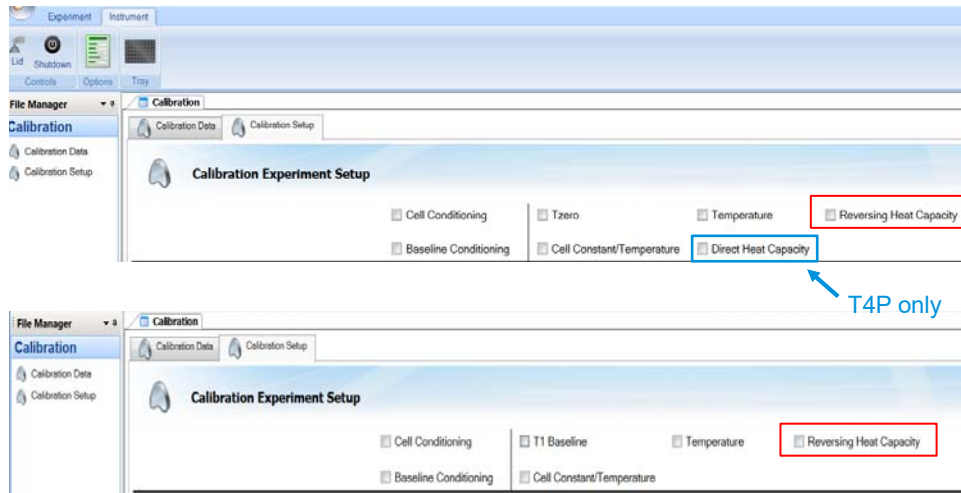

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MDSC Calibration – Discovery Series

- Calibrate your DSC as normal
  - Tzero™
  - Cell Constant
  - Temperature
- Cp Calibration is Optional
- If measuring absolute quantitative Cp then…
- Need to calibrate Reversing Heat Capacity or Direct Heat Capacity (DSC2500 only)
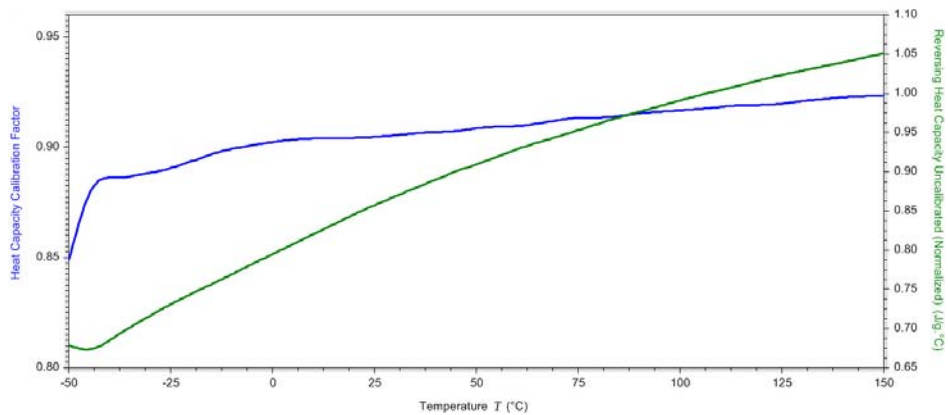
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Cp Calibration in Trios

T4P only

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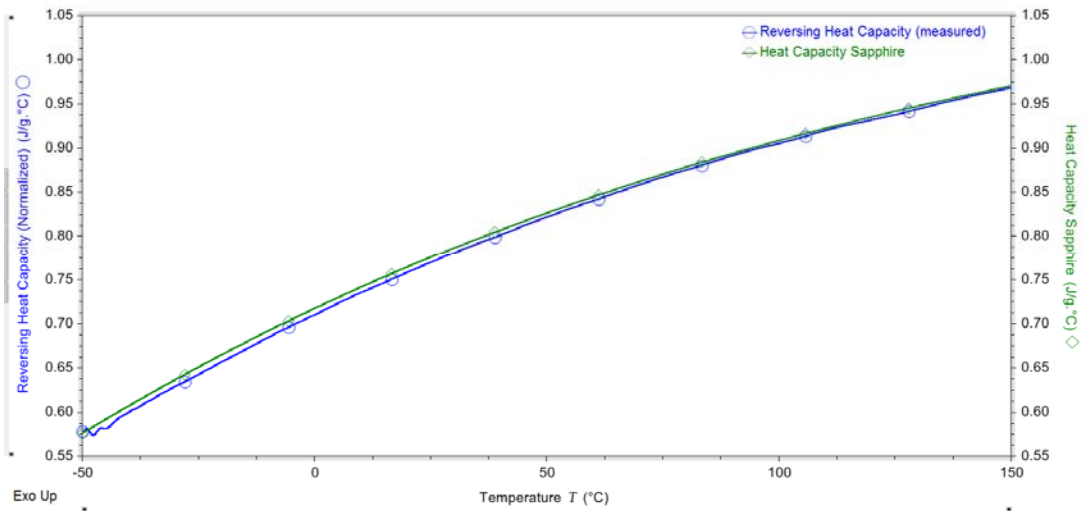# MDSC *Cp* calibration using TRIOS

KCp is determined as a continuous function of temperature in the Discovery DSC.

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MDSC *Cp* verification using TRIOS

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Experimental Design: Instrument Set Up

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Instrument Hardware and Gas Selection Considerations

Temperature Range Dependent On The Cooling System
- Finned Air Cooling System (FACS): Ambient to 725°C
- Quench Cooling Accessory (QCA): -180°C to 400°C
- Liquid Nitrogen Cooling System (LN2P): -180°C to 550°C
- RCS120: -120°C to 400°C
- RCS90: -90°C to 550°C
- RCS40: -40°C to 400°C

Purge Gas Selection
- **Nitrogen**
  - inert, inexpensive and readily available
  - flow rate of 50ml/min
- **Helium**
  - a high thermal conductivity gas which improves response time and cooling capabilities
  - the recommended purge gas when using the LN2 accessory at temperatures below -100°C
  - flow rates of 10-25ml/min are typically used; cell constant affected by flow rate
- **Air/Oxygen**
  - used when studying oxidative stability of materials

Sample Press and Pan Selection
- Aluminum: max. temperature of 600°C
- Gold
- Copper
- Graphite, Alumina
- Platinum
- Stainless Steel

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Cooling Accessories

- Finned Air Cooling System (FACS): Ambient to 725°C
- Quench Cooling Accessory (QCA): -180°C to 550°C *
- Liquid Nitrogen Cooling System (LNCS): -180°C to 550°C
- RCS120: -120 °C to 400 °C
- RCS90: -90°C to 550°C
- RCS40: -40°C to 400°C

RCS40: -40˚C to 400˚C
RCS90: -90˚C to 550˚C
RCS120: -120˚C to 400˚C
LN2P: -180˚C to 550˚C
With Quench Cooling Accessory
FACS: RT to 725˚C
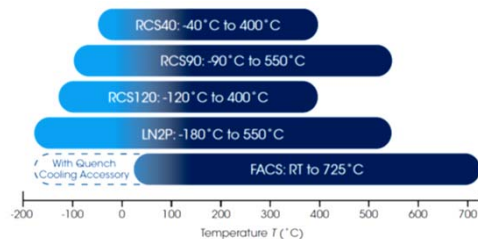
Temperature T (˚C)

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* Isothermal or slow heating ramp experiments above 400°C are not recommended.

Selecting the Cooler – Discovery DSC

This is used to select the cooler type

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Selecting the Purge Gas – Discovery DSC

This is used to specify the type of gas connected to Gas #1 and Gas #2 inlets

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Setting the Purge Gas Flow Rate – Discovery DSC

This is used to select which gas is going to the DSC cell and the flow rate for that gas.

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Recommended Purge Gas Flow Rates

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

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

- If purge gas is too fast – excessive noise

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Experimental design:
Sample Preparation and Considerations

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TGA for DSC Experimental Design

- Thermogravimetric Analysis (TGA) measures weight loss or gain as a function of temperature, time and atmosphere.

- General applications of TGA include:
  - thermal stability
  - residual solvent, out gassing, moisture sorption/desorption
  - filler/fiber content
  - weight loss on cure

- TGA measurements are extremely useful in selecting experimental conditions for DSC experiments and for interpreting results.

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Typical TGA data: TGA of Drug A Monohydrate

Sample: Drug A Monohydrate
Size: 15.1740mg
Heating Rate: 10°C/min
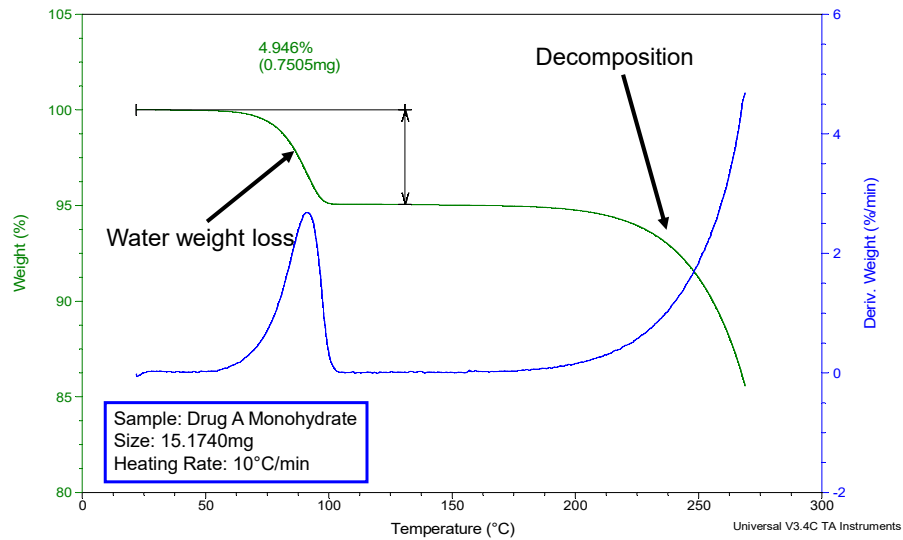
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Selecting Optimum Experimental Conditions

- Use TGA data to help select DSC experimental conditions
  - Standard (non-hermetic) vs. Hermetic (sealed) pans
    - Use hermetic pan if sample loses approximately 0.5% weight or more.
    - Use hermetic pan with pin hole lids if sample loses volatiles such as water
  - Maximum Temperature
    - Excessive decomposition will contaminate the DSC cell between runs
  - When comparing samples, always use the same experimental conditions

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DSC Pan Selection

- High thermal conductivity – aluminum, gold, copper, platinum
- Inert - alodined aluminum, ceramic, graphite
- Flatness of the pan for optimal thermal contact
- Standard, non-hermetic vs. hermetic sealing
- Capacity/sample volume
- Temperature range

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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

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Sample Shape

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

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TA Instruments Tzero Pans (Aluminum)

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 non-hermetic or hermetic use. P/N 901683.901 Tzero Pans (pkg. of 100)

- The Tzero Low-Mass Pan is designed for the highest sensitivity when sample mass is limited. P/N 901670.901 Tzero Low-Mass Pans (pkg. of 100). Can only be used with the non-hermetic Tzero lid.
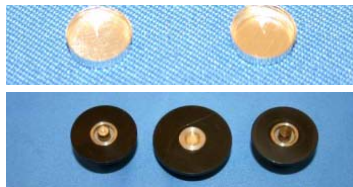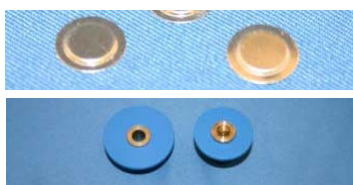
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TA Instruments Tzero Pans

Tzero Lid

- Tzero Lid (P/N: 901671.901) - Lightweight aluminum lids for use in sample encapsulation with the Tzero Pans and the Tzero Low-Mass Pans. The seal is not hermetic.

Tzero Hermetic Lid

- Tzero Hermetic Lid (P/N: 901684.901) (pkg. of 100) and P/N: 901685.901 Tzero Hermetic Pinhole Lid (75 micron diameter pinhole) (pkg. of 50). Used only with the Tzero pan, not the low mass Tzero pan

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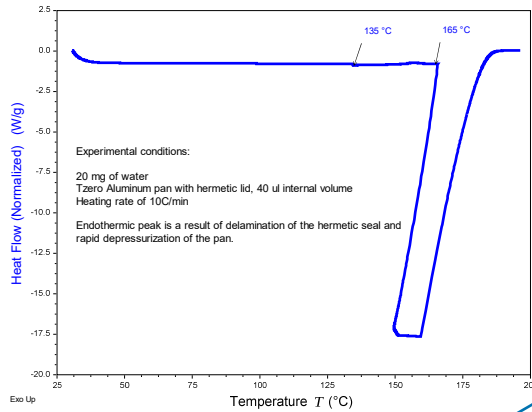
Standard Series DSC Other Pans (Non Hermetic)

- Standard pans are available in:
  - Gold (p/n 900866.901 pan, p/n 900868.901 lid):up to 725°C
  - Graphite (p/n 900874.901 pan, p/n 900873.901 lid):   up to 725°C (in N_2)

- Standard Pans with no lids available
  - Platinum (p/n 900578.901): up to 725°C
  - Copper (p/n 900867.901) : up to 725°C

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Hermetic DSC Pans

Experimental conditions:

20 mg of water
Tzero Aluminum pan with hermetic lid, 40 ul internal volume
Heating rate of 10C/min

Endothermic peak is a result of delamination of the hermetic seal and rapid depressurization of the pan.

Aluminum Hermetic 3 atm

Sample:
1. Liquid
2. Solid with volatile content

High Volume Stainless Steel 40 atm

Gold Hermetic 6 atm

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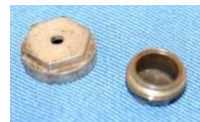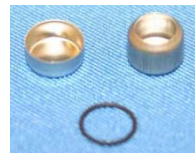# Hermetic Pans Summary

- Hermetic Pans are available in:
  - Aluminum: <600°C; <3 atm (300 kPa gauge)
  - Alodined Aluminum: <200°C; <3 atm (300 kPa gauge)
  - Gold: <725°C; <6 atm (600 kPa gauge)

- Specialized Sealed Pans
  - High Volume: 100µL; <250°C; 37 atm (575 psi)
  - P/N 900825.901

  - High Pressure: 35µL; <300°C; 100 atm (1450 psi)
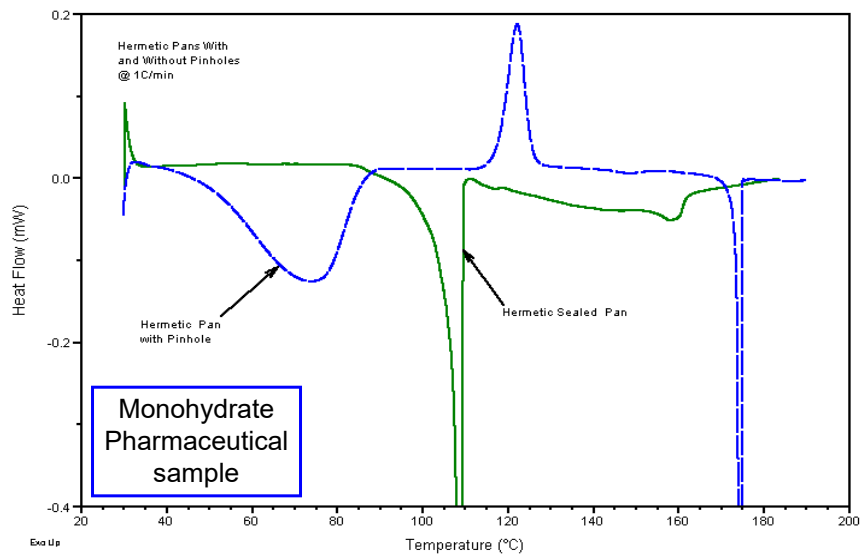 - P/N 900808.901

  Note: 3 atm is approximately 44 psi

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It Can Matter What Pan You Use

What if Sample Spills out 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

Cleaning the Cell

- Use solvent – slightly damp swab with an appropriate solvent
    - Heat cell to 200°C for 10 min to drive off any remaining solvent

- If the cell is still dirty
    - Clean w/ brush
    - Be careful with the Tzero™ thermocouple
    - **Fibers in cell from cleaning brush need to be removed**

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Cleaning Cell: Bake Out Procedure

- Bake out
    - Should be used as a last resort if none of the previous steps are effective
    - Involves Air purge and/or an open lid
    - Heat at 20°C/min to appropriate temp (max of 550°C on Q series, max. 400°C in Discovery)
    - Do NOT hold Isothermal at the upper temperature
    - Cool back to room temp & brush cell again

- Irrespective of the cleaning method used, always verify the baseline at the end of the cleaning procedure, and recalibrate the DSC if required

- Check out the TA Tech tip video on cleaning the DSC cell:
    - https://www.youtube.com/watch?v=cclJXrbUICA

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Method Development
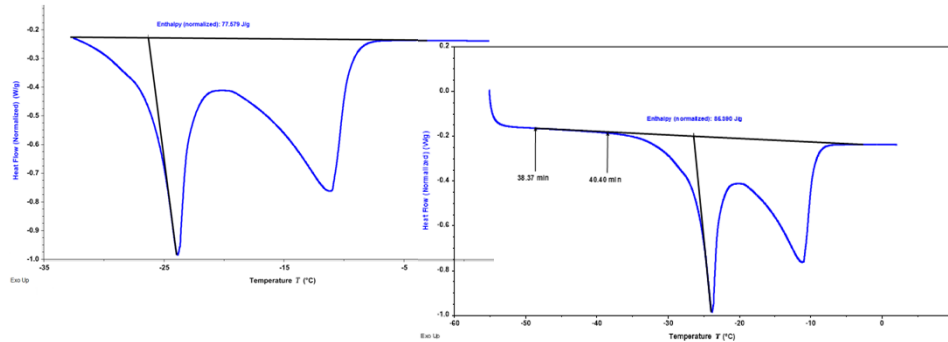
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DSC General Method Recommendations

- Run a Heat-Cool-Heat at 10-20 °C/min
- Use specific segments as needed, i.e. gas switch, abort, etc.
- Ensure that the starting temperature of the experiment is chosen to encompass the entire transition (see next slide)
- Modify heating rate based on what you're looking for

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Have 2 Minutes of Baseline

- 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

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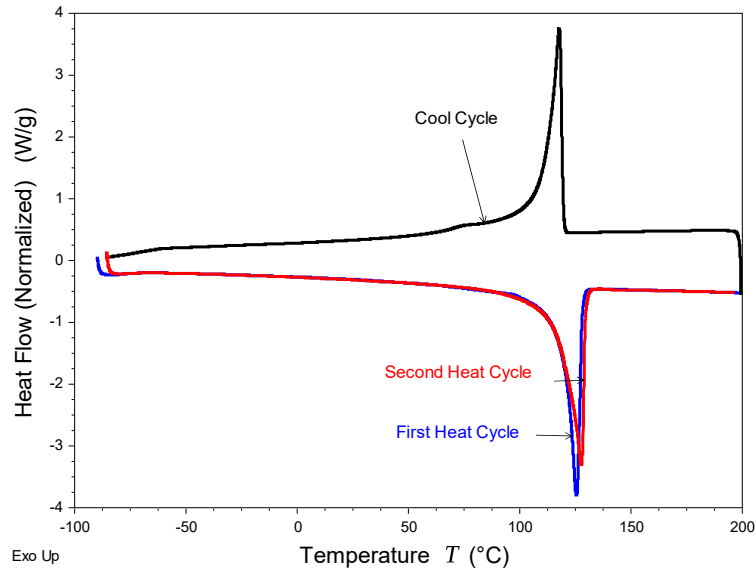## Method Development

A Heat Cool Ramp Method

1) Ramp 10°C/min to -90°C or Equilibrate to -90°C
2) Ramp 10°C/min to 200°C
3) Ramp 10°C/min to -90°C
4) Ramp 10°C/min to 200°C

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Heat Cool Heat Cycles of High Density Polyethylene (HDPE)

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Exo Up

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How to Program MDSC?

Period	• Typically 60 seconds for transitions • Typically 120 seconds for Cp
Heating rate	• Typically 2-3°C/min
Amplitude	• Typically ±1°C for amorphous transitions and Cp • Use Heat-Iso amplitude for crystalline transitions

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Starting Guidelines for Determining the Tg in Amorphous Materials – Conventional MDSC®

- Conventional MDSC conditions
  - Period: 60 second
    - Minimum period depends on pan type and pan mass
      - Can use 40 sec for low-mass Tzero pans
      - Use 200 sec for Hi-volume pans
  - Amplitude: ±1°C
    - Increase for added sensitivity
  - Heating Rate 3°C/min
    - Slow down heating rate for sharper transitions or large enthalpic recovery peaks

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Starting Guidelines for crystallinity/melting studies: MDSC® Heat Only Conditions
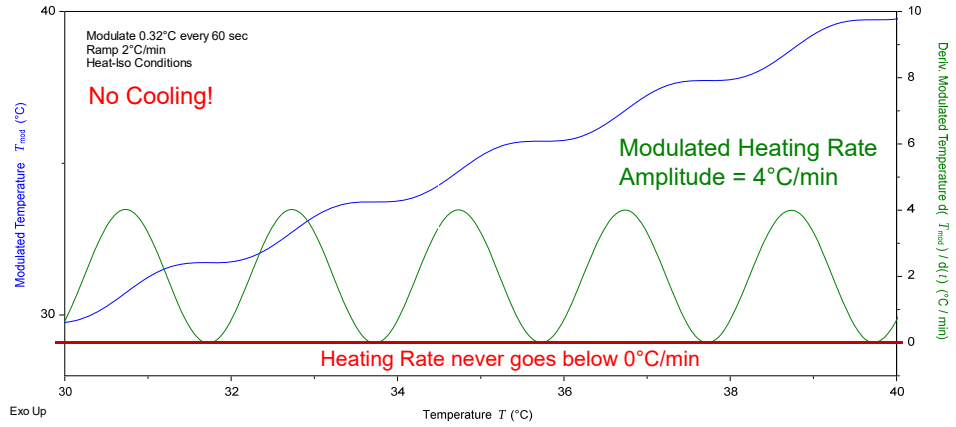
- MDSC Heat-Only Conditions
  - Period: 60 second
    - Minimum period depends on pan type and pan mass
      - Can use 40 sec for low-mass Tzero pans
    - Heating Rate 2-3°C/min
      - Ensure 4-5 cycles through peak @ half-height of melt
    - Amplitude Heat-only (Heat-Only/Heat-Iso)
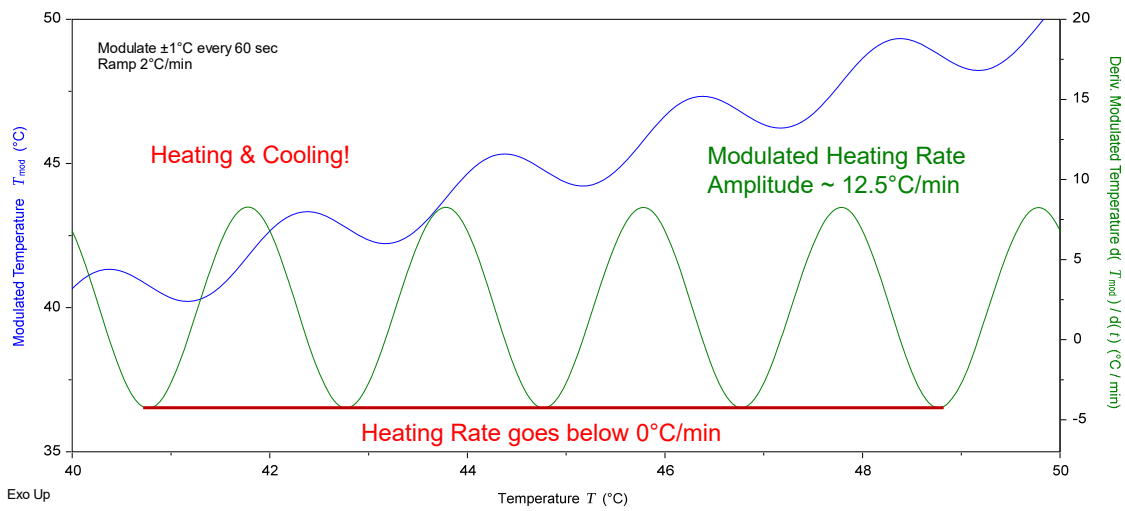
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MDSC – Heat-only Temperature Modulation

Modulate 0.32°C every 60 sec
Ramp 2°C/min
Heat-Iso Conditions

No Cooling!

Modulated Heating Rate
Amplitude = 4°C/min

Heating Rate never goes below 0°C/min

Exo Up

Temperature *T* (°C)

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MDSC – Heat-Cool Temperature Modulation

Modulate ±1°C every 60 sec
Ramp 2°C/min

Heating & Cooling!

Modulated Heating Rate
Amplitude ~ 12.5°C/min

Heating Rate goes below 0°C/min

Exo Up

Temperature *T* (°C)

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Parameters for Heat Capacity (Cp)

- **Conventional MDSC** conditions
  - Period 120 seconds
    - Can use 100 seconds with low-mass Tzero pans
  - Amplitude ±1°C
  - Heating Rate 3°C/min
    - Can also do Quasi-isothermal for specific temperatures

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MDSC Conditions for Discovery SDT 650

- Used to measure Heat Capacity
- Amplitude = ±3°C
- Period = 200 seconds
- Heating Rate = 5°C/min
- Best above 300 or 400°C

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MDSC Parameters: The Modulation Period

- The modulation period should be long enough to allow for a quantitative measurement of heat flow between the sensor and the sample.
  - Too short a period may result in poor data due to thermal resistances between the sensor and the pan, the pan and the sample, and the sample itself.
  - Too long a period requires a lower average heating rate resulting in potential signal to noise issues and longer experiment time.
- Suggested starting periods:
  - Thermal transitions: 60 seconds
  - Heat capacity measurement: 120 seconds
- The default conditions are also a good starting point for MDSC experiments.

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Modulation Period: Summary Guidelines

- Choice of period will also be dependent to some extent on the pan you use:
- For transitions:
  - Use 40 sec for pans <30mg (Tzero Low Mass)
  - Use 60 sec for pans ~50mg (Tzero Std & Hermetic)
  - Use 200 sec for Hi-Volume Pans
- For quantitative Heat Capacity measurements:
  - Use 100 sec for pans <30mg (Tzero Low Mass)
  - Use 120 sec for pans ~50mg (Tzero Std & Hermetic)

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MDSC® Parameters: The Modulation Amplitude

- Factors Considered Choosing Modulation Amplitude:
  - Signal to Noise: Larger amplitudes will result in greater sensitivity, but if too large may effectively smear a transition (loss of resolution) and may adversely affect the linearity of the heat flow response.
  - Cooling? – Amplitude is selected based on whether cooling (negative heating) is desired during the modulation.
    - Amplitudes utilizing cooling are effective for determining heat capacity or changes in heat capacity such as glass transitions.
    - Amplitudes resulting in only positive or minimum zero heating rates are effective in analysis of melt transitions.

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MDSC Parameters: The Modulation Amplitude

- The software will allow choice of amplitudes between +/-0.001 and 10 °C.
- The practical range is +/- 0.1 and 2 °C, with lower amplitudes yielding poor sensitivity and high amplitudes decreasing resolution.

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Modulation Amplitude: Summary Guidelines

- For amorphous transitions and measuring heat capacity:
  - Start with ±1°C
  - Increase amplitude for added sensitivity
- For crystalline transitions:
  - Use Heat-Only

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MDSC Parameters: Average Heating Rate

- The average heating rate is chosen to maximize signal to noise while balancing the need to obtain 4-6 modulations through the temperature range of interest.
- For melting transitions, the range of interest is determined at the half-height of the melting peak.
- For glass transitions, it is determined where the transition is changing fastest.
- Typically a heating rate from 1-3 °C / min is chosen.
- The heating rate is the best parameter to vary when 'fine tuning' the MDSC experiment.

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## Selecting MDSC® Underlying Heating Rate

- Check your data by plotting the modulated heat flow and the total heat flow signals. You should obtain 4-6 modulations through the transition of interest.

- Faster rates improve signal quality and sensitivity balanced by the need for sufficient modulations.

- Often MDSC optimization is an iterative process, so its not unusual to repeat an experiment.

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MDSC Parameters: Sufficient Modulations Through Melting Transition
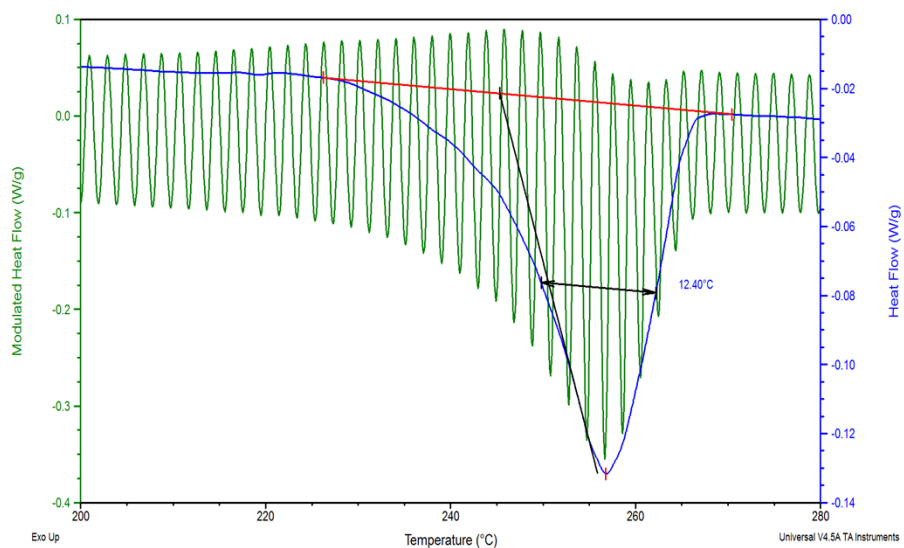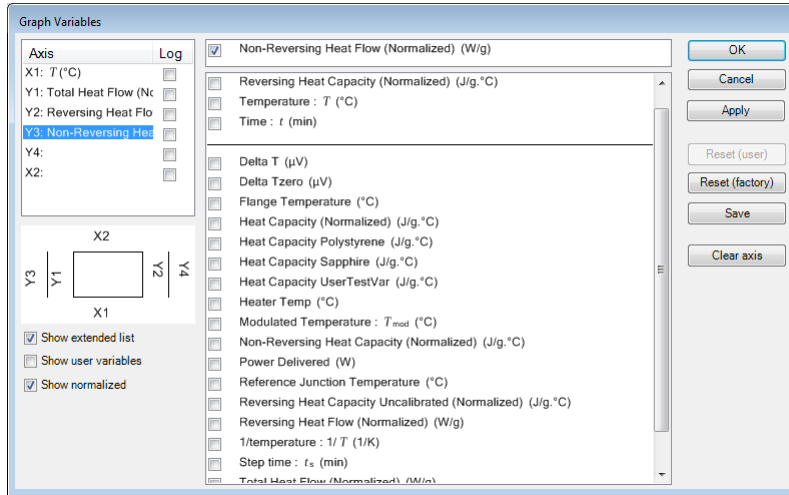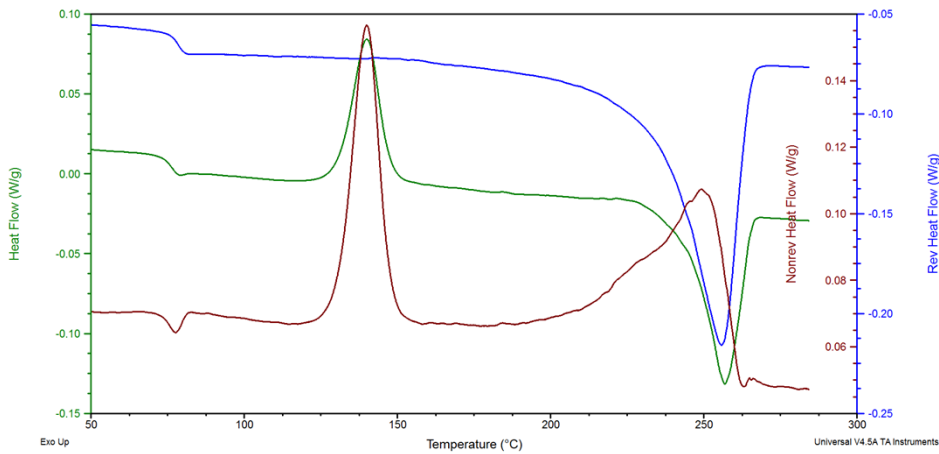

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Selecting Signals for Plotting (TRIOS)

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MDSC® of PET

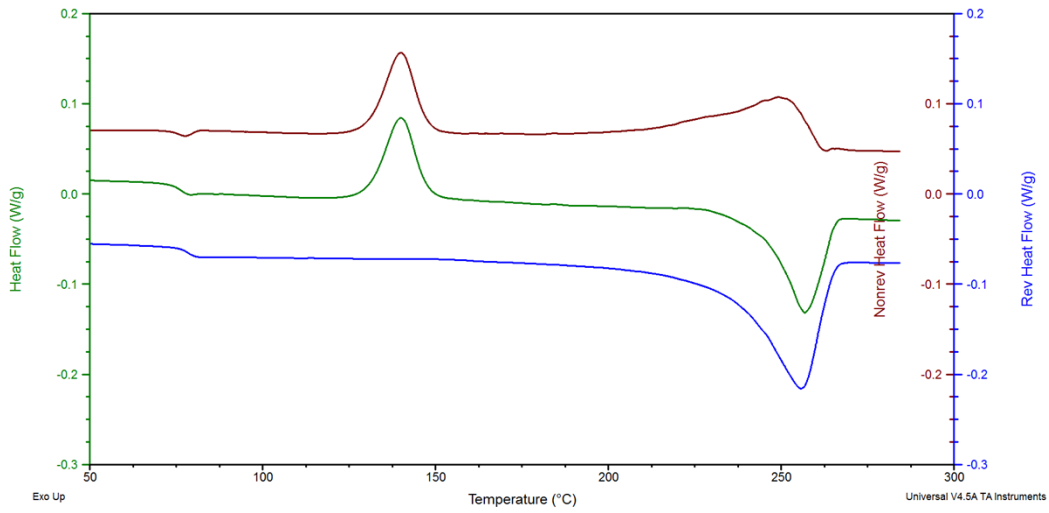Default Universal Analysis Presentation of Data

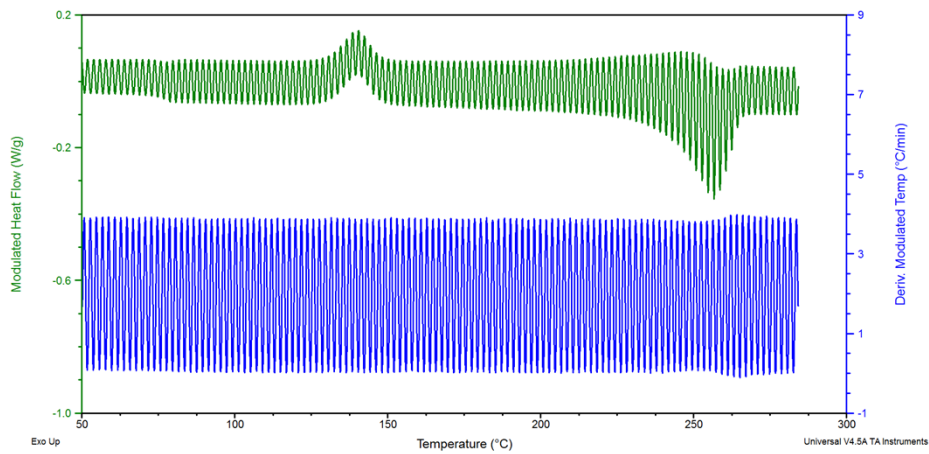100

100

MDSC® of PET (Normalized Data)

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MDSC® of PET – Raw Signals

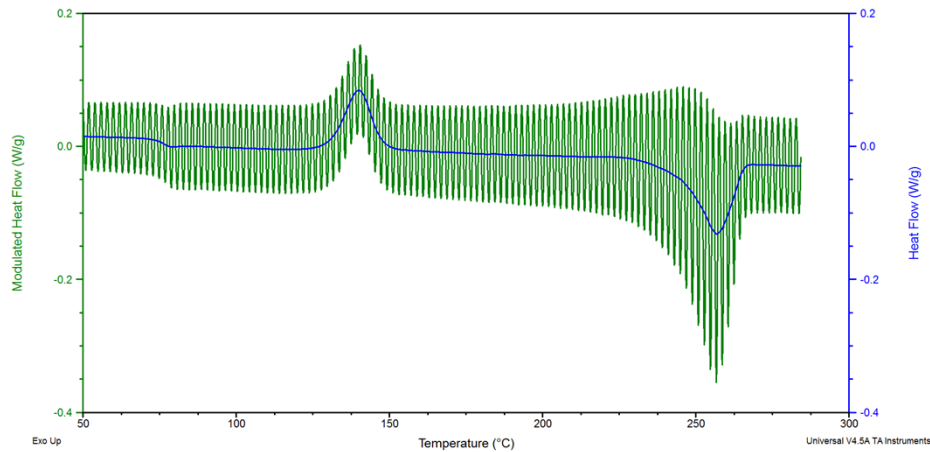102

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MDSC® of PET

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Summary for Method Development

- Typical starting sample mass – depends on the size of the transition
  - 5-10mg for most polymers
  - 3-5 for chemical melting
  - <1 for explosives
- Typical starting ramp rate = 10°C/min (Heat-Cool-Heat)
  - Faster for better sensitivity
  - Slower for better resolution
- Change above as needed
- MDSC® as needed

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What if I need help?

- TA Tech Tips
    - http://www.youtube.com/tatechtips
- TA Instruments Applications Helpline available from the TA website
    - http://www.tainstruments.com/support/applications/applications-hotline/
- Check out our Website
    - http://www.tainstruments.com/

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- TA Instruments Applications Helpline available from the TA website
    - http://www.tainstruments.com/support/applications/applications-hotline/
- Check out our Website
    - http://www.tainstruments.com/

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- For additional questions:
- Email thermalsupport@tainstruments.com
- Please put Online Training Questions in the subject line
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