# Differential Scanning Calorimetry (DSC)


Q-series
Discovery
DSC2500
DSC250
DSC25

# Agenda for the course

- **Understanding heat flow measurements on a DSC**
- Calibrations and Verification
- Experimental design and method development
- Applications

# TA Instruments DSC Models

DSC 25
DSC 250
DSC 2500

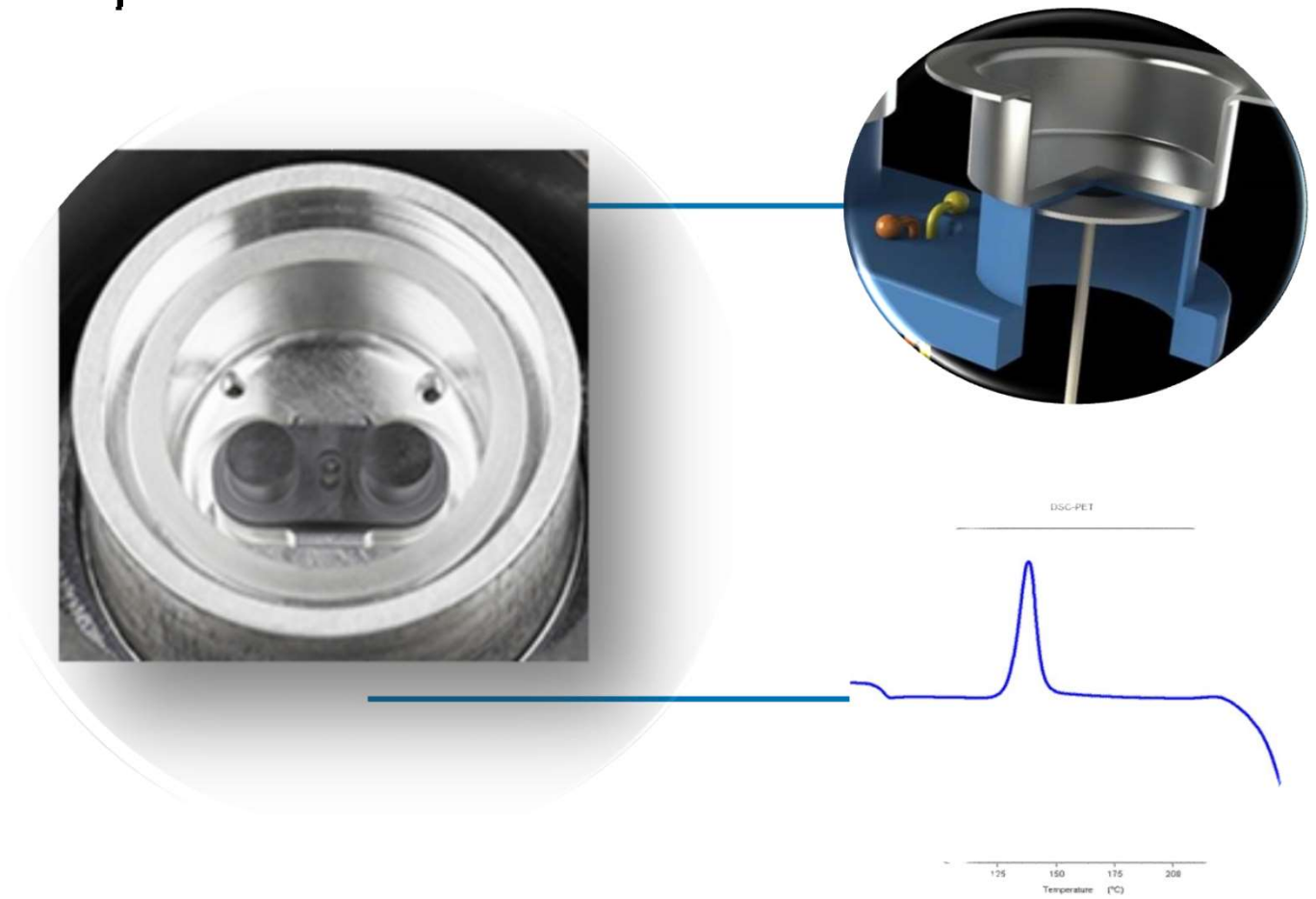
AutoQ20

Discovery DSC

Q2000

# 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



# Simple Heat Flux DSC Cell Schematic


## Reference Sensor

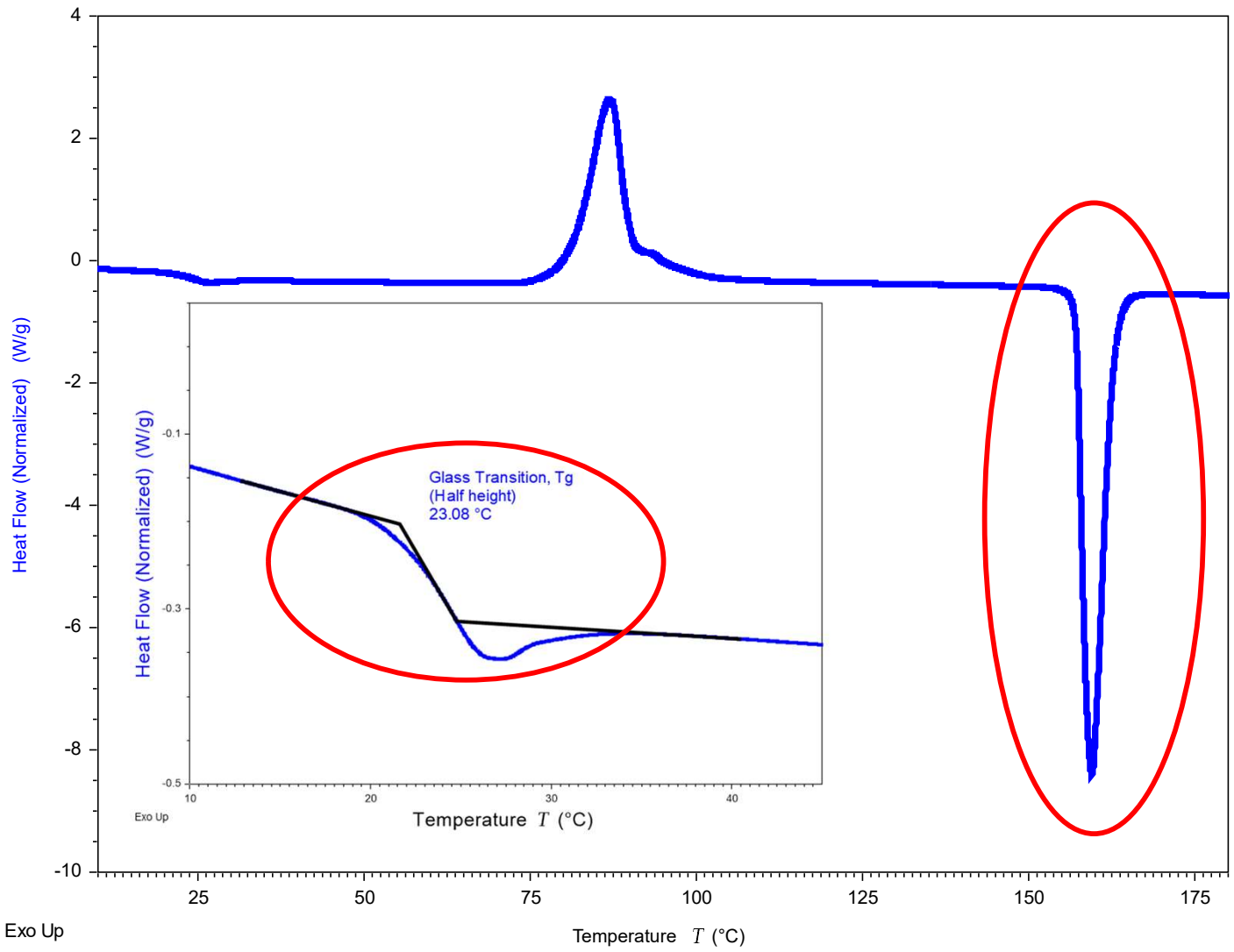
An empty pan on the reference sensor should react similarly to the pan on the sample sensor, thus canceling out any pan contribution

## Sample Sensor

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

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

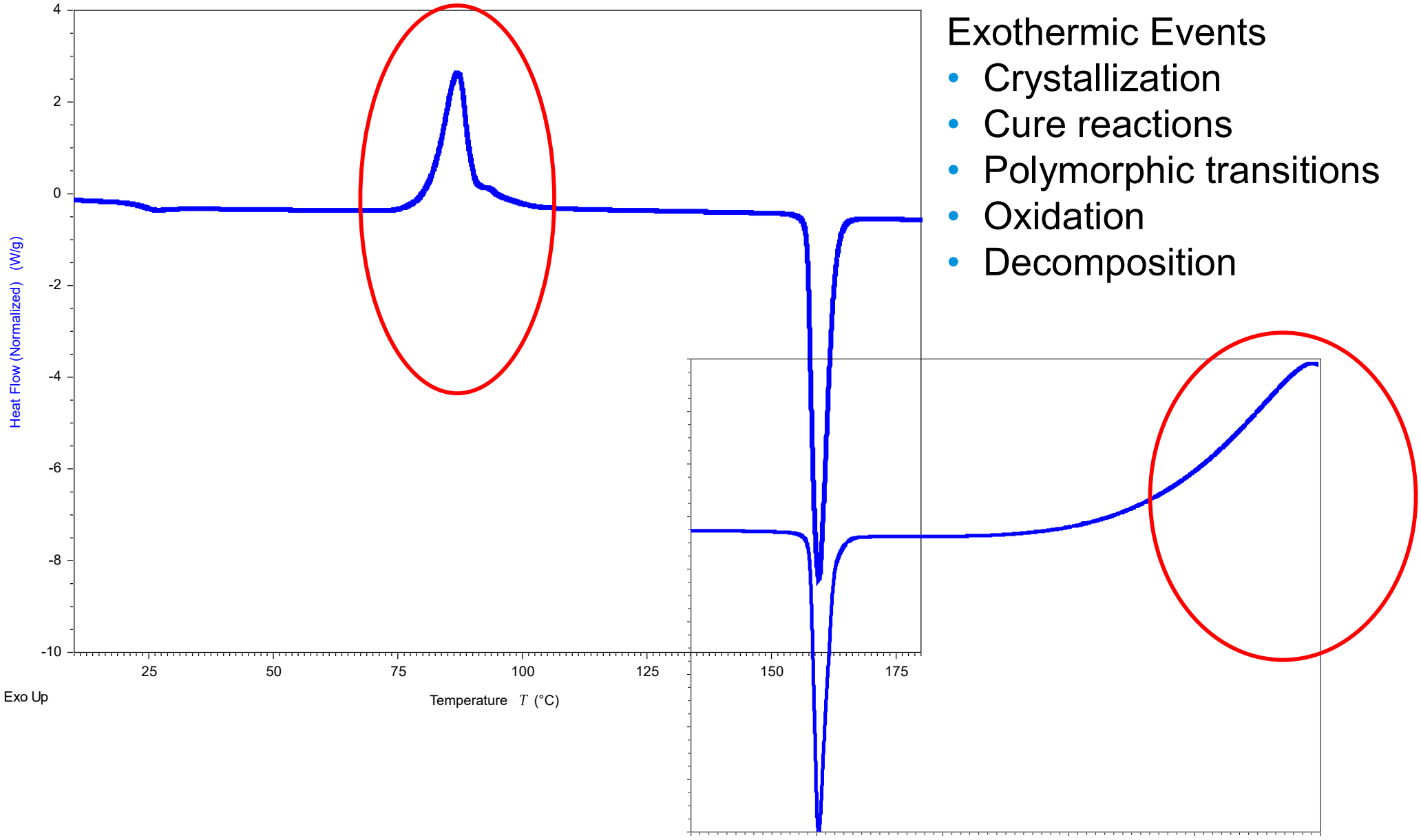
# Endothermic Heat Flow – Heat Absorbed by Sample




Endothermic Events

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

# Exothermic Heat Flow – Heat Released by Sample




Exothermic Events

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

# DSC Heat Flow

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

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

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 (°C/min)

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

# DSC Heat Flow

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

**Heat Capacity**

- Glass Transition
- Some Melting

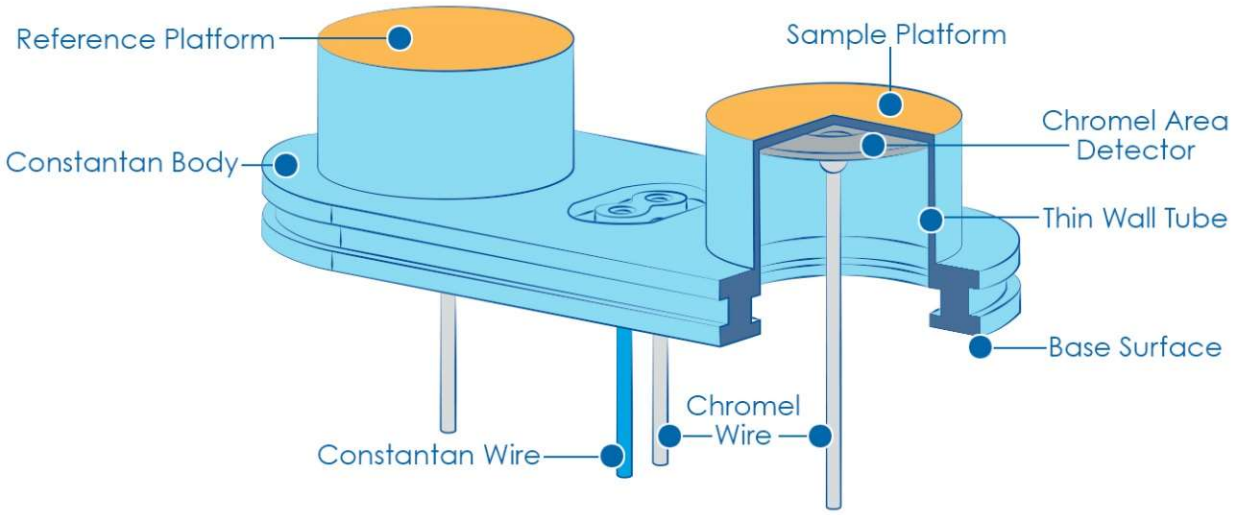
**Kinetic**

- Crystallization
- Some melting
- Cure reactions
- Volatilization
- Decomposition
- Denaturation

# DSC heat flow modes – T1 vs T4 vs T4P mode

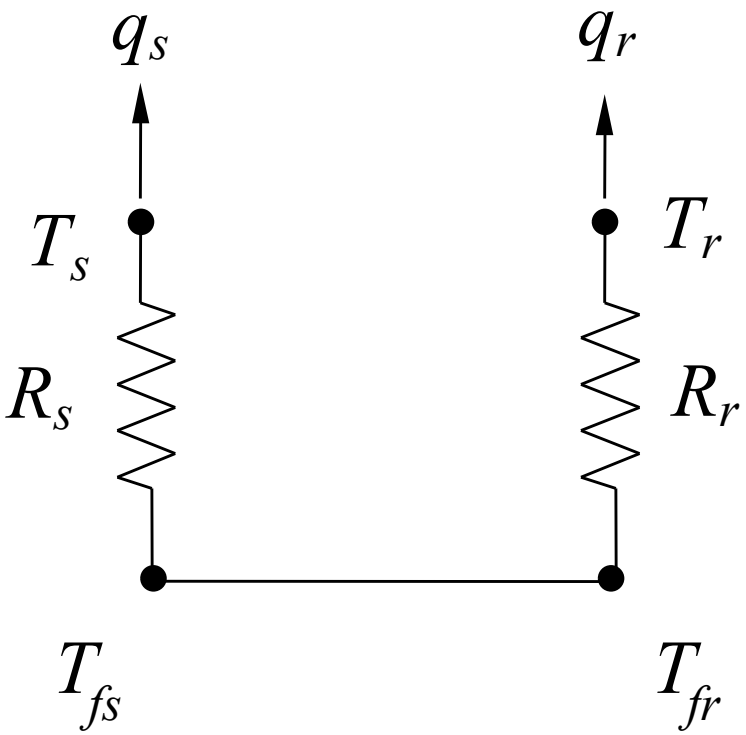
# Measurement of Temperature

- What temperature is being measured and displayed by the DSC?
  - Sample Sensor Temperature
    - Used by most DSCs
    - Measured at the sample platform with a thermocouple, thermopile or PRT
- The actual temperature of the sample is never measured by DSC
  - There is no thermocouple in direct contact with the sample



# Conventional DSC Measurements, T1 Heat Flow

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

$$q = q_s - q_r$$

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

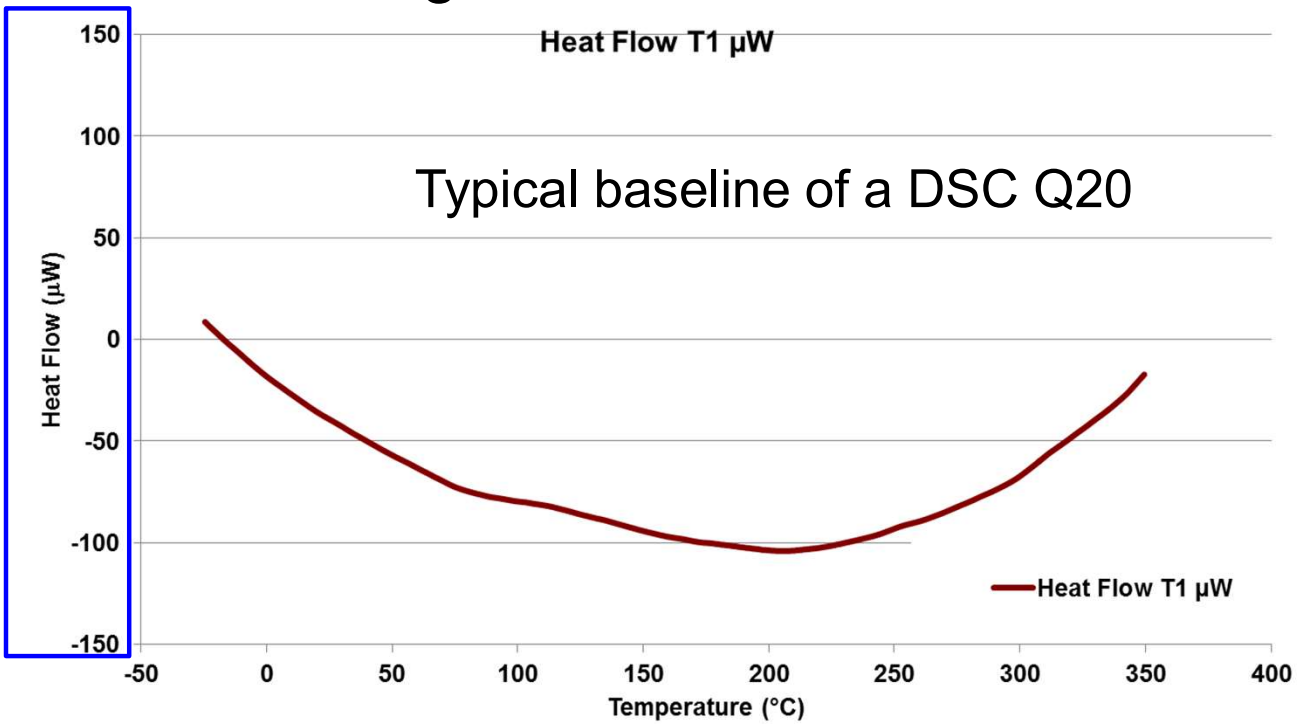
This model assumes that the sample and reference calorimeter thermal resistances are identical and that the furnace temperature is uniform throughout the cell.

# Conventional DSC - Assumptions

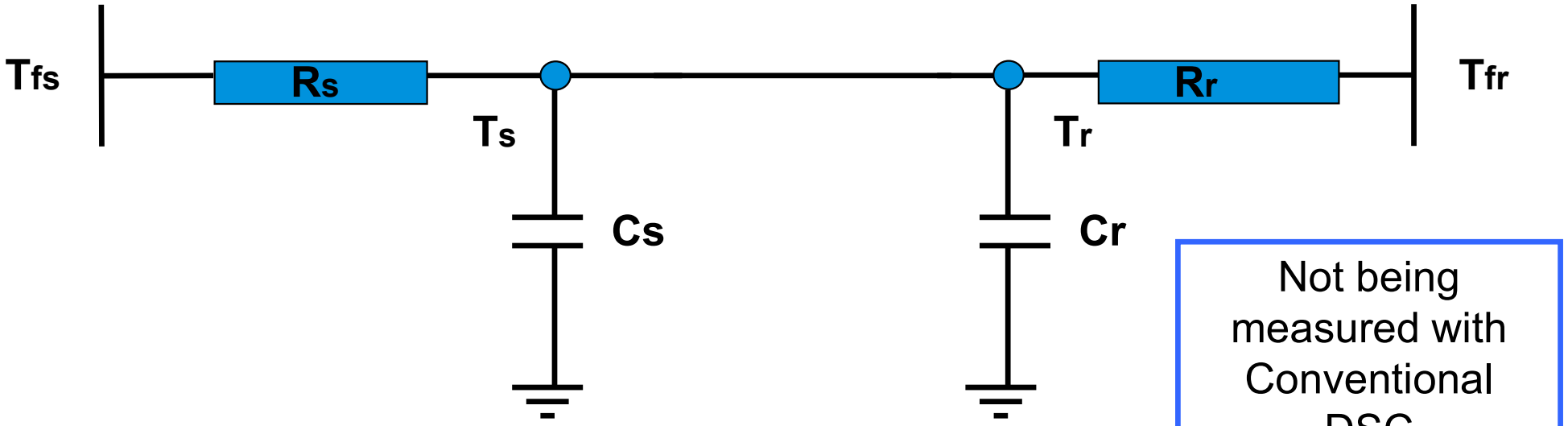
- The heat flow rate of an empty, perfectly symmetrical twin calorimeter should be zero
  - The heat flow is almost never zero because the DSC is rarely perfectly symmetrical as assumed due to the inevitable result of manufacturing tolerances and is unavoidable
    - To achieve a 1% thermal resistance imbalance between the sample and reference sensors would require a manufacturing tolerance of 0.00005" (0.00127mm)
- The thermal resistances between the sample sensor and the furnace is the same as the resistance between the reference sensor and the furnace
- The pan and sensor heat capacities are ignored
- The measured temperature equals sample temperature
- No heat exchange with the surroundings

# Consequences of the Assumptions

- The heat flow baseline is usually curved and has large slope and offset. Loss of sensitivity as a result of curvature in the baseline.
- The heating rate of the sample and reference calorimeters are not identical, resulting in reduced resolution.



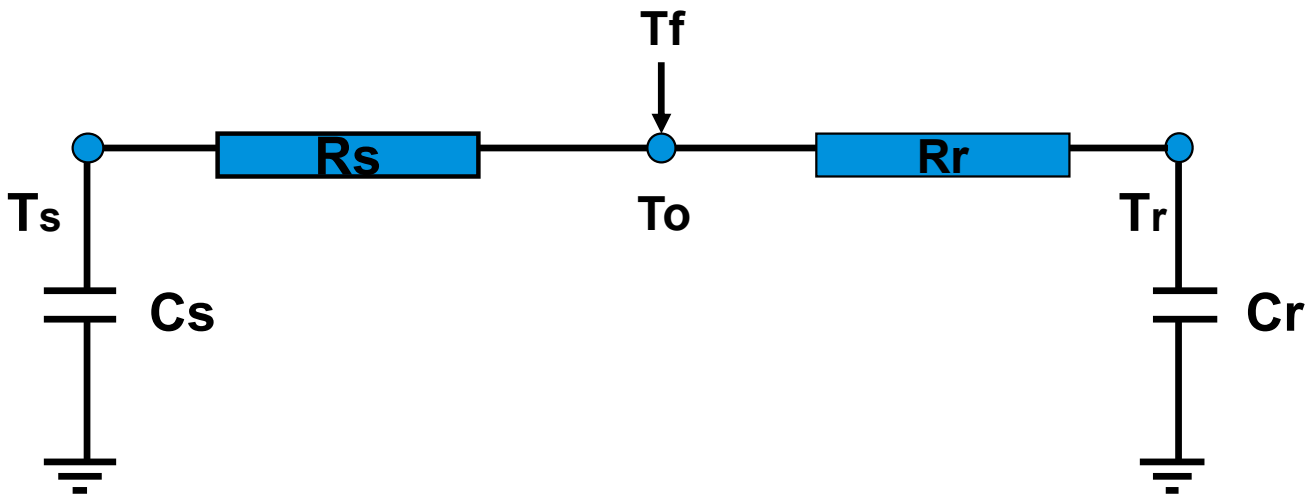
# Expanded Principles of DSC Operation Accounting for Imbalances

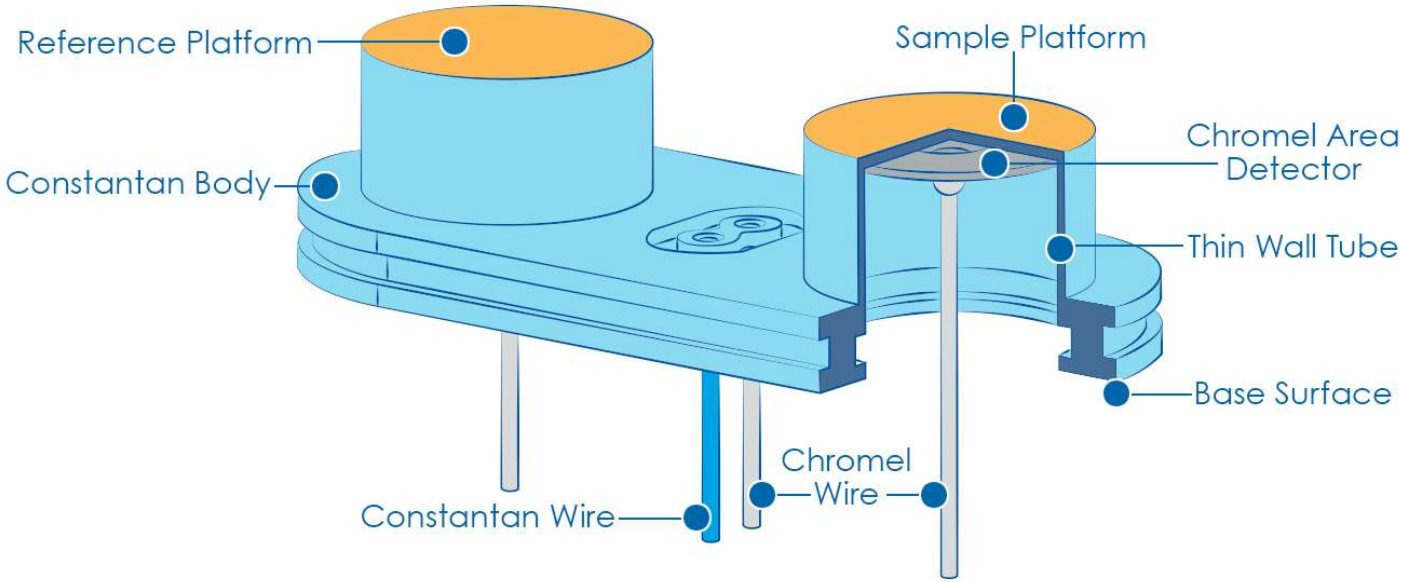



Not being measured with Conventional DSC

$$Q = \frac{Ts - Tr}{R} + \underbrace{A}_{\text{Thermal Resistance Imbalance}} + \underbrace{B}_{\text{Thermal Capacitance Imbalance}} + \underbrace{C}_{\text{Heating Rate Imbalance}}$$

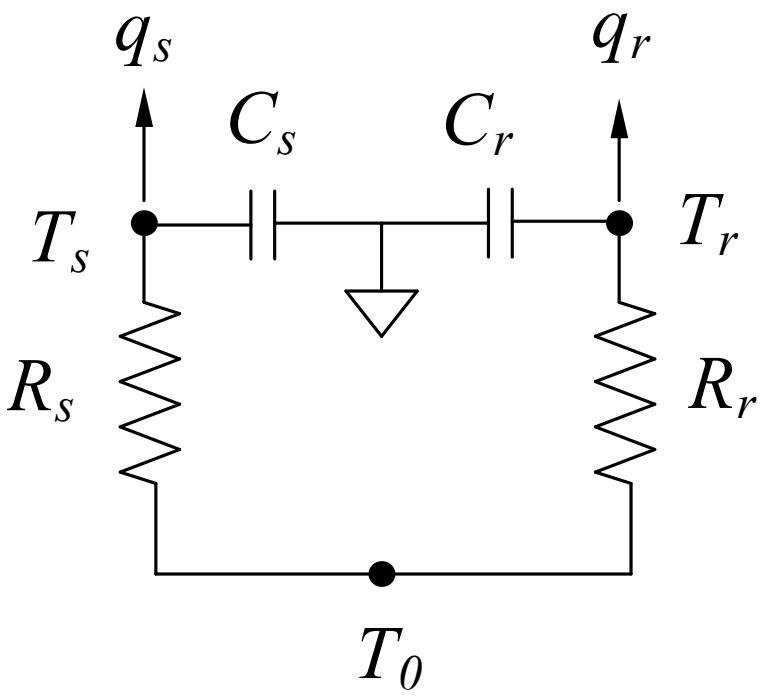
# What is Tzero Technology? (T4/T4P Heat Flow)



# 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

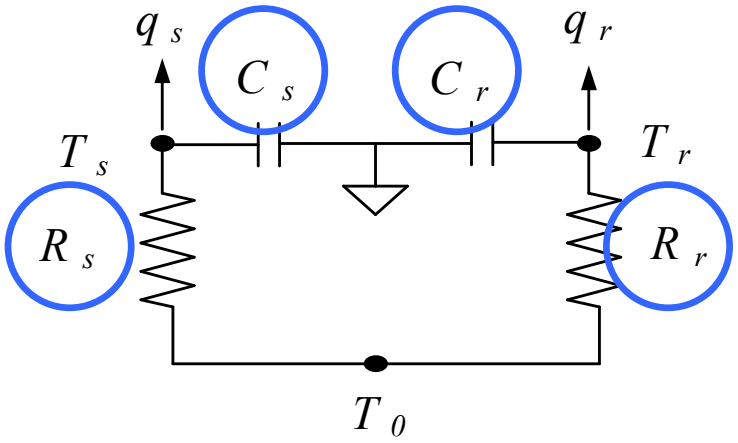
$$q_s = \frac{\Delta T_0}{R_s} - C_s \frac{dT}{dt}$$

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

*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 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?

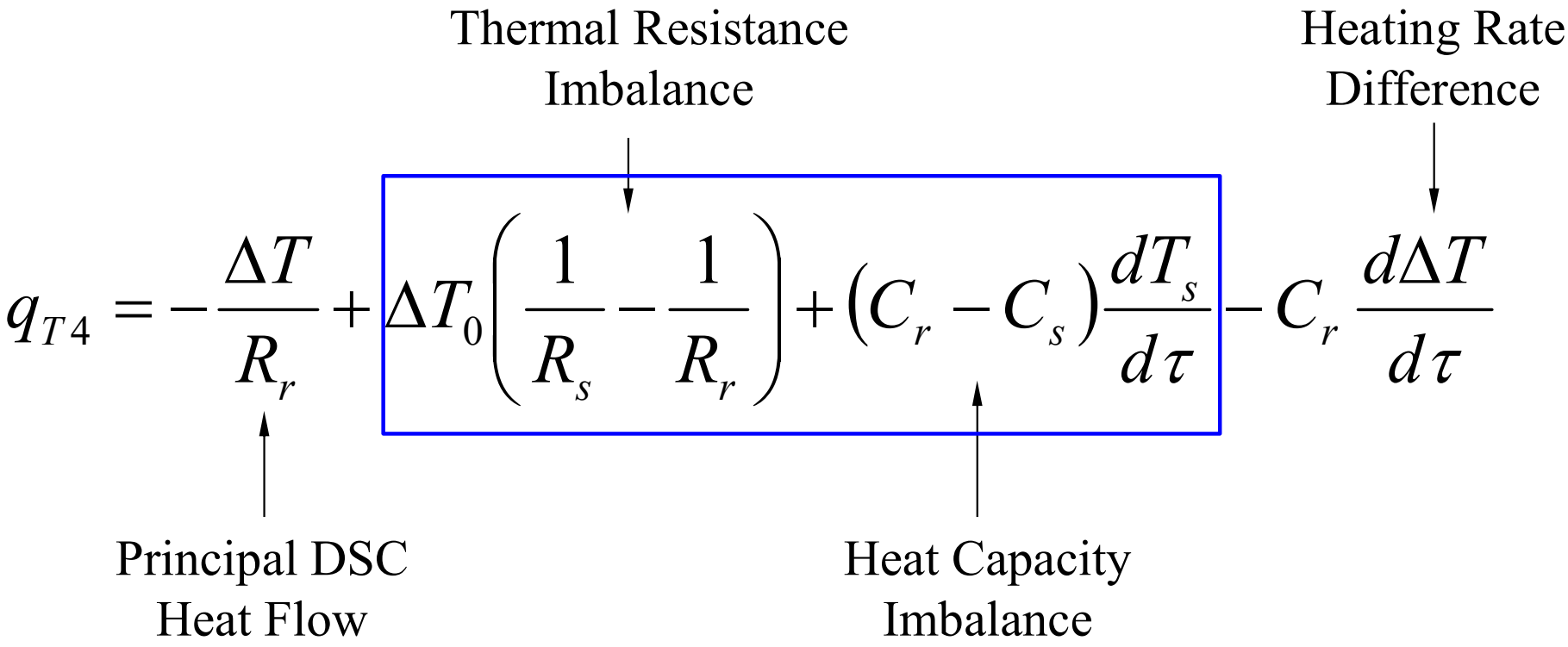
$$q = -\frac{\Delta T}{R_r} + \Delta T_0\left(\frac{1}{R_s} - \frac{1}{R_r}\right) + (C_r - C_s)\frac{dT_s}{d\tau} - C_r\frac{d\Delta T}{d\tau}$$

# Measuring the Sensor C's and R's

- The Tzero measurements are used to determine the C's and R's using two experiments
  - A temperature ramp of an empty cell
  - A temperature ramp with two sapphire disks placed directly on the DSC sensors

- On determination of the capacitance and resistance of the reference and sample side of the cell, these values are inputted into the expanded heat flow equation corresponding to T4 heat flow

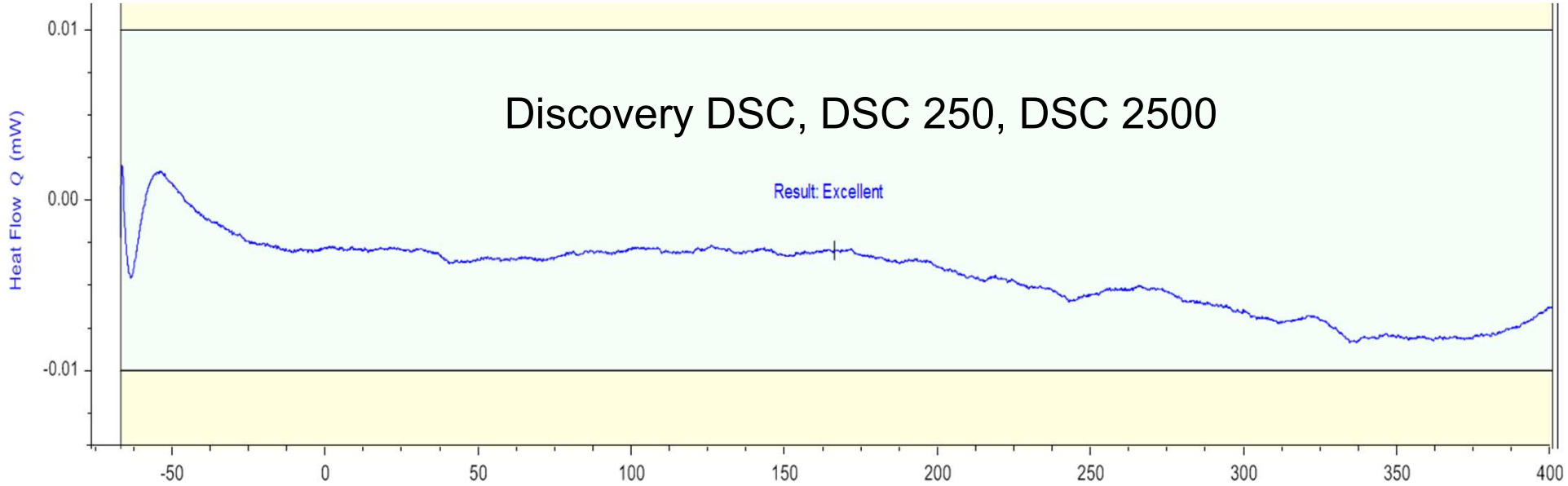
# Tzero™ Heat Flow Equation

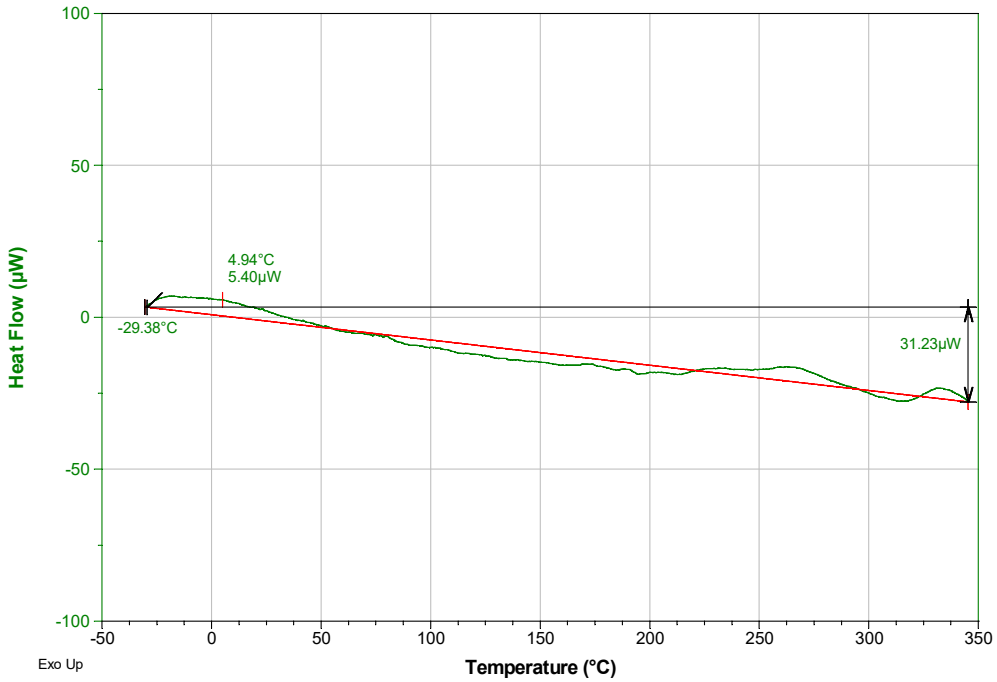


# Benefit of the Tzero heat flow measurements

- 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.

# Empty cell baseline using the Tzero™ heat flow equation

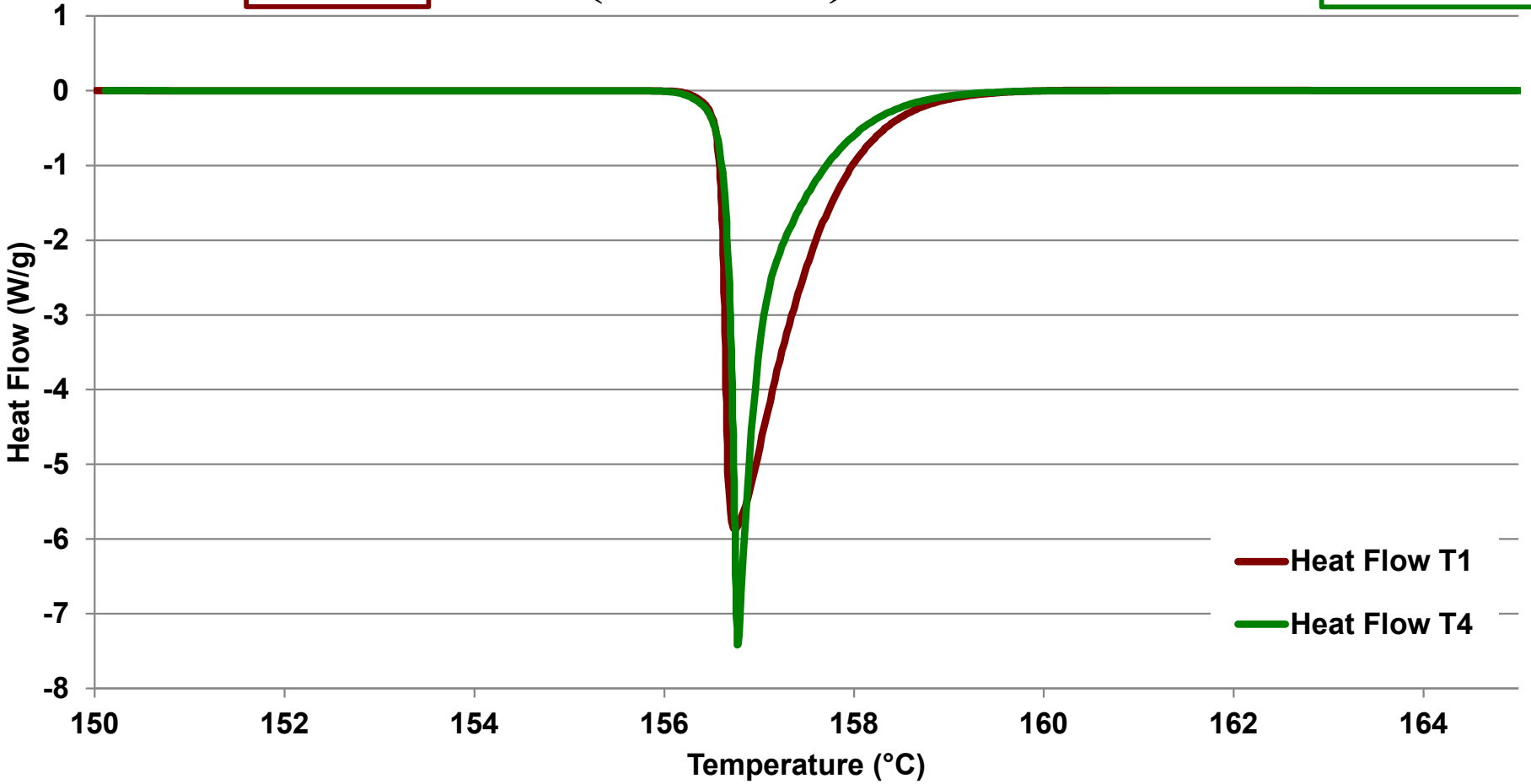



DSC Q2000

# Tzero Benefit: Improved Peak Resolution

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



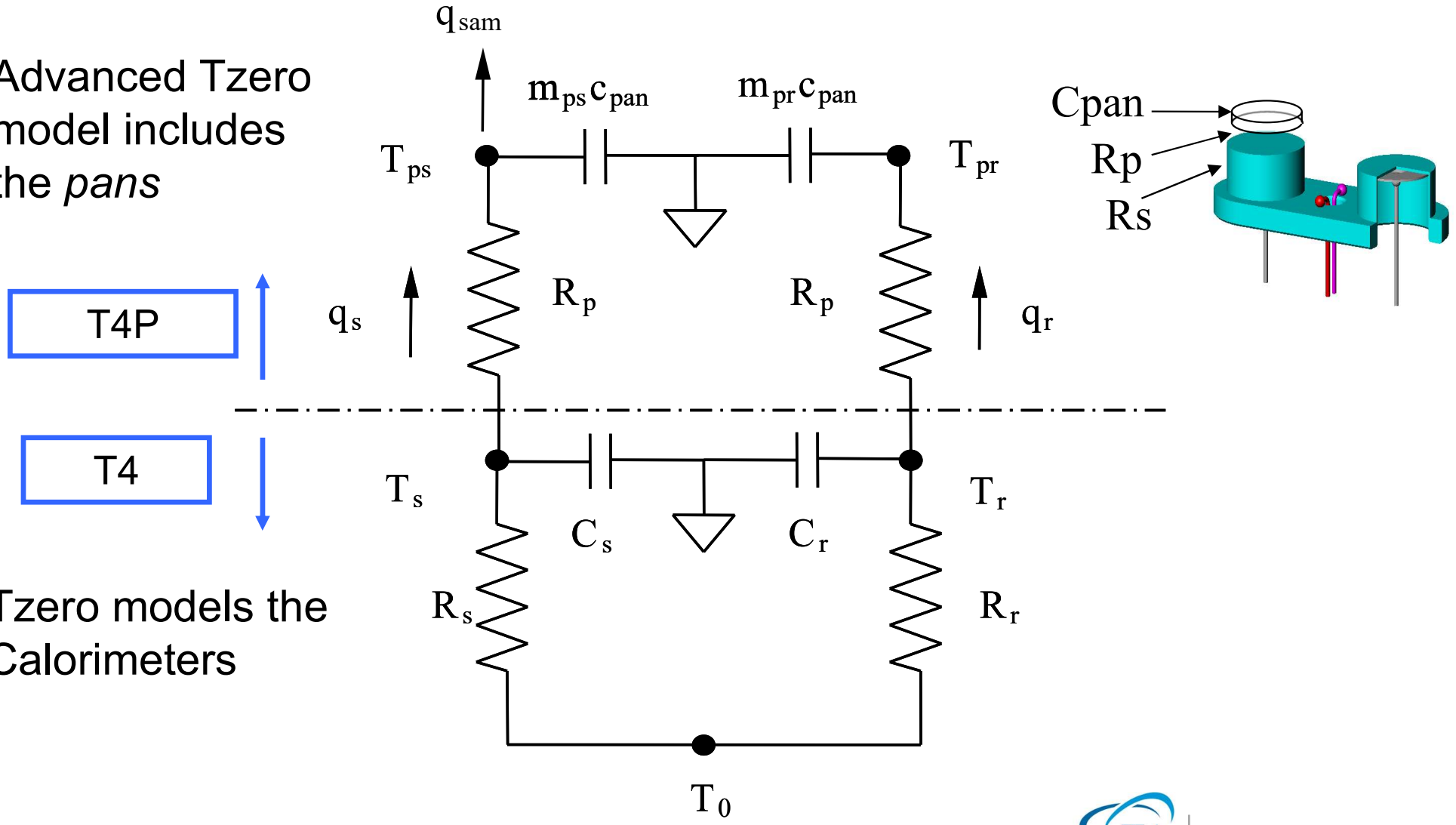
# Advanced Tzero Technology (T4P)

- 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; sample and reference pans rarely have the same mass.
- Advanced Tzero includes the capacitance and resistance of the pans so that the heating rate differences between the sample and reference calorimeters and pans can be corrected for.
- As a result peaks are taller and sharper; both resolution and sensitivity are dramatically improved.

# Advanced Tzero™ Model

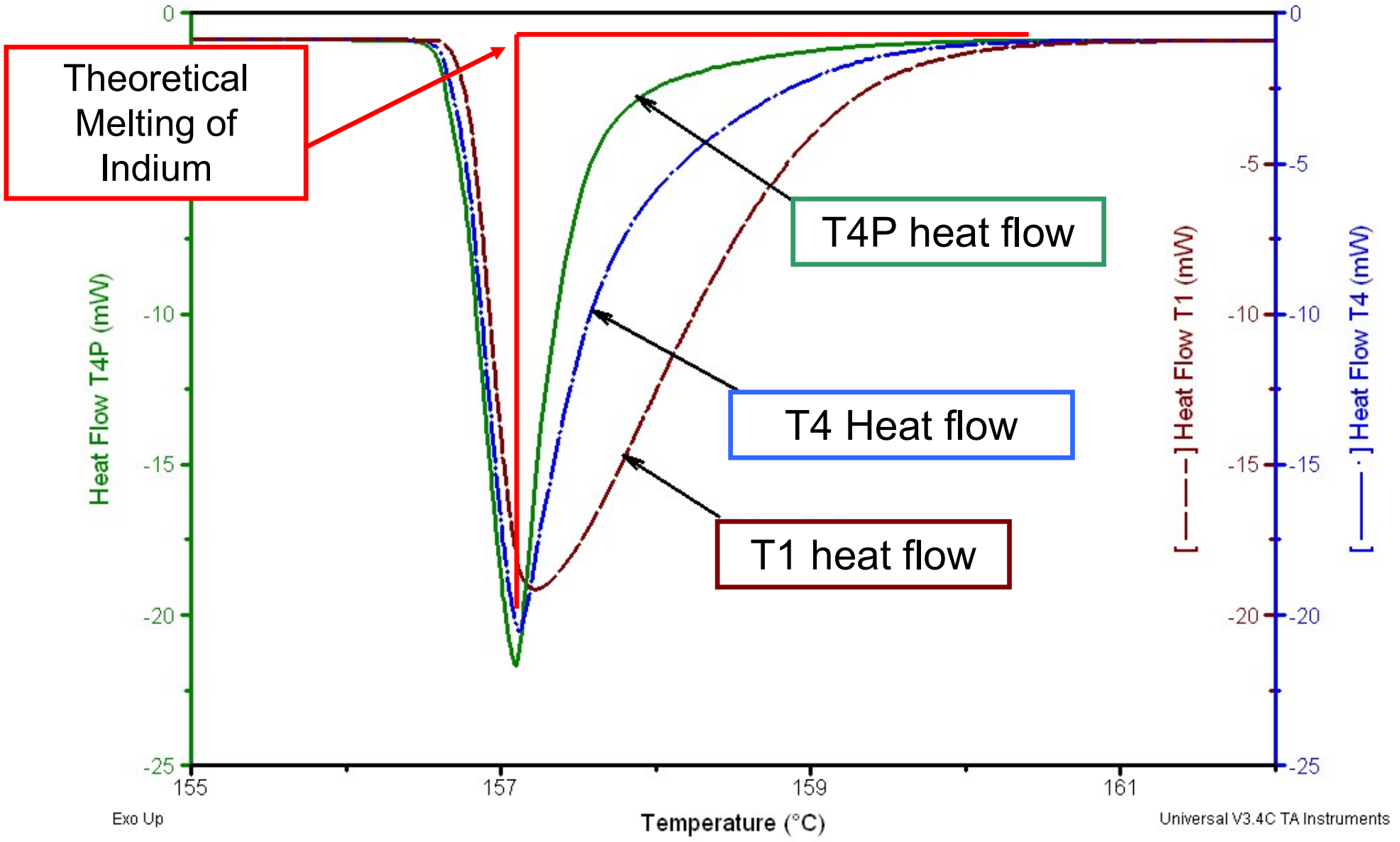
Advanced Tzero is a further refinement of the Tzero model and takes the measurement up to the sample pan, ***one step closer to the actual sample***

Advanced Tzero model includes the *pans*




Tzero models the Calorimeters

# Indium with T1, T4 and T4P Heat Flow Signals Improvements to Sensitivity and Resolution



# Modulated DSC® Theory (MDSC®)

# 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.

# MDSC® Theory: Heat Flow Signals

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

**Total Heat Flow**

- All Transitions

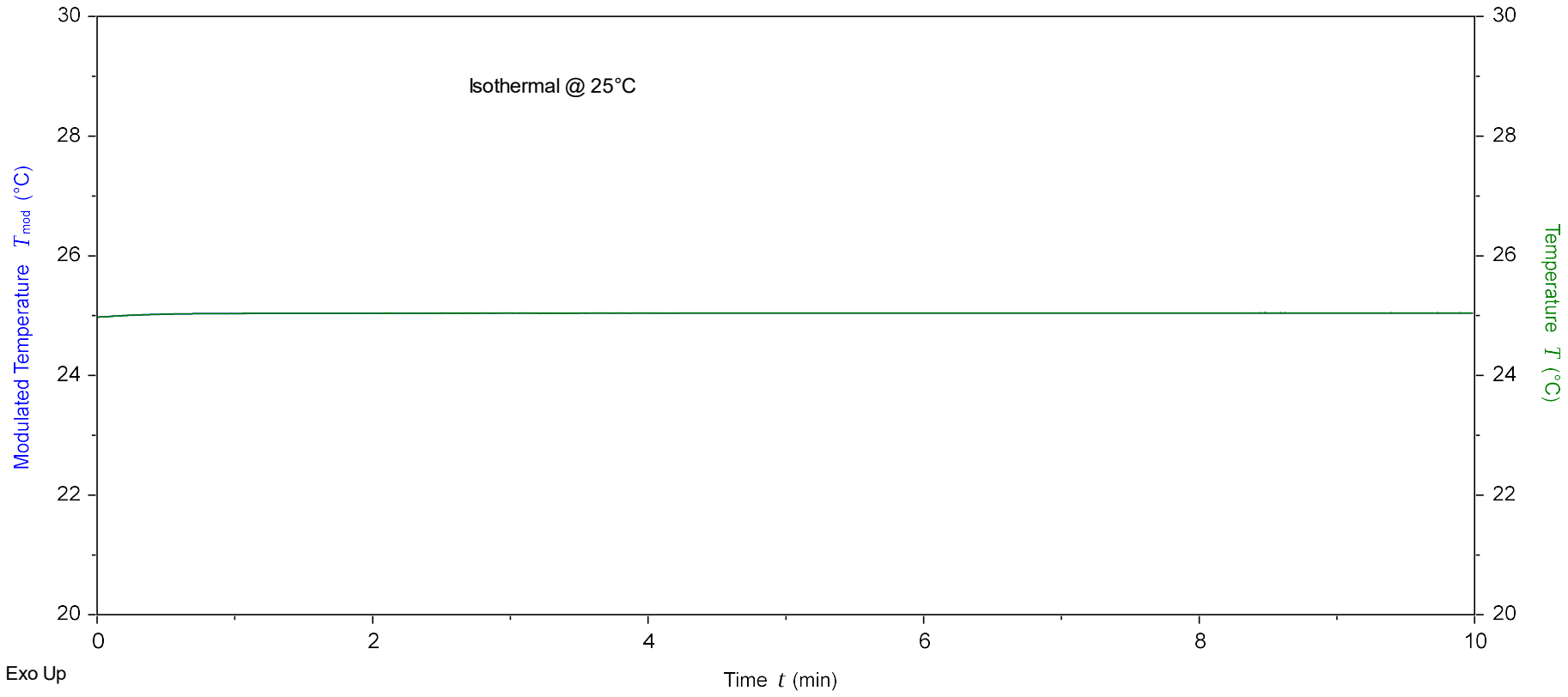
**Reversing Heat Flow**

- Heat Capacity
- Glass Transition
- Melting

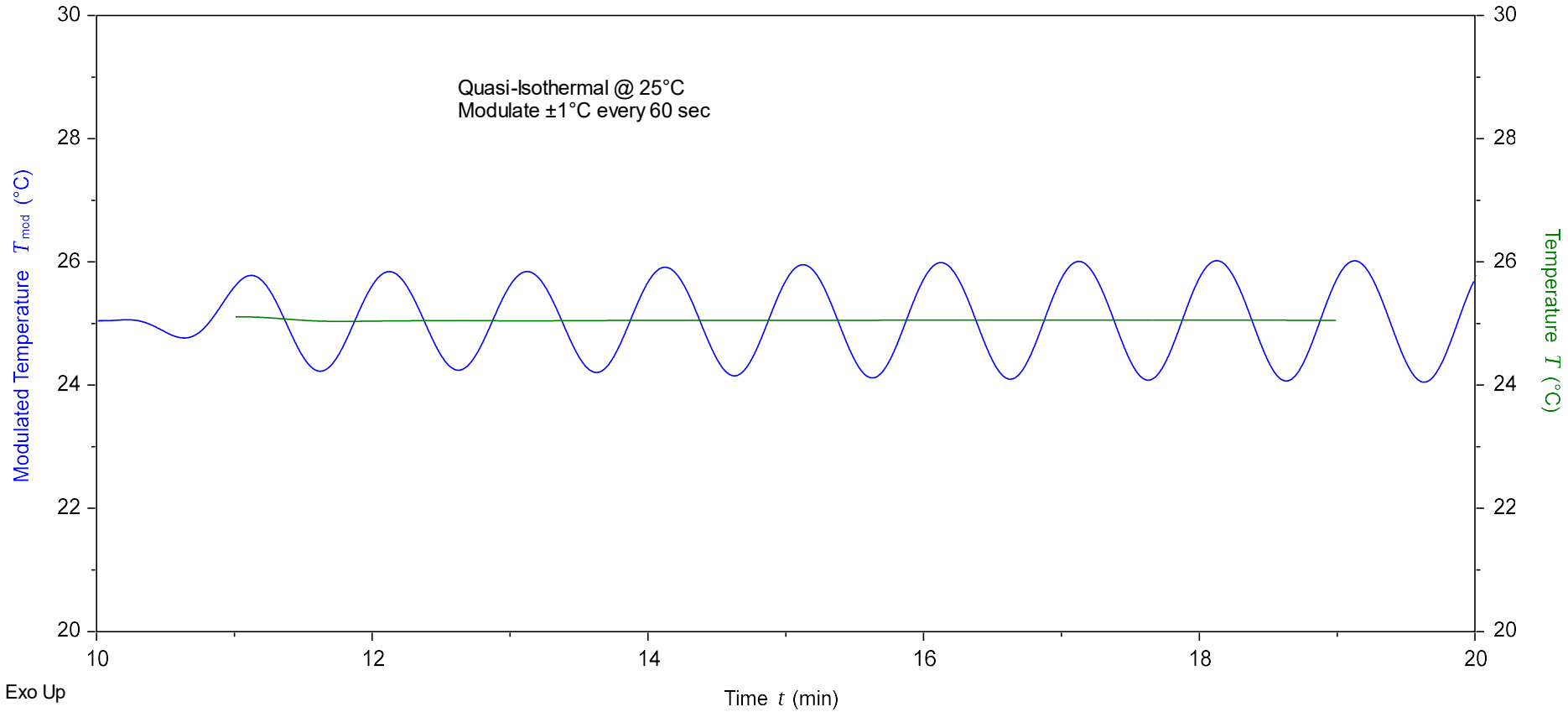
**Non-Reversing Heat Flow**

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

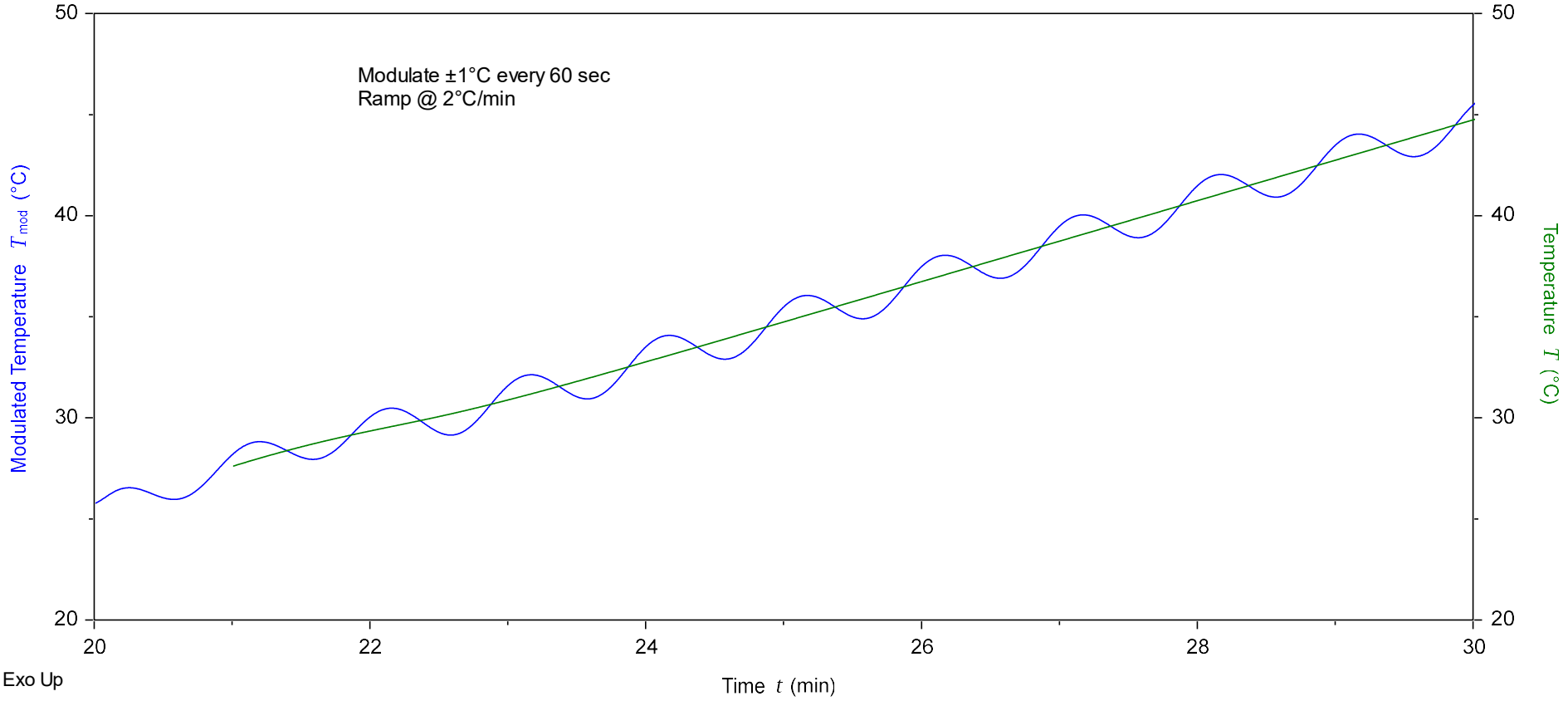
# Isothermal @ 25°C



# MDSC - Quasi-Isothermal @ 25°C



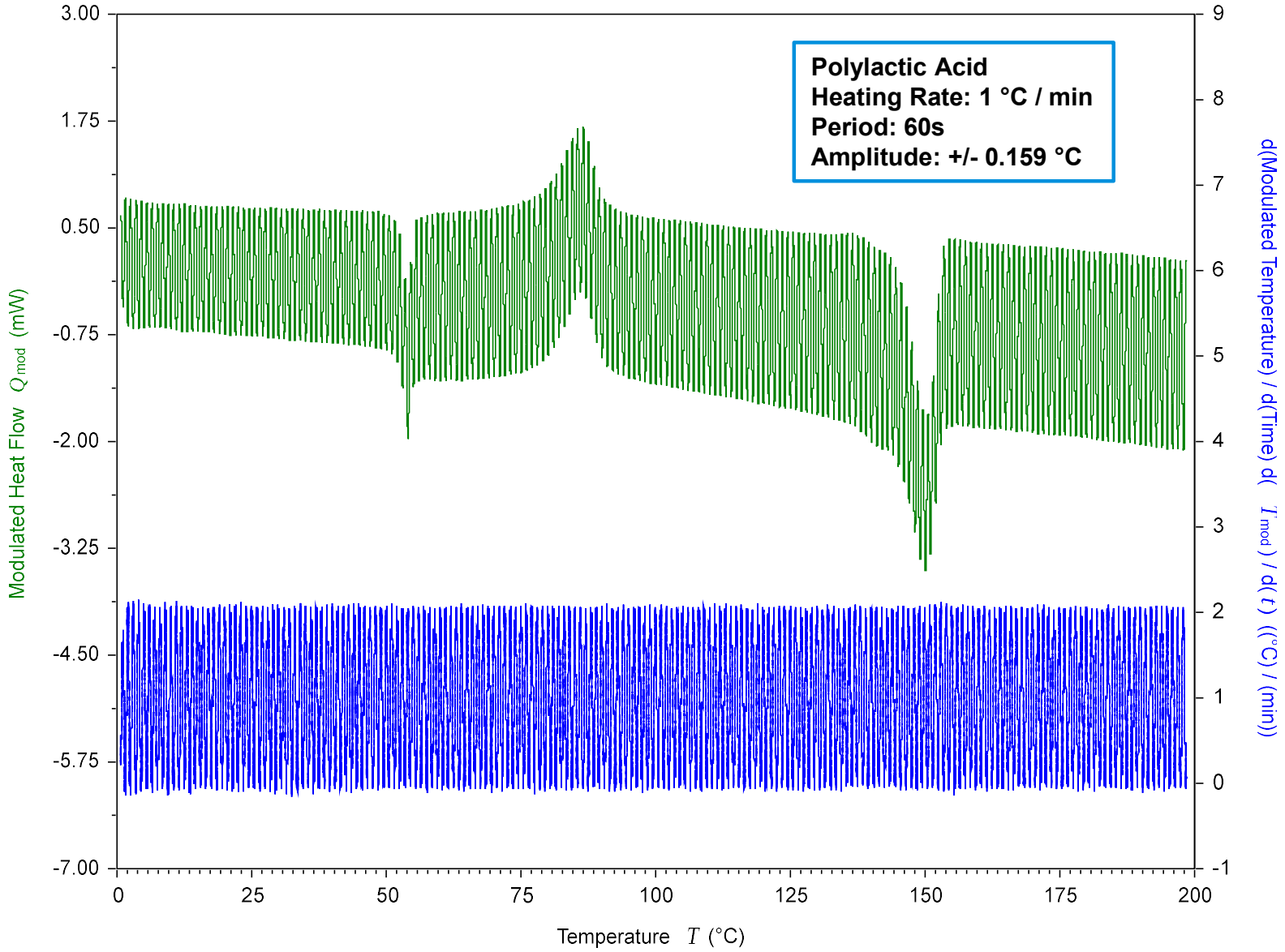
# MDSC – 1°C amplitude, every 60 sec, @ 2°C/min



# 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)

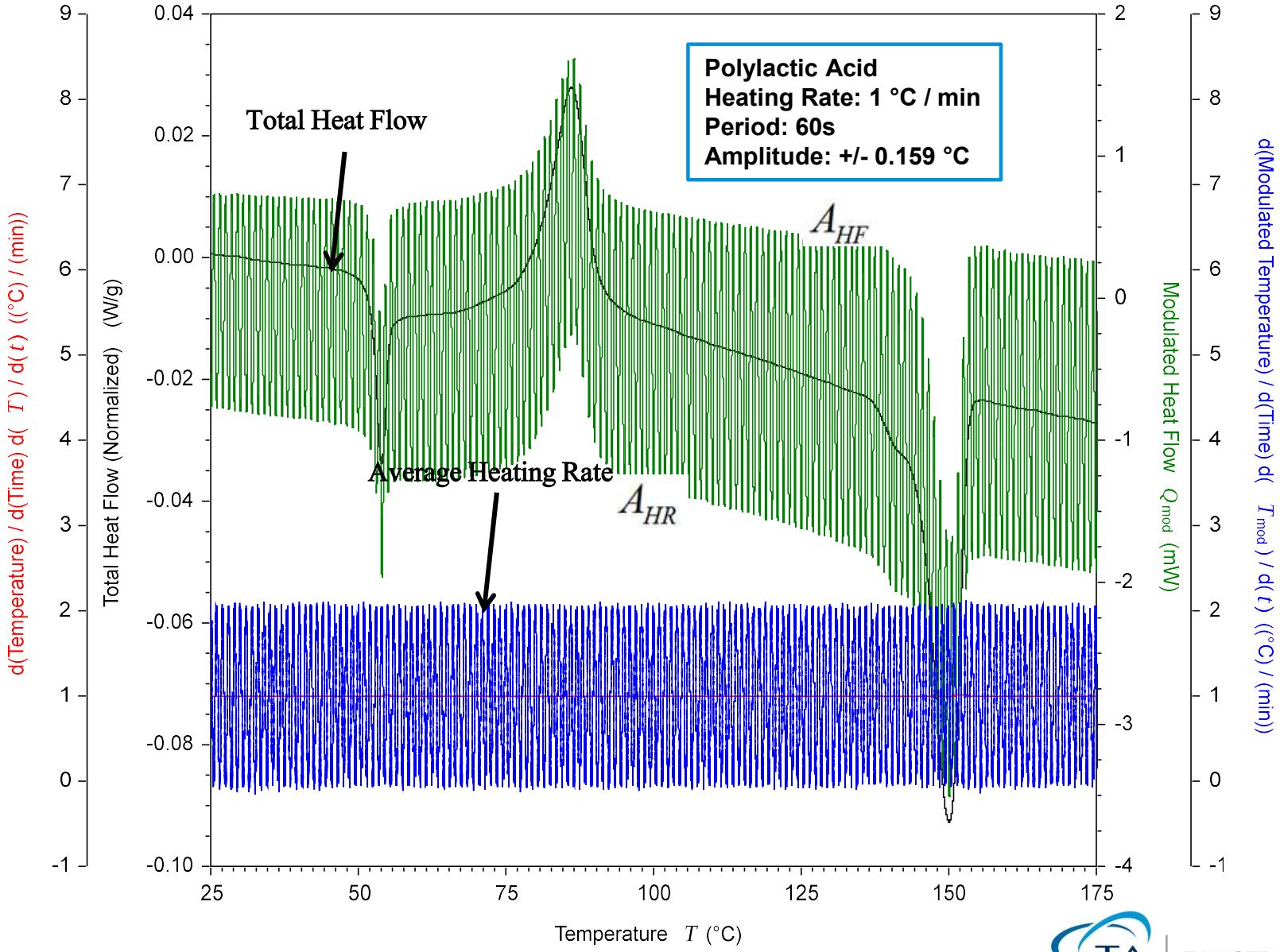
# MDSC® Raw Data Signals



# 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:
  - $\langle dQ/dt \rangle$ = average heat flow; Q = heat
  - $A_{HF}$= Amplitude of heat flow modulation
  - $A_{HR}$ = Amplitude of modulated heating rate

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



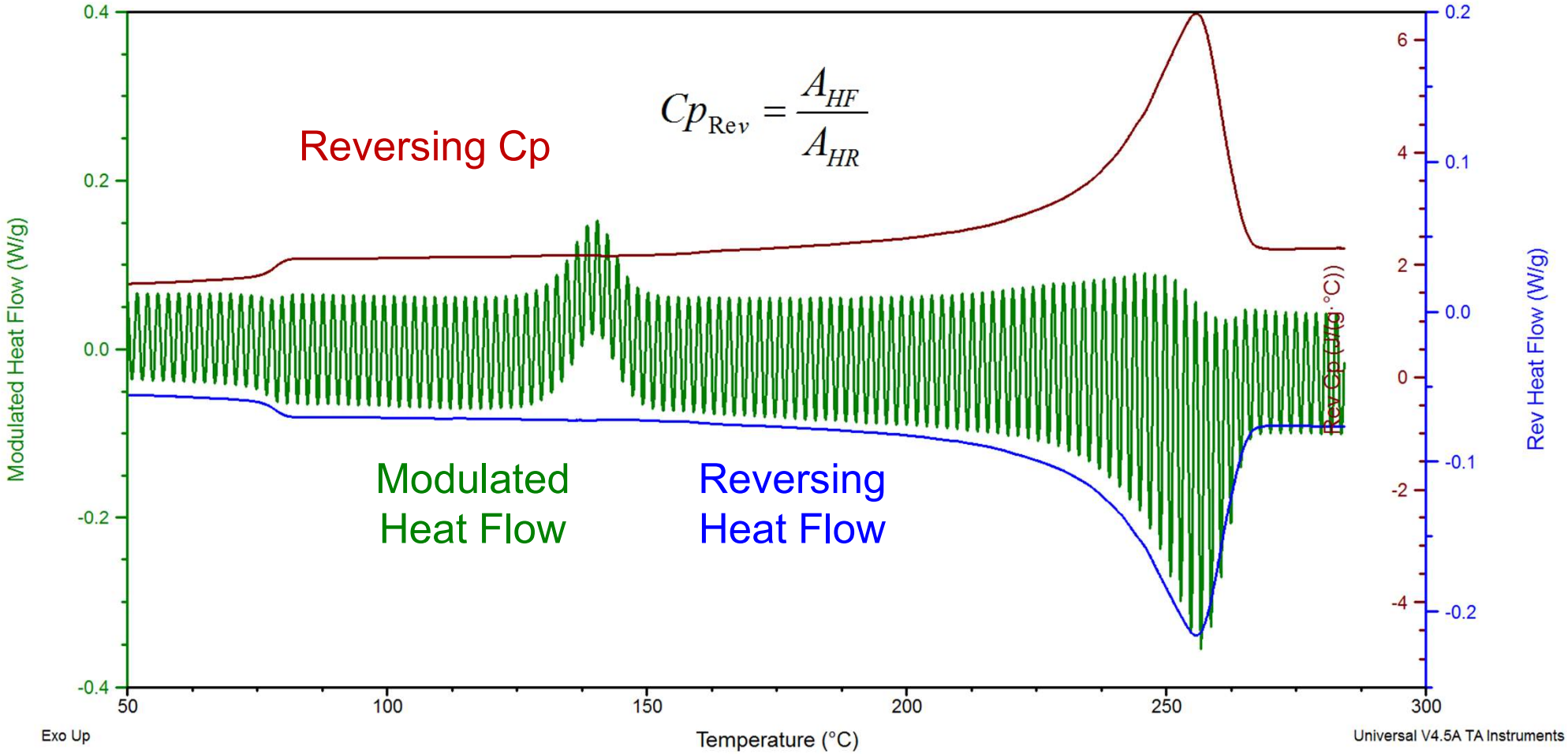
# MDSC Theory: Heat Flow Signals

$$\langle dQ/dt \rangle = \text{Average Heat Flow}$$

$$Cp_{Rev}\beta = \text{Reversing Heat Flow}$$

$$\langle dQ/dt \rangle - Cp_{Rev}\beta = \text{Non-Reversing Heat Flow}$$

# MDSC® Theory: Calculation of MDSC® Reversing Heat Flow and Reversing *Cp*

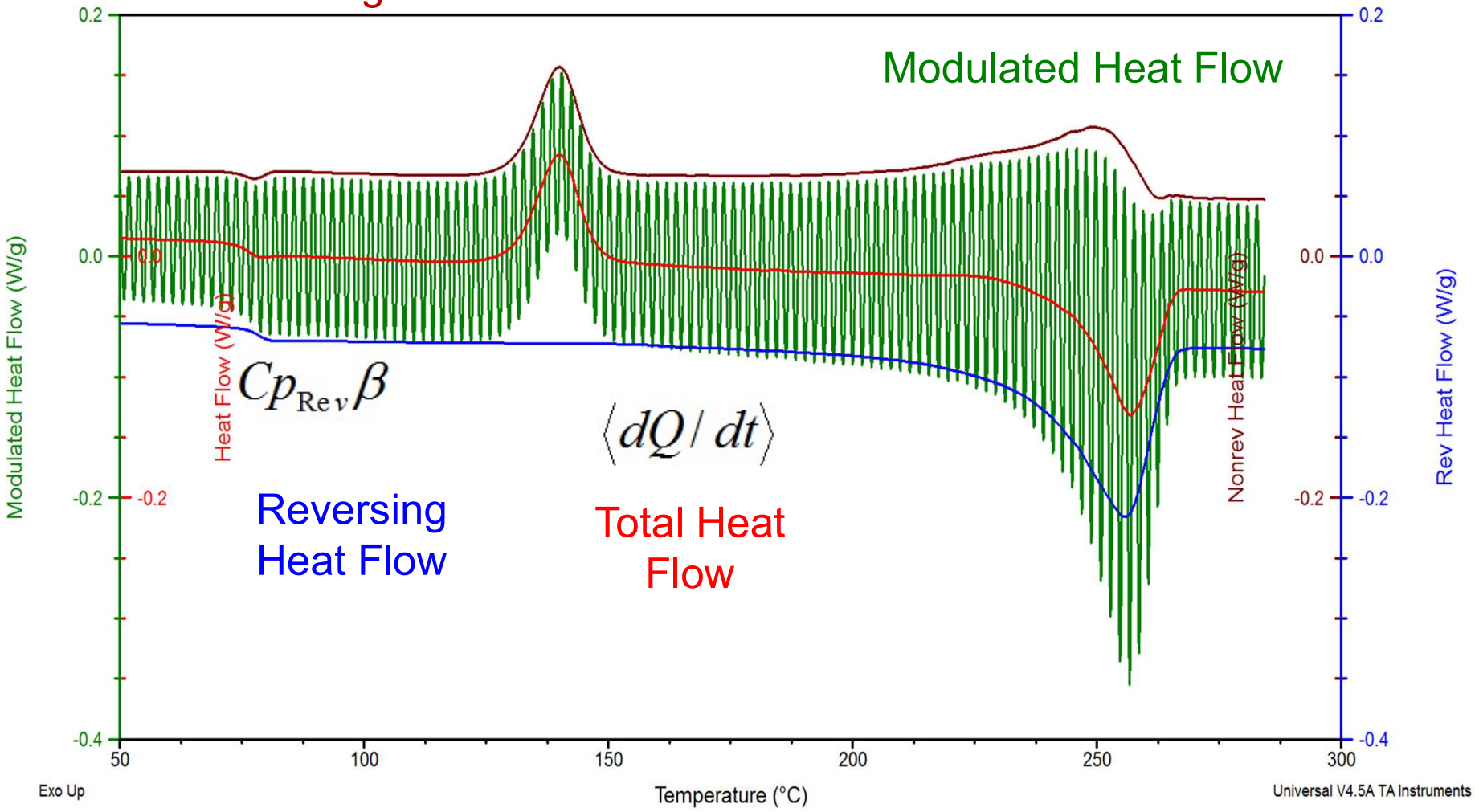


# MDSC® Theory: Calculated MDSC® Heat Flow Signals Summary

$$\langle dQ/dt \rangle - Cp_{Rev}\beta$$

$$\frac{dQ}{dt} = Cp(\beta + \omega A_T \cos \omega t)$$

Non-Reversing Heat Flow



# Calibration & Verification

# The DSC Heat Flow Rate Equation

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

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

- A DSC is calibrated for the heat flow enthalpy and temperature. Baseline calibrations are performed per manufacturers recommendations.

# International Standards pertaining to DSC calibrations

- American Society of Testing and Materials, ASTM
  - www.astm.org
- International Organization of Standards, ISO
  - www.iso.org
- Deutsches Institut für Normung/German Institute for Standardization, DIN
  - www.din.de/en

# ASTM Standards for DSC Heat Flow, Temperature and Enthalpy Calibration

- ASTM E 967 - Standard Test Method for Temperature Calibration of Differential Scanning Calorimeters and Differential Thermal Analyzers

- ASTM E 968 - Standard Practice for Heat Flow Calibration of Differential Scanning Calorimeters

# Calibration of specific instrument models

**Tzero**

Measurement of Rs and Cs

- DSC2500
- DSC250
- Q2000
- Q200

**Baseline calibration**

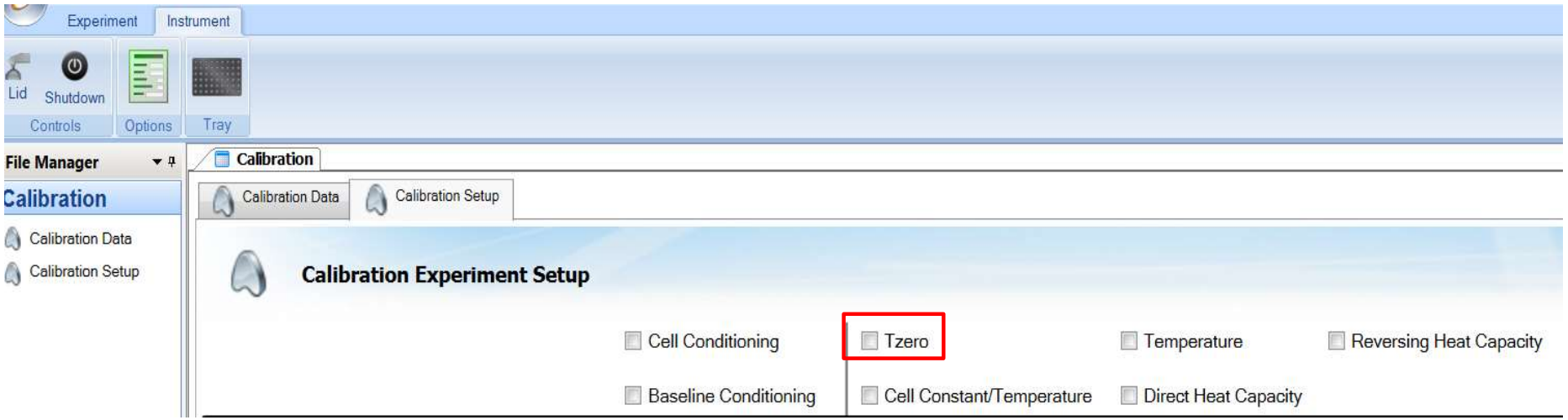
Measurement of slope and offset

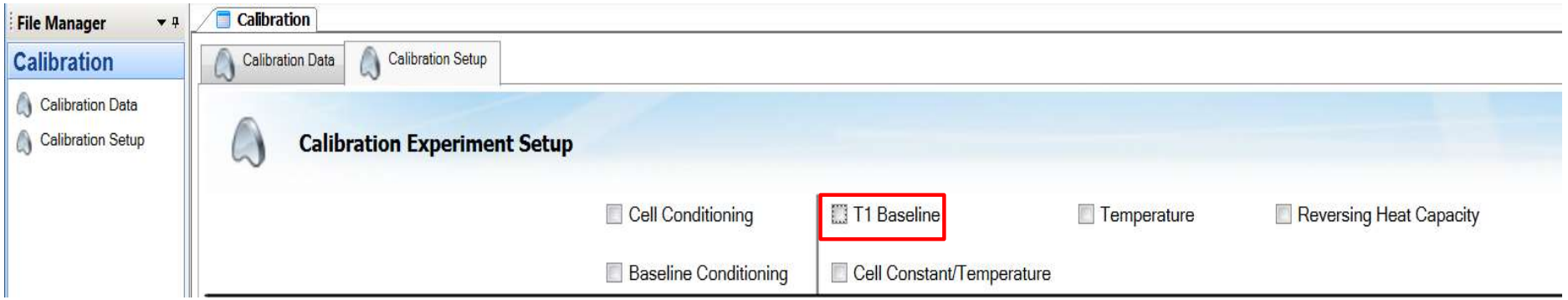
- DSC 25
- Q20

**Cell constant and temperature**

- All DSCs

# Calibration Setup in Trios



# General calibration and verification guidelines

- Calibration
  - Use Calibration Mode
  - Calibrate upon installation
  - Re-calibrate if does not pass verification or if instrument setup is modified (see previous slide)

- Verification
  - 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

# 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

# ASTM E 967 - Standard Test Method for Temperature Calibration of DSC's

- For transition temperature, calibration is required with known reference standards.
  - Pure metals (indium, lead, etc.) typically used
  - Extrapolated onset is used as melting temperature
  - Sample is fully melted at the peak

- This test method consists of heating the calibration materials at a controlled rate in a controlled atmosphere through a region of known thermal transition. The heat flow into the calibration material or the difference of temperature between the calibration material and a reference is monitored and continuously recorded. A transition is marked by the absorption of energy by the specimen resulting in a corresponding endothermic peak in the heating curve.

# Instrument setup factors affecting calibration

- Purge Gas
  - 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

# ASTM E 967 - Temperature Calibration of DSC's


Indium (156.6°C)

Can be re-used, can pre-melt


Tin (231.9°C)

Has multiple crystalline forms,

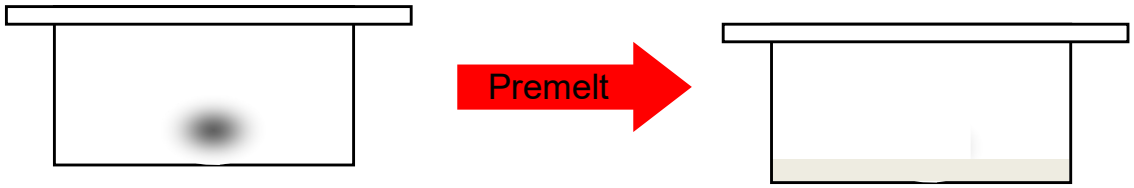
use once – no pre-melt


Zinc (419.5°C)

Can easily oxidize and alloy with container, use once – no pre-melt

# Temperature and Cell Constant Calibration

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




- Verify at least once a month

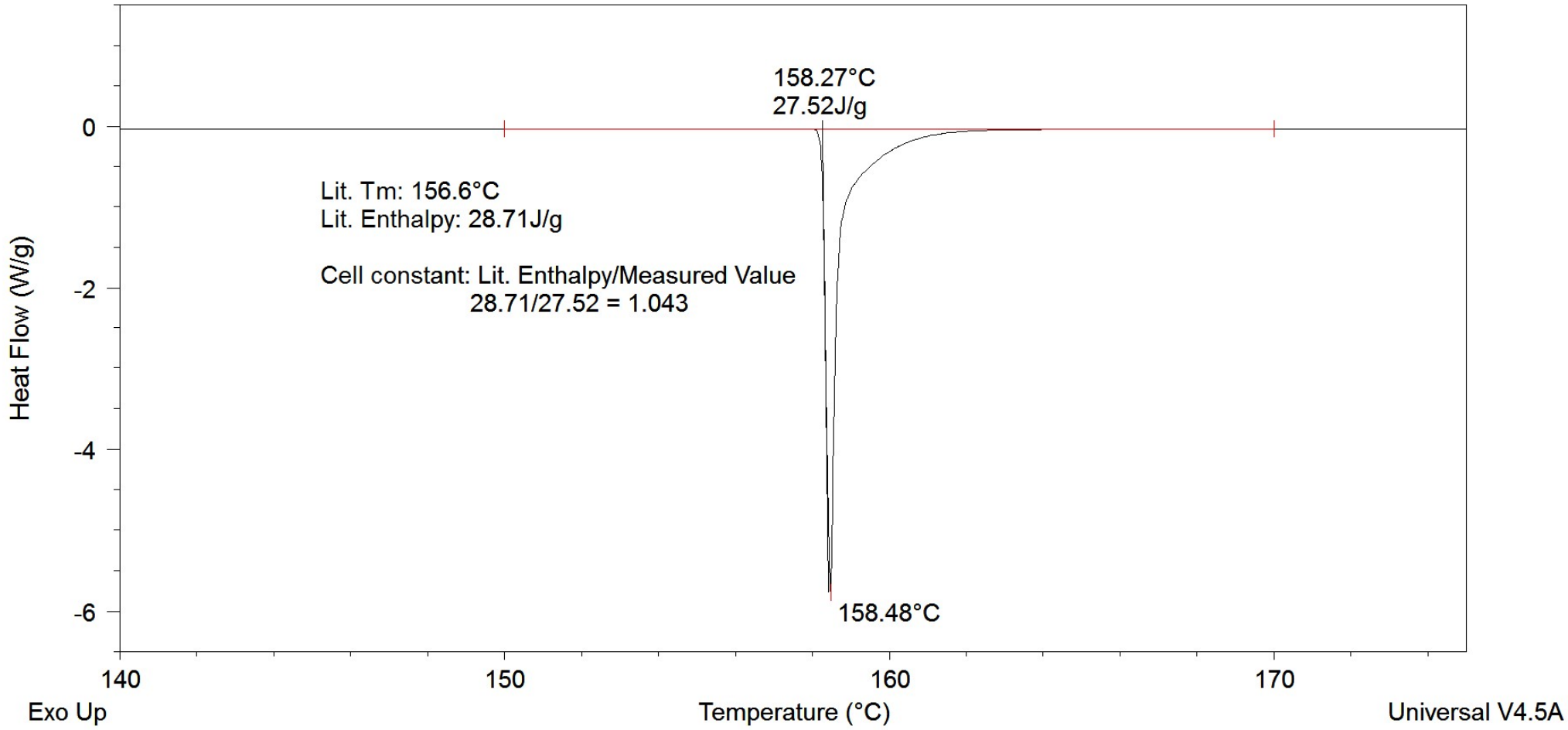
- Typical values for cell constant:
  - 0.9 to 1.2 (in N2)
  - Helium will typically give higher values for the cell constant

# Verifying Cell Constant & Temperature

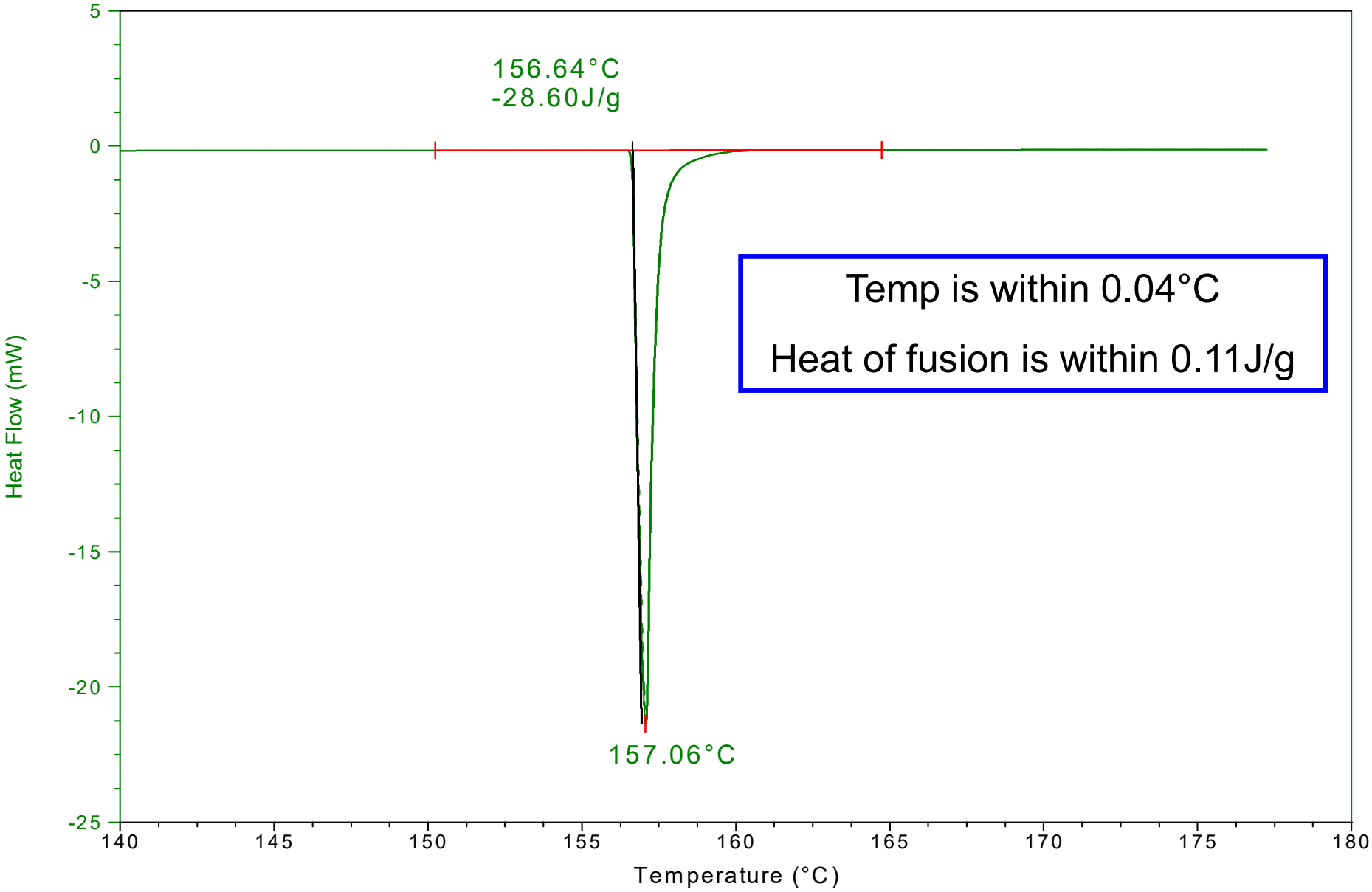
- Run Indium as a sample (i.e. in standard mode not calibration mode)
- Analyze melt and record melt onset & heat of fusion
- Compare to known values
  - Melting of In 156.6°C
  - Heat of Fusion 28.71J/g

# Calorimetric and Temperature Calibration (Un-calibrated Data – No Correction Factors Applied)

Sample: Indium



# Verifying Cell Constant & Temperature



# Temperature Calibration of DSC's

- 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
  - Water # 0°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

# A note on certified and 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

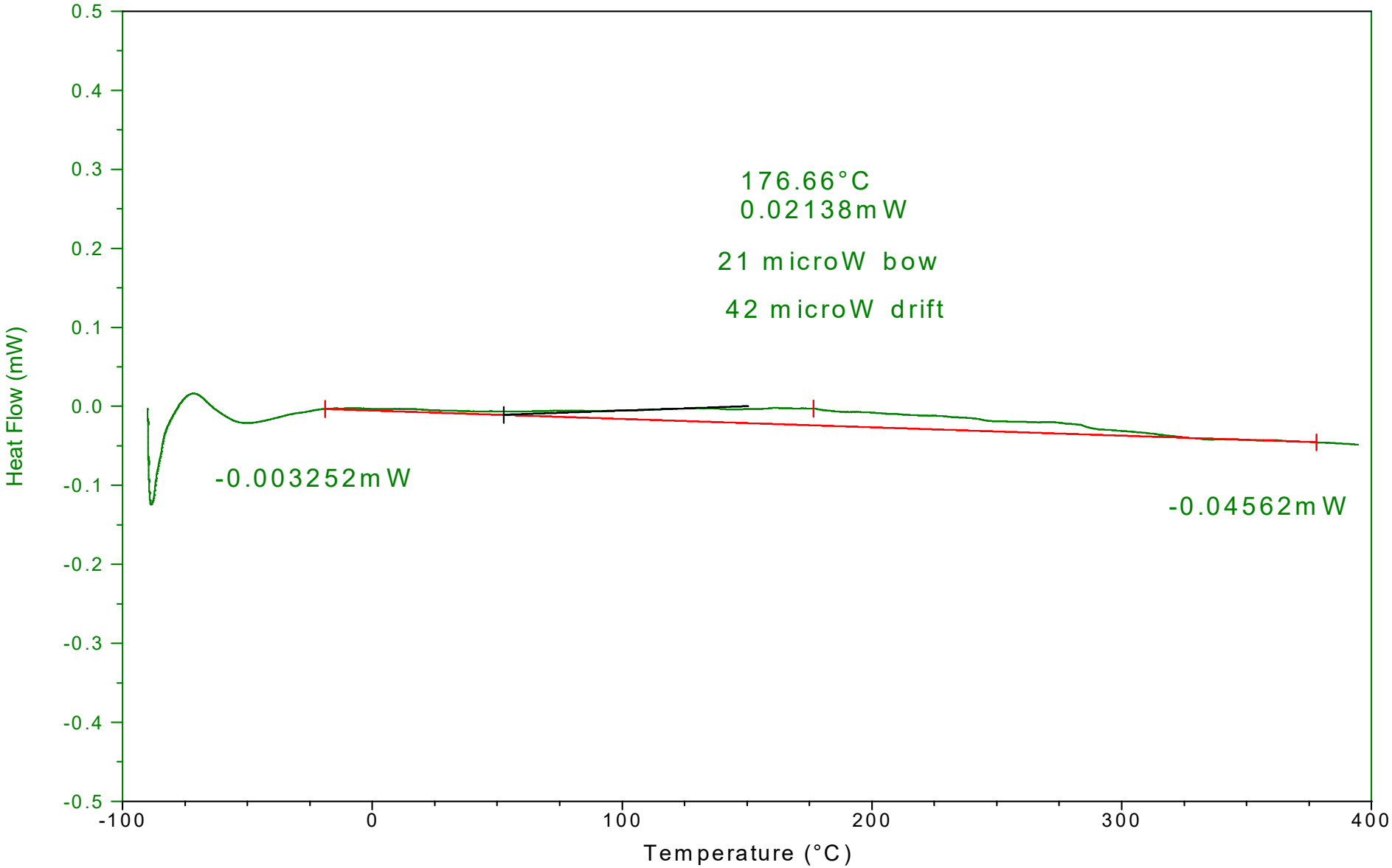
# Verifying Baseline

- 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 bow, drift and compare to instrument specifications.
  - Verify performance periodically

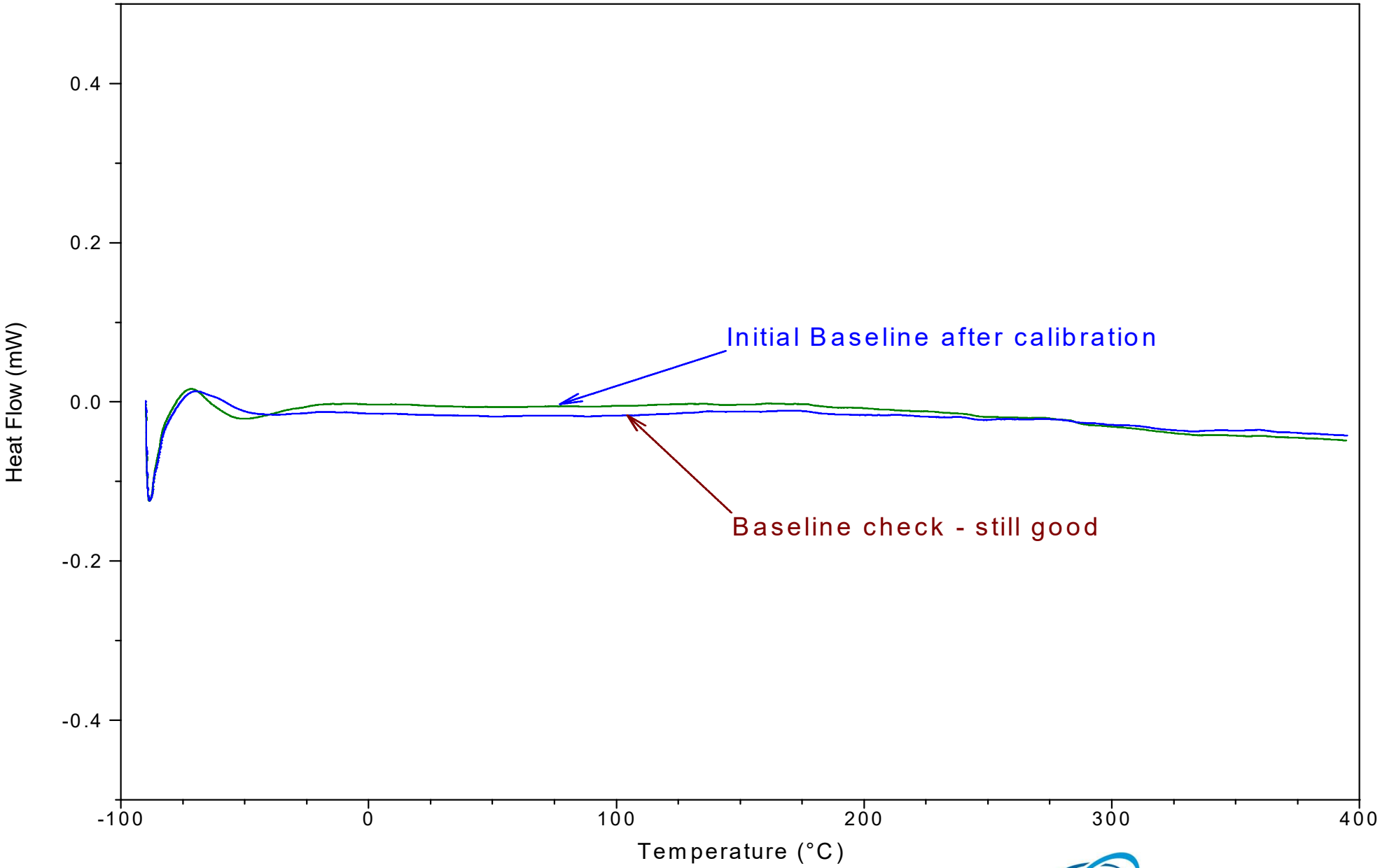
# Verifying Baseline

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

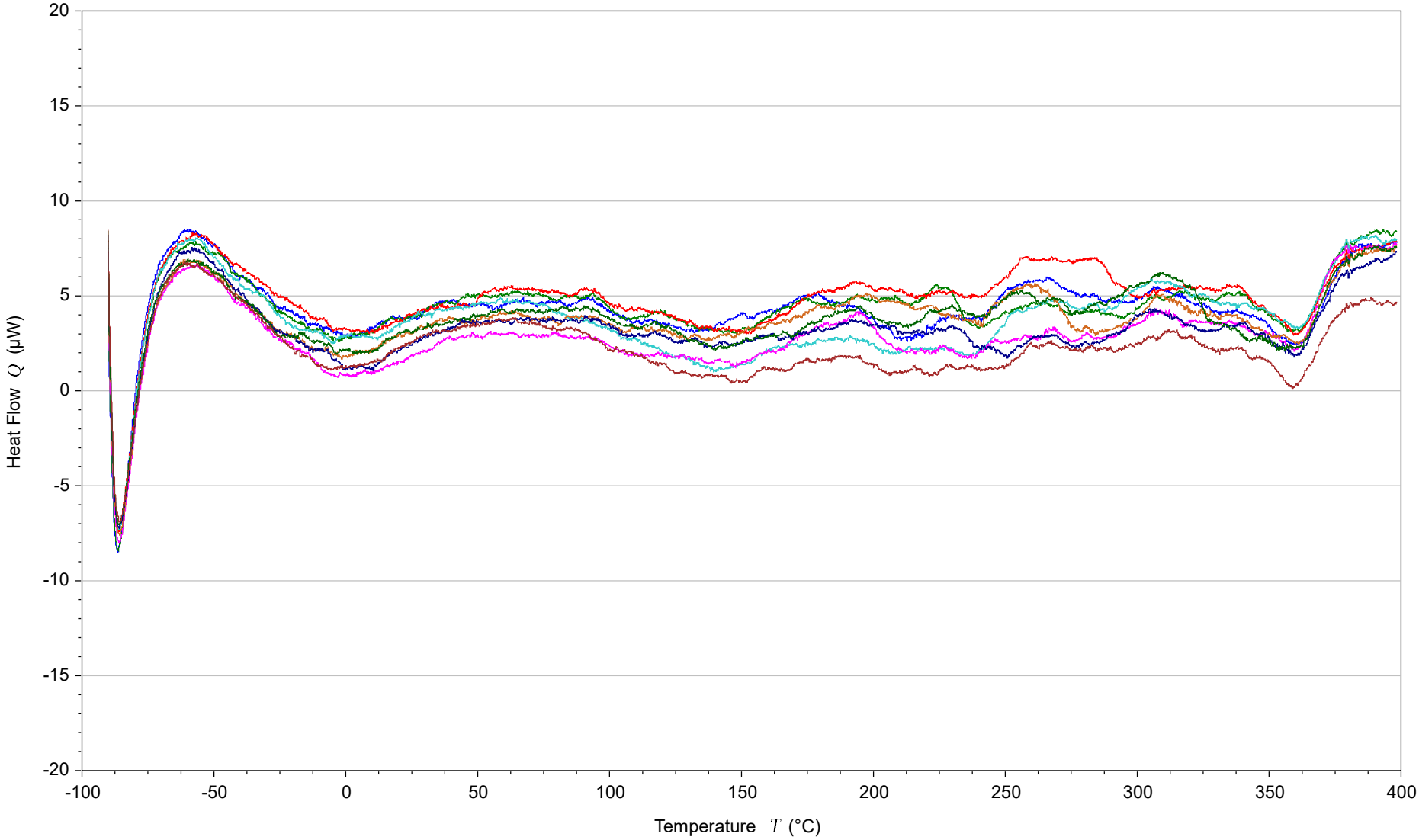
# Verifying Baseline



# Verifying Baseline



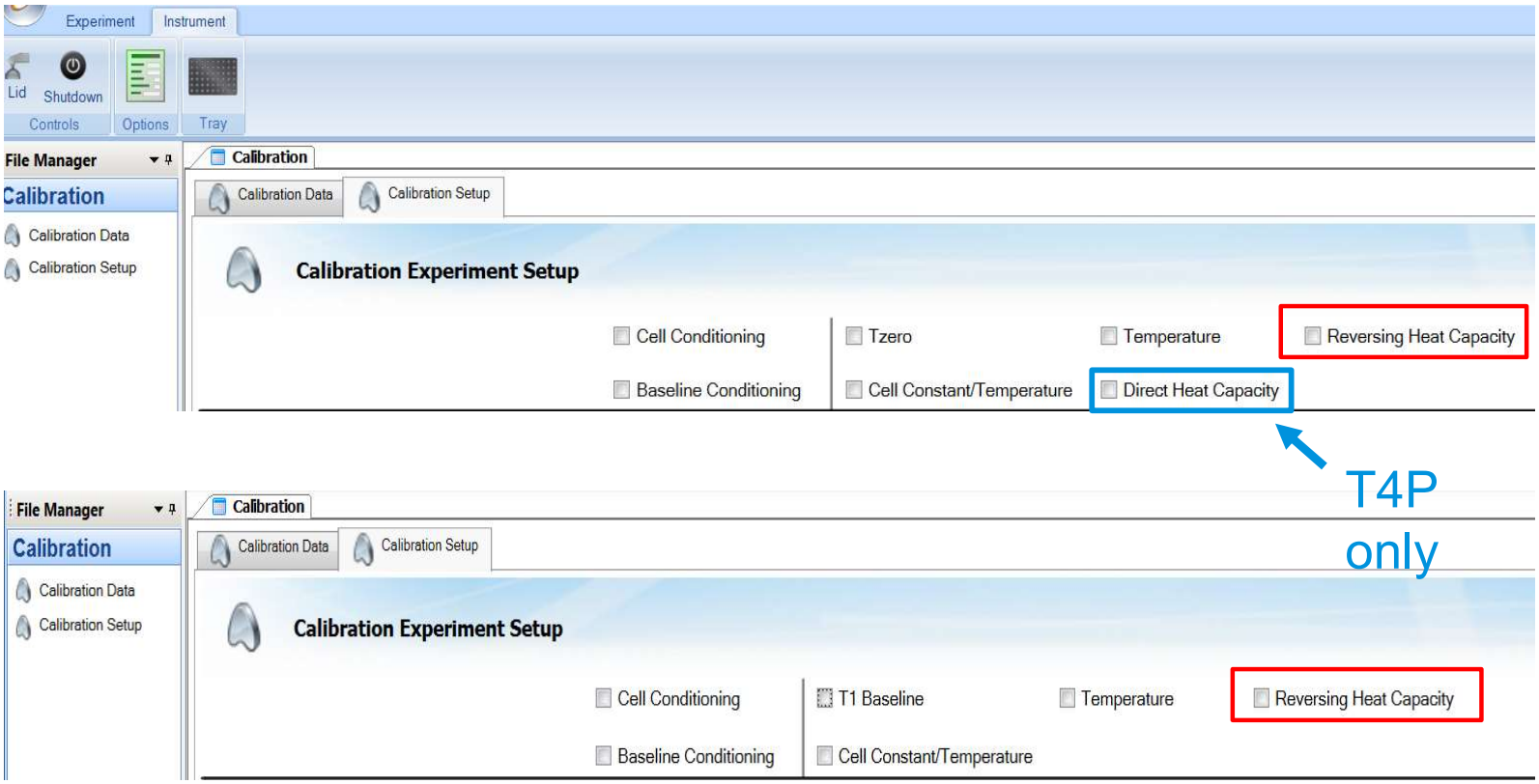
# Empty Cell Baseline at 20 deg/min – DSC2500



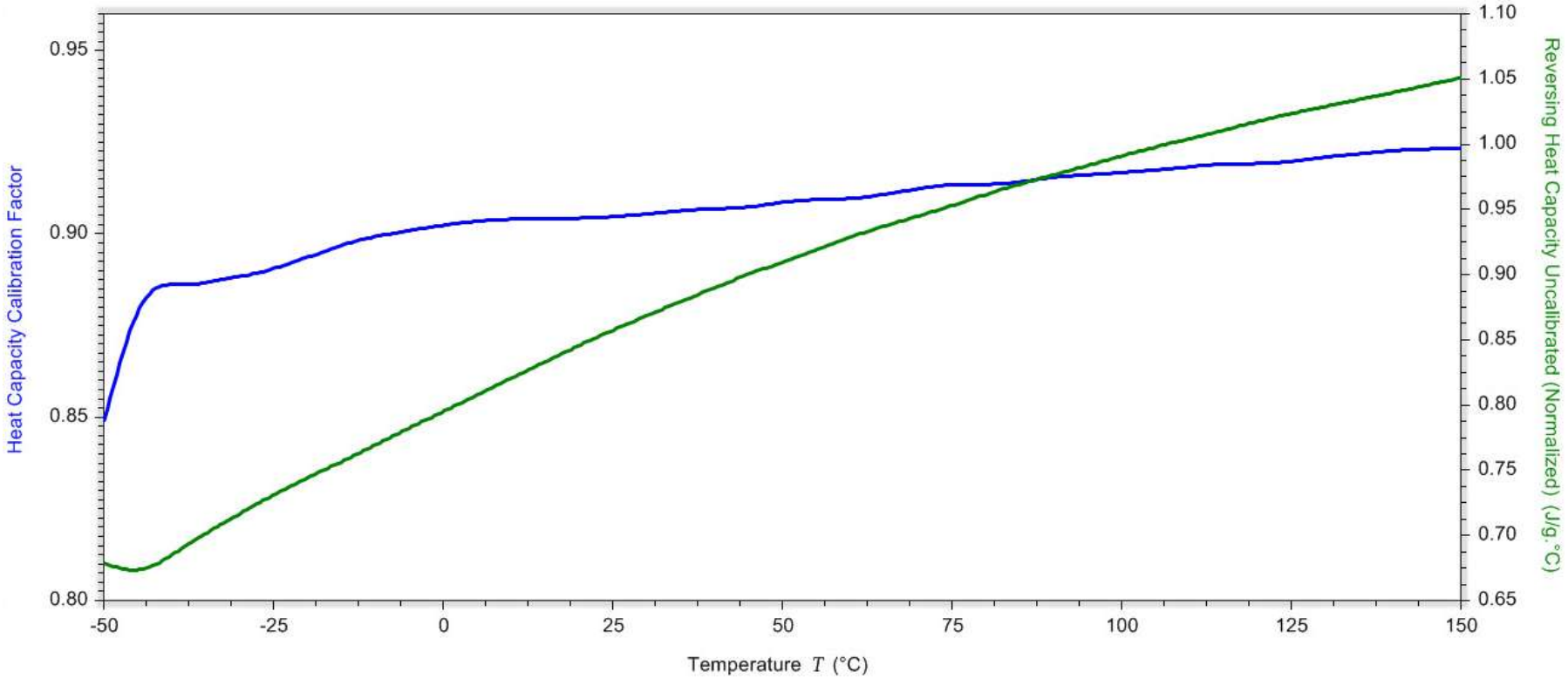
# MDSC Calibration – Discovery Series

- 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)

# Cp Calibration in Trios

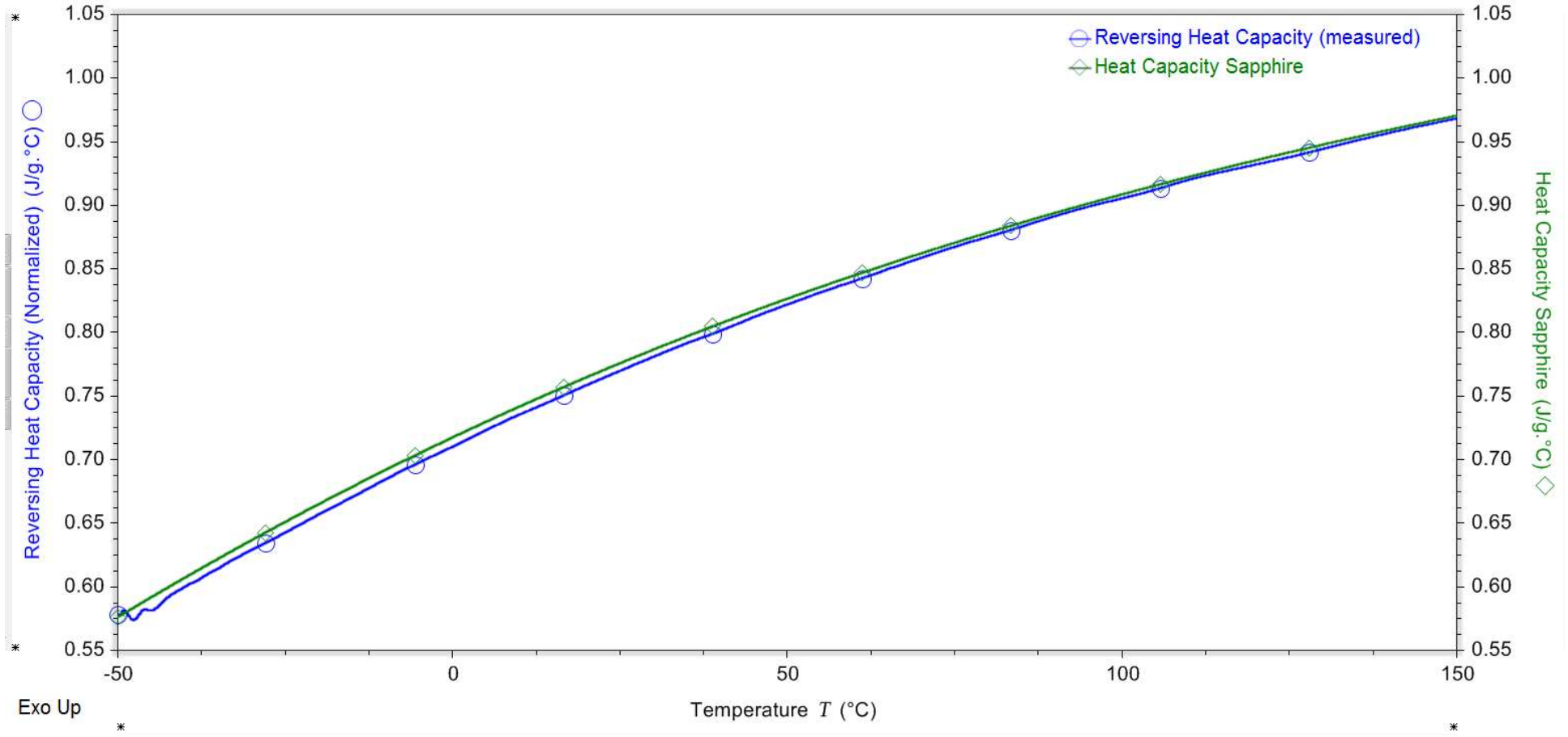


# MDSC Cp calibration using TRIOS




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

# MDSC Cp verification using TRIOS



# Experimental Design: Instrument Set Up

# 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

# 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

# Performance of the cooling accessories

RCS90 Controlled Cooling Rates, from 550°C (upper limit)*

| Controlled Rate | To Lower Temperature |
|---|---|
| 100°C/min | 300°C |
| 50°C/min | 120°C |
| 20°C/min | -20°C |
| 10°C/min | -50°C |
| 5°C/min | -75°C |
| 2°C/min | -90°C |

RCS40 Controlled Cooling Rates, from 400°C (upper limit)*

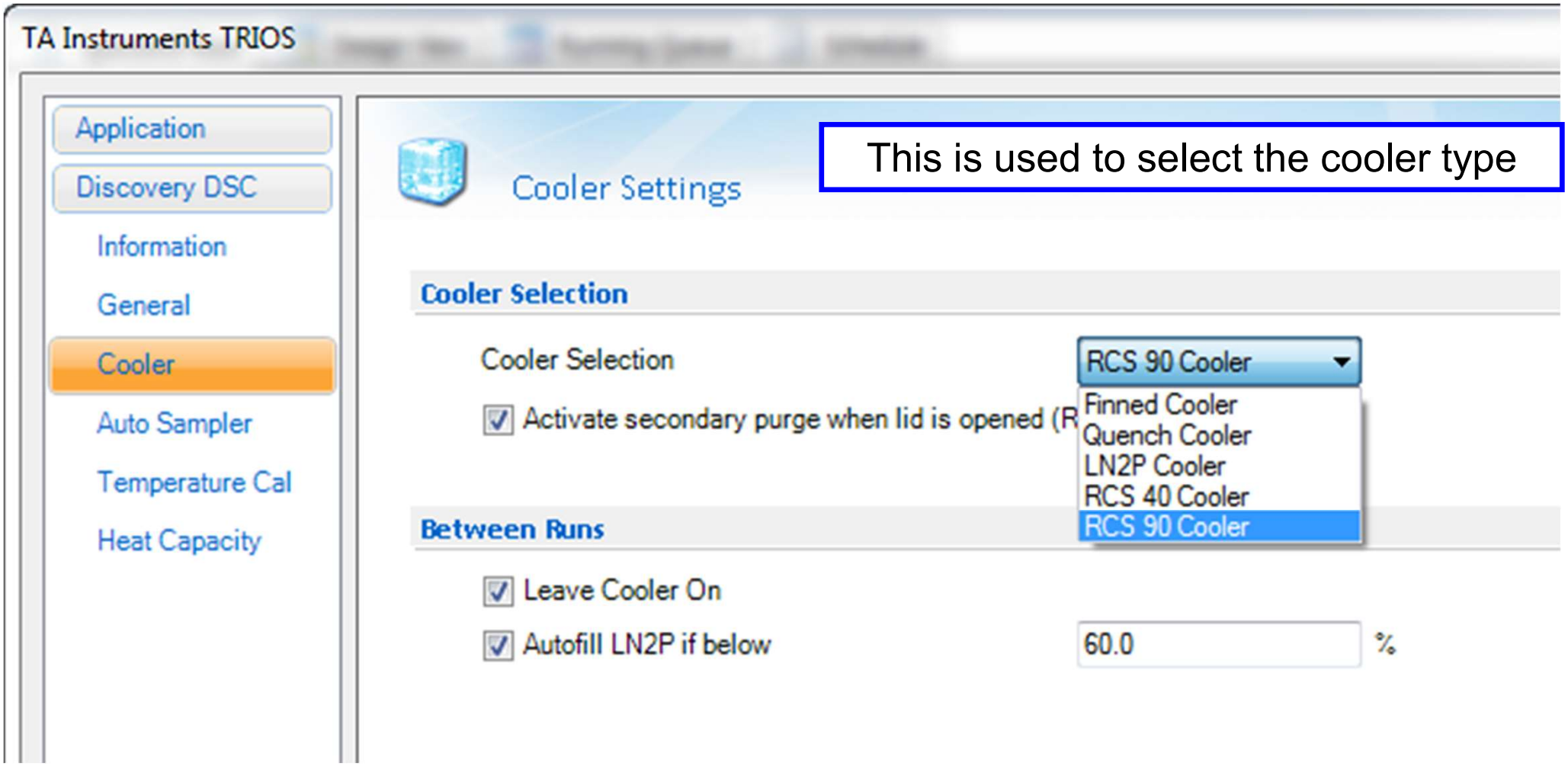
| Controlled Rate | To Lower Temperature |
|---|---|
| 65°C/min | 250°C |
| 50°C/min | 175°C |
| 20°C/min | 40°C |
| 10°C/min | 0°C |
| 5°C/min | -15°C |
| 2°C/min | -40°C |

LNCS Controlled Cooling Rates, from 550°C (upper limit)*

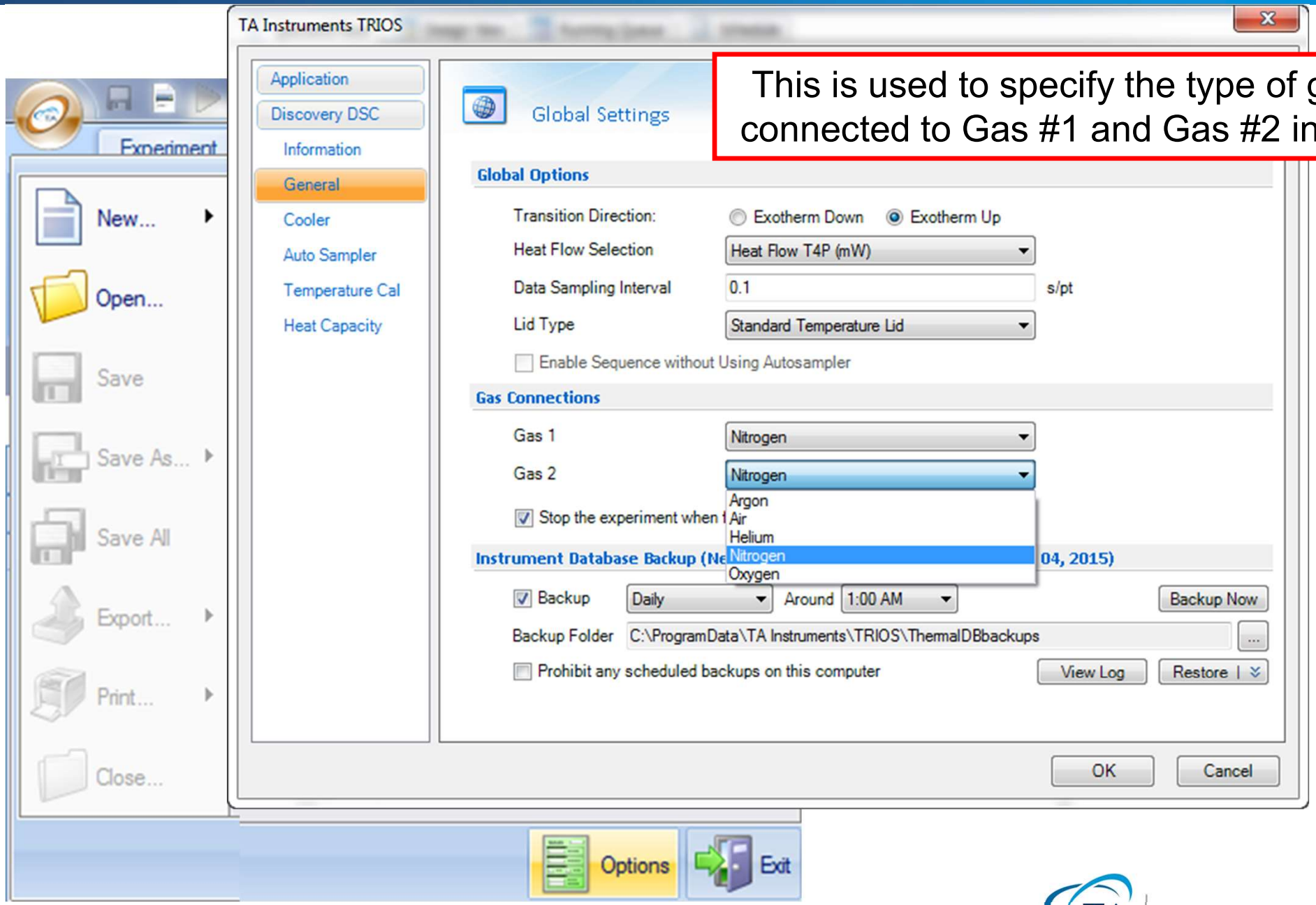
| Controlled Rate | To Lower Temperature |
|---|---|
| 100°C/min | 200°C |
| 50°C/min | 0°C |
| 20°C/min | -100°C |
| 10°C/min | -150°C |
| 5°C/min | -165°C |
| 2°C/min | -180°C |

* Performance may vary slightly, depending on laboratory conditions.

# Selecting the cooler – Discovery DSC

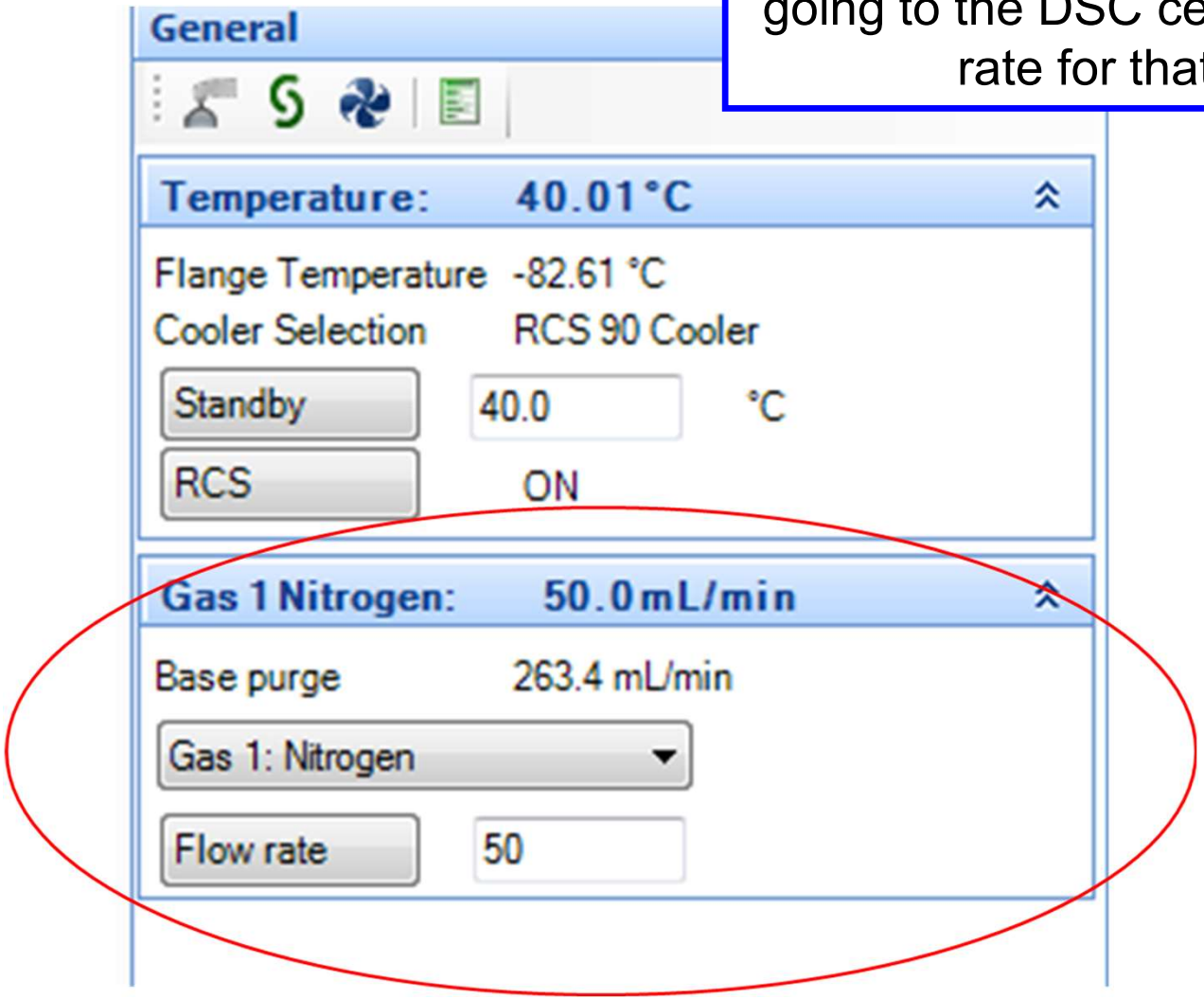


# Selecting the purge gas – Discovery DSC



# 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.



# 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

# Experimental design:
# Sample Preparation and Considerations

# TGA for DSC Experimental Design

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

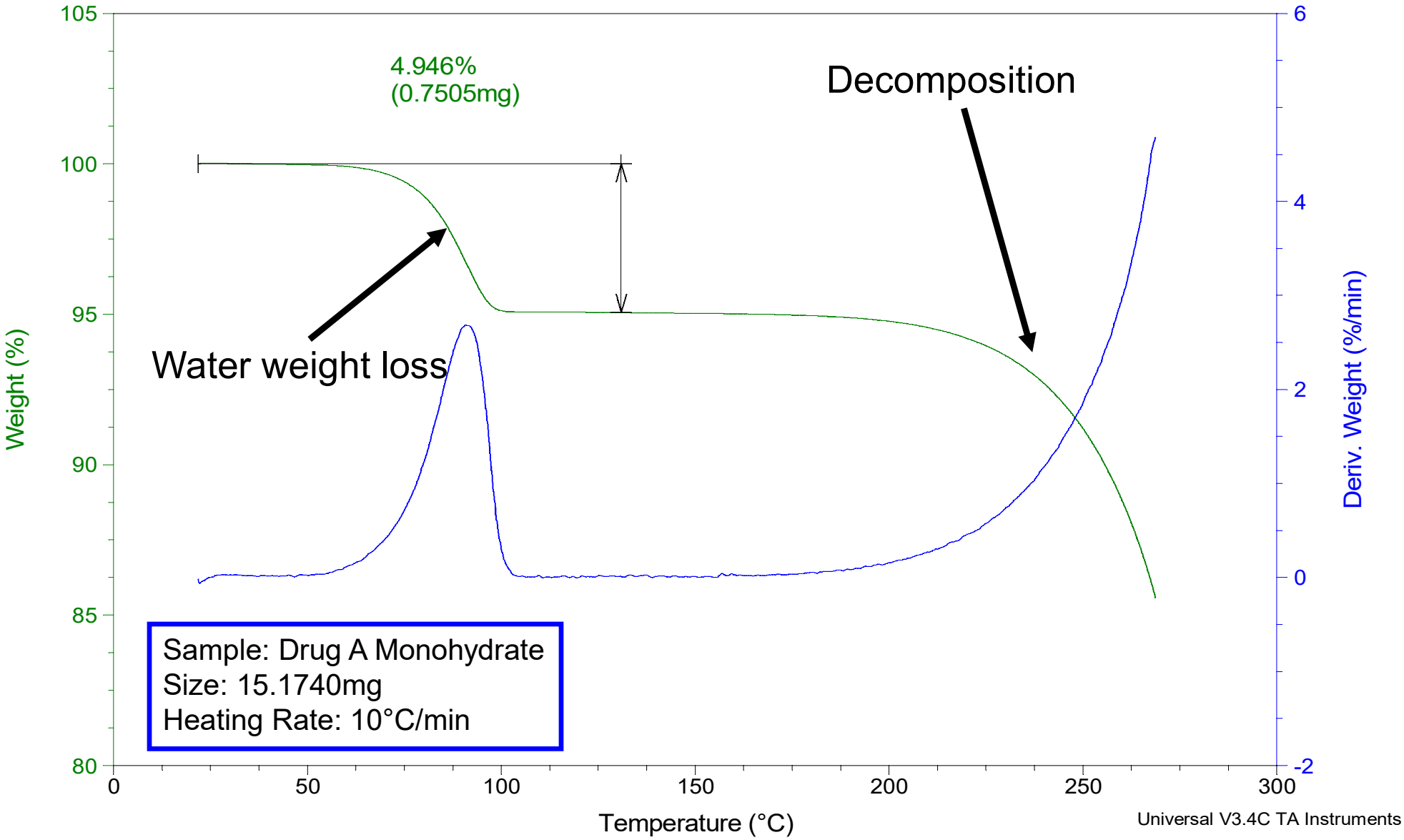
- General applications of TGA include:
  - thermal stability
  - residual solvent, out gassing, moisture sorption/desorption
  - filler/fiber content
  - weight loss on cure

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

# Selecting Optimum Experimental Conditions

- If possible, 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 slower heat rates

# Typical TGA data: TGA of Drug A Monohydrate



# 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

# DSC Pan Selection

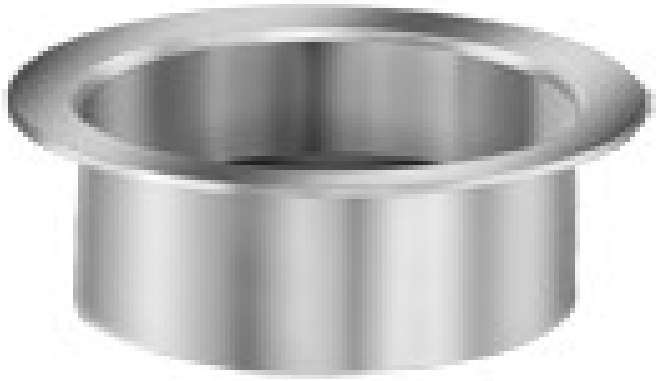
- High thermal conductivity – aluminum, gold, copper, platinum
- Inert - alodined aluminum, ceramic, graphite
- Flatness of the pan for optimal thermal contact
- Standard, non-hermetic vs. hermetic sealing
- Capacity/sample volume
- Temperature range

# 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

# 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 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.

# Tzero Press (P/N 901600.901)

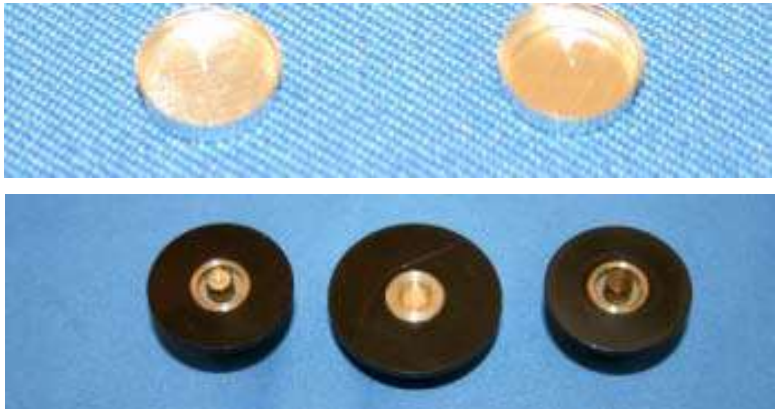
Tzero Press kit includes die sets for:

1. Tzero Pans / Tzero Lids and Tzero Low-Mass Pans / Tzero Lids (Black)
2. Tzero Pans / Tzero Hermetic Lids (Blue)
3. Standard Aluminum Pans / Lids (Green)
4. Standard Hermetic Pans / Lids (White)

The kit also includes one box each of Tzero Pans (100) and Tzero Lids (100).

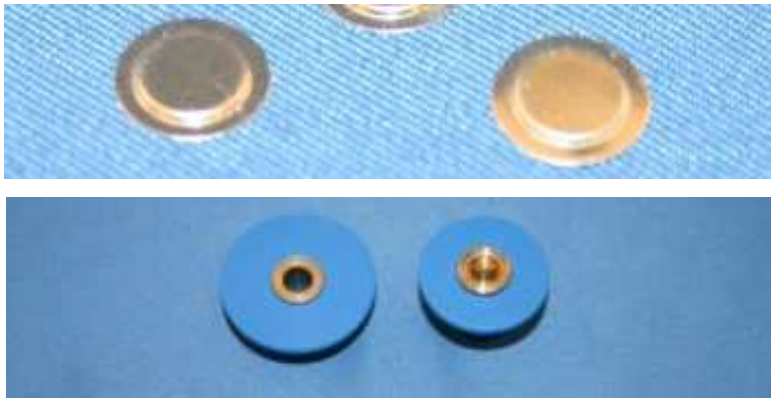
# TA Instruments Tzero Pans

## 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 Tzero Hermetic Lids (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

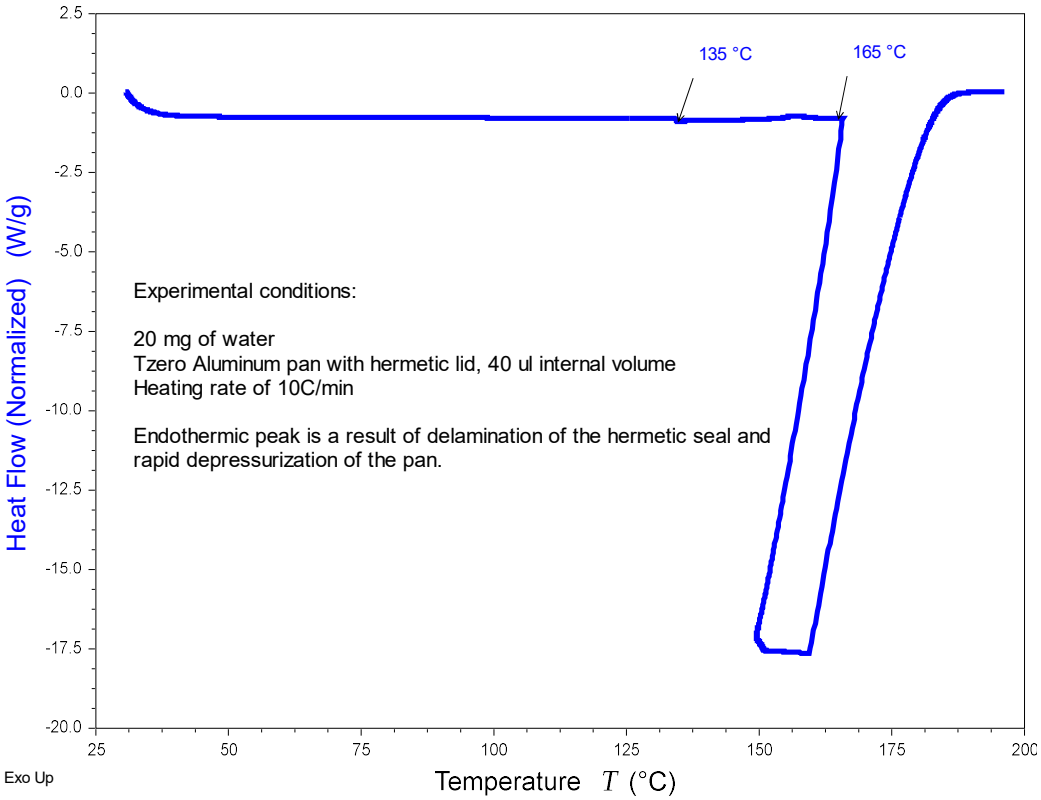
# Standard Series DSC Pans (Crimped lid)

- Part numbers for the pans and lid
  - 900760.901 Classic Aluminum Pans (pkg. of 200) (higher sidewall compared to the standard aluminum sample pans to accommodate larger samples)
  - 900786.901 Aluminum Sample Pans (pkg. of 200)
  - 900779.901 Aluminum Lids (pkg. of 200)
- 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

# Sample Shape

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

# Hermetic DSC Pans




Aluminum Hermetic
3 atm

Sample:
1. Liquid
2. Solid with volatile content

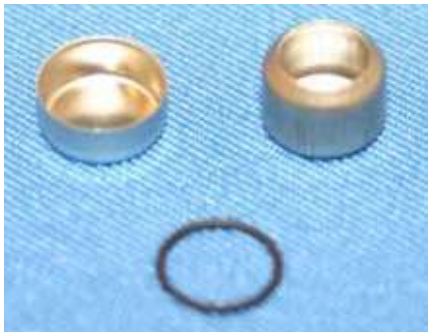
High Volume Stainless Steel
40 atm

Gold Hermetic
6 atm

# Hermetic Pans (Sealed)

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

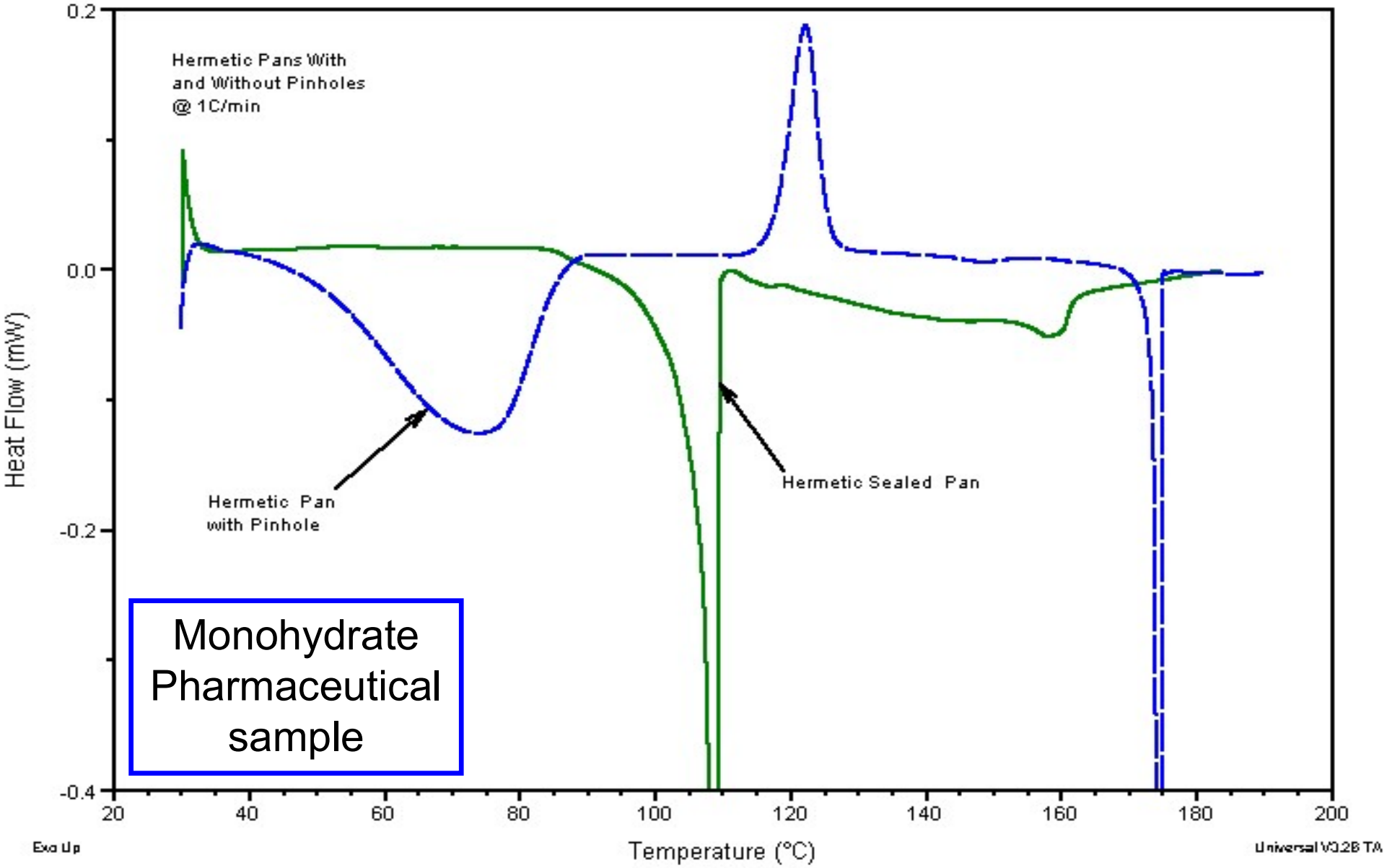
- Specialized Sealed Pans
  - High Volume:  100µL; <250°C; 600 psig
  - P/N 900825.901



  - High Pressure:  35µL; <300°C; 1450 psig
  - P/N 900808.901

Note: 3 atm is approximately 44 psig

# It Can Matter What Pan You Use



# What if Sample Spills out of the Pan? Keeping the DSC Cell Clean

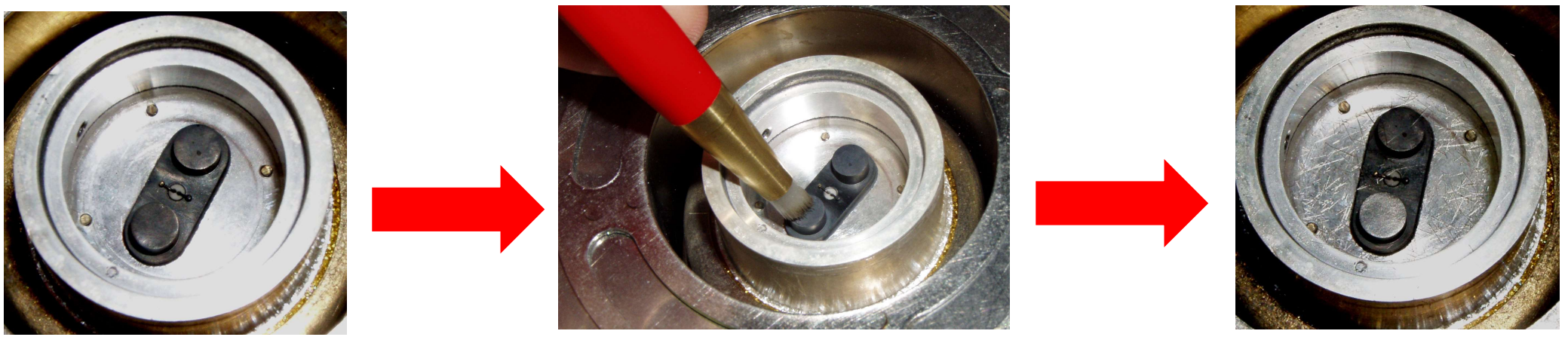
- One of the first steps to ensuring good data is to keep the DSC cell clean

- 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



# Cleaning Cell: Bakeout procedure

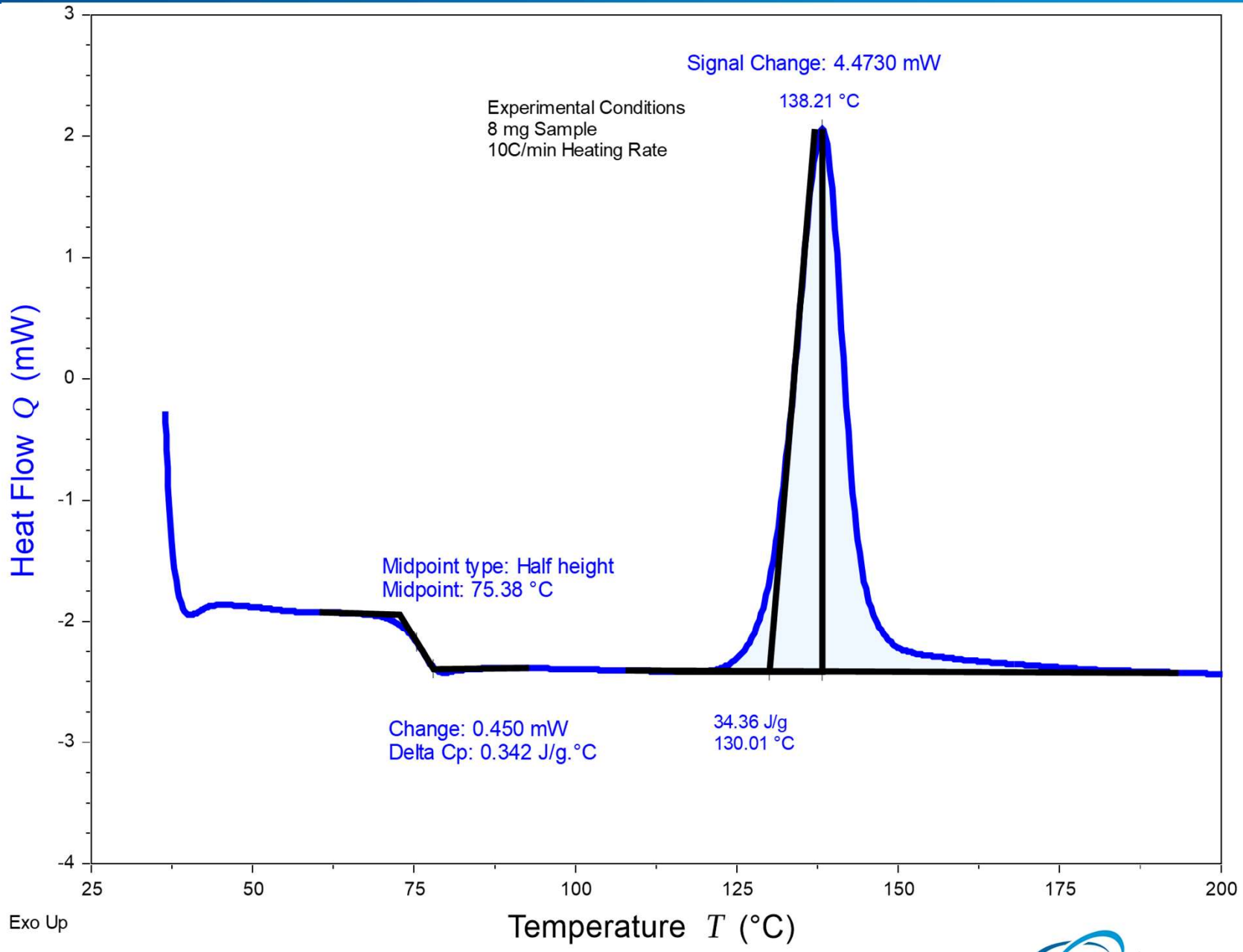
- Bake out
  - Should be used as a last resort if none of the previous steps are effective
  - Involves Air purge and/or an open lid
  - Heat @ 20°C/min to appropriate temp (max of 550°C on Q series, max. 400°C in Discovery)
  - Do NOT hold Isothermal @ the upper temperature
  - Cool back to room temp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

# Sample preparation: Optimization of Sample Mass

- Sample Preparation
  - Weight of 5-10 mg for polymers; 10-15 mg for cross-linked thermosets; 3-5 mg for metal or chemical melting
  - Goal is to achieve a change of 0.1-10mW heat flow in going through the transition

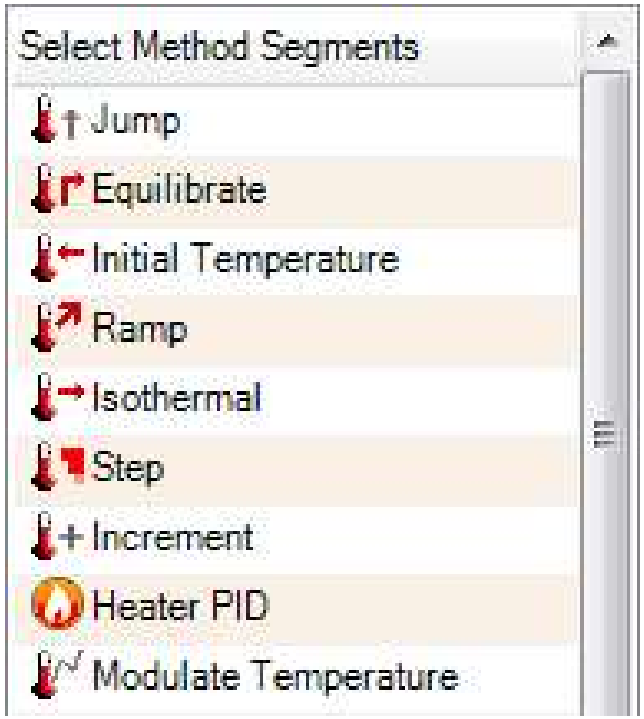
$$\frac{dH}{dt} = Cp\frac{dT}{dt} + f(T,t)$$

# Heat Flow Change During a Transition



# Method development

# Method Design: DSC Segment List

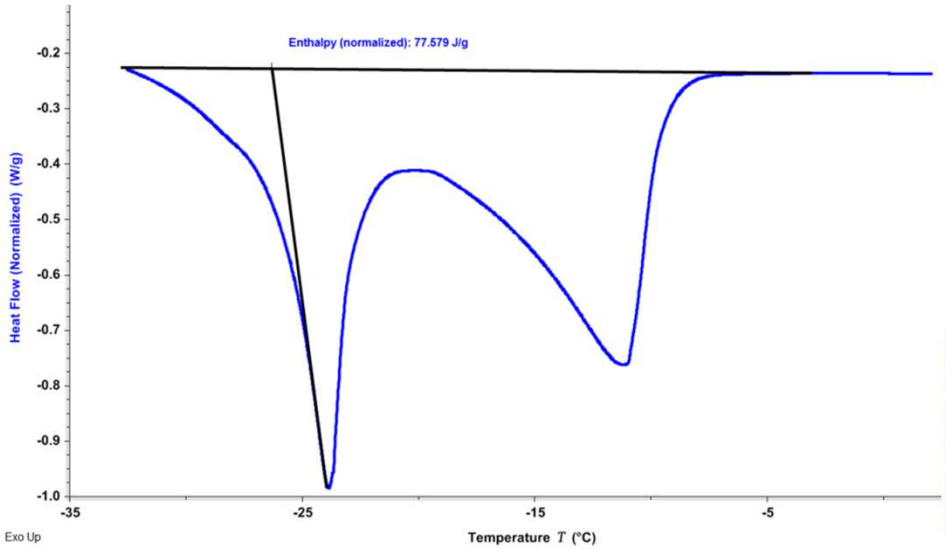


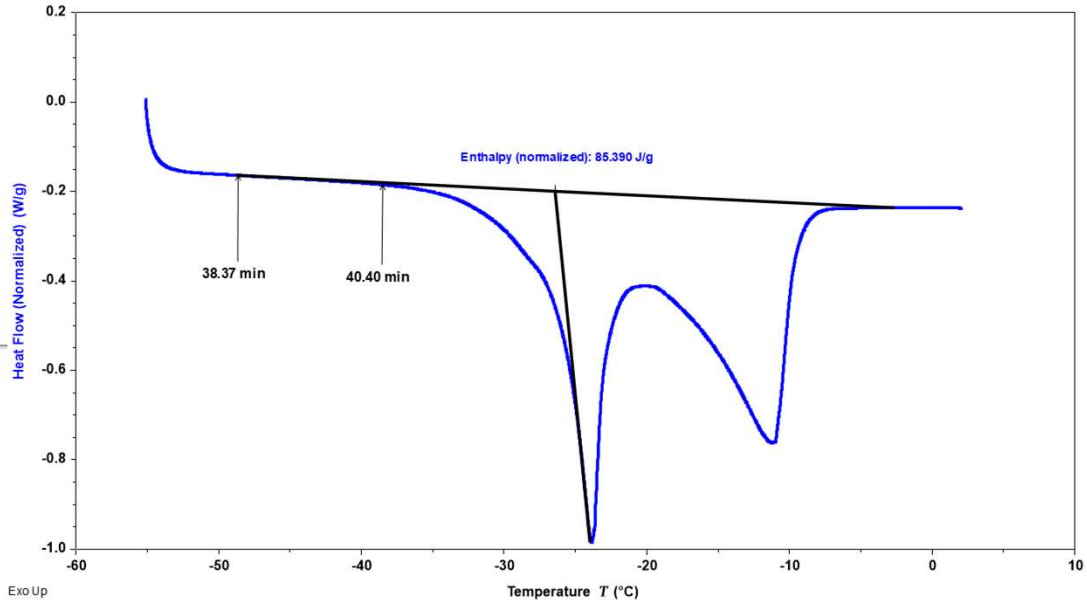

- The Ramp segment heats or cools the sample at a fixed rate until it reaches the specified temperature, producing a linear plot of temperature versus time
- The Equilibrate segment heats or cools the furnace to the defined temperature, stabilizes the furnace at that temperature, then continues to the next segment.
- The Select Gas segment controls the switching of gas between Gas 1 and Gas 2 for an instrument with a gas delivery module. This segment is used to synchronize gas switching at a specific time or temperature in an experiment.

# DSC General Method Recommendations

- Run a Heat-Cool-Heat @ 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

# Why 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

# Heating/Cooling Methods

- Typical Heating Method
  1) Equilibrate at -90°C
  2) Ramp 10°C/min. to 300°C

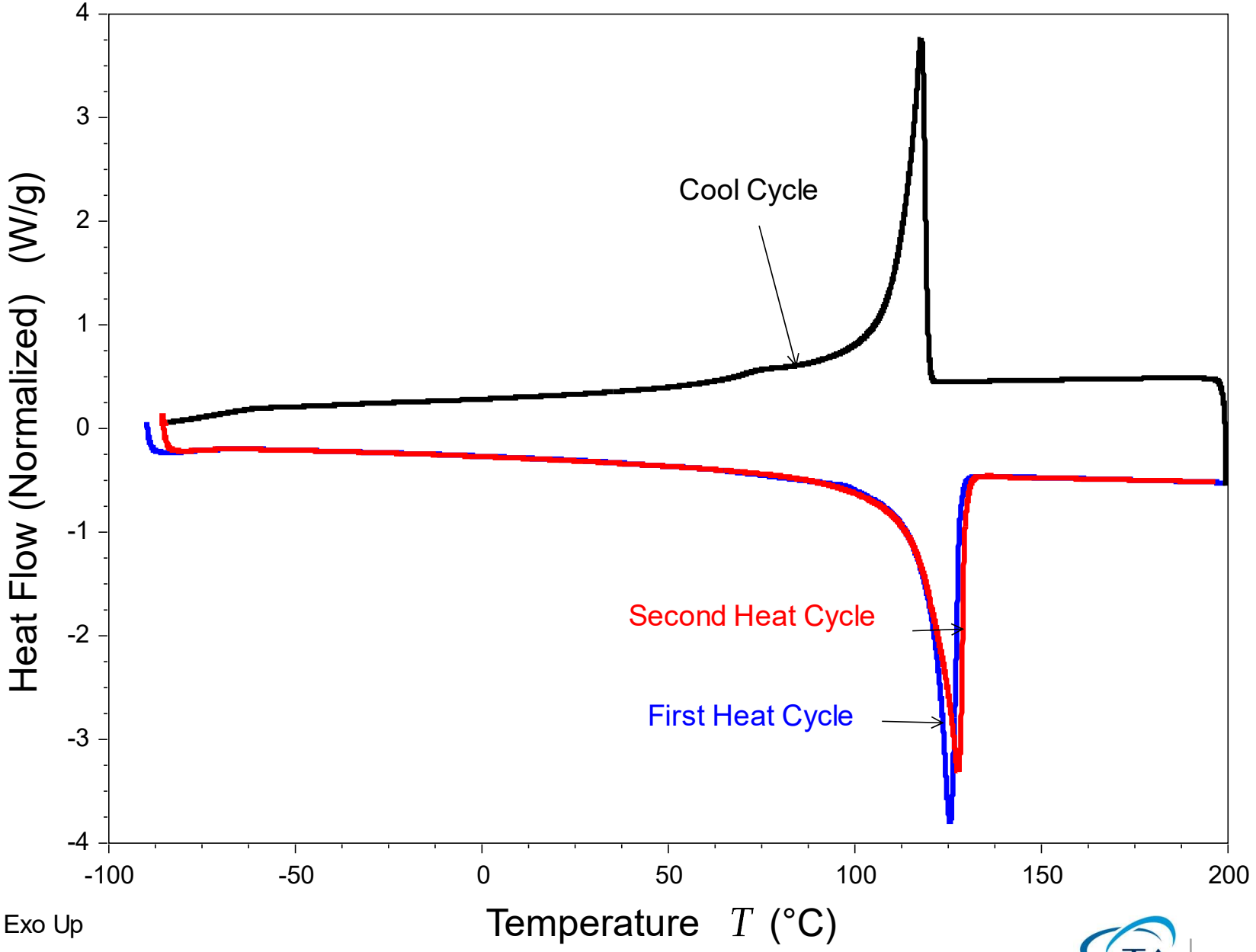
- Typical Cooling Method
  1) Equilibrate at 300°C
  2) Ramp 10°C/min. to 25°C

# 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

# Heat Cool Heat Cycles of High Density Polyethylene (HDPE)

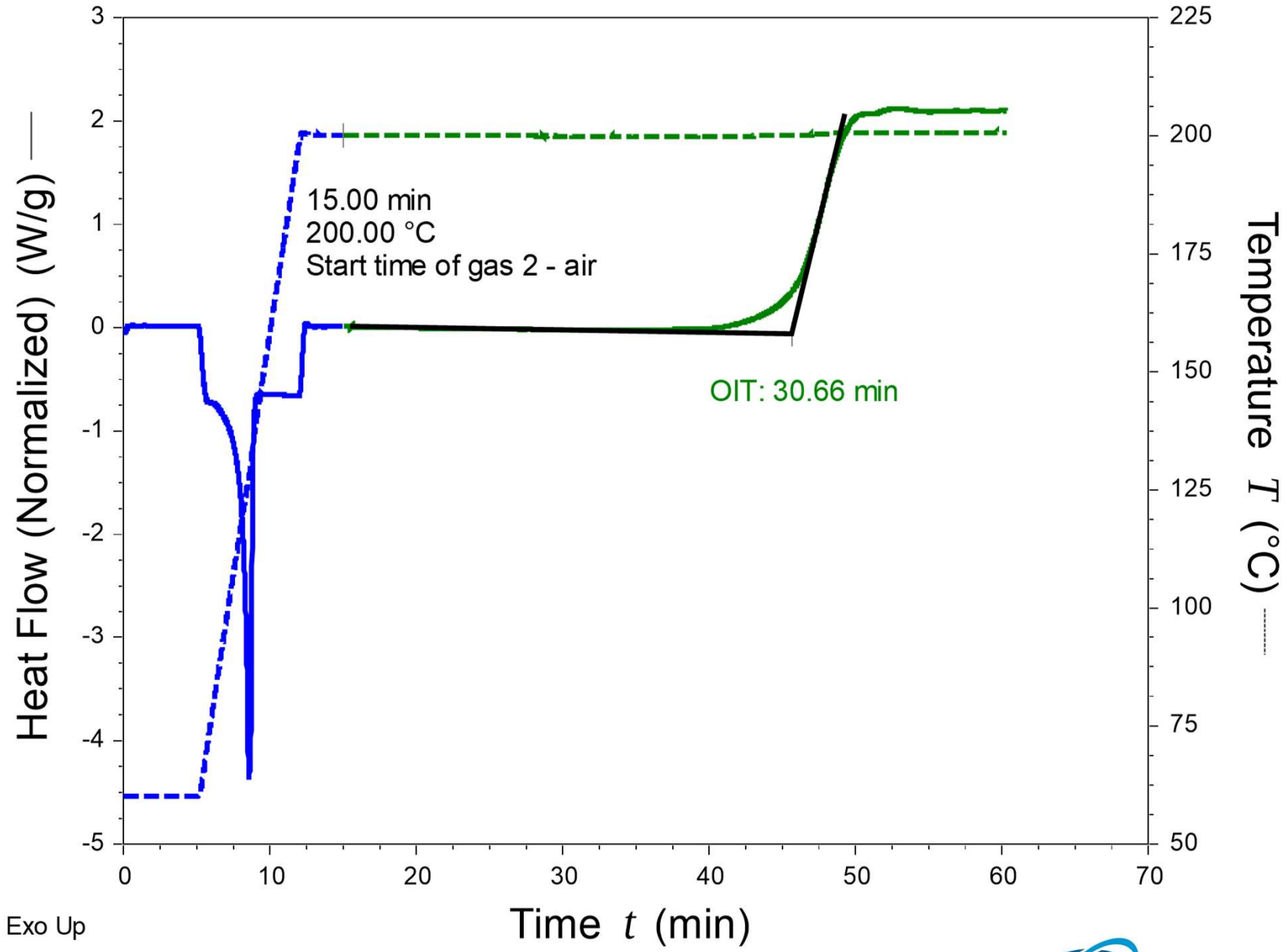


# Oxidative Stability (OIT) Method

An OIT Method

1) Isothermal for 5.00 minutes in Nitrogen
2) Ramp 20°C/min. to 200°C
3) Isothermal for 5.00 minutes
4) Select gas: 2 (air or oxygen)
5) Isothermal for 100.00 minutes (hold to a time where the exotherm reaches a peak to get accurate OIT)

# Oxidative Induction Time of Polyolefin Film

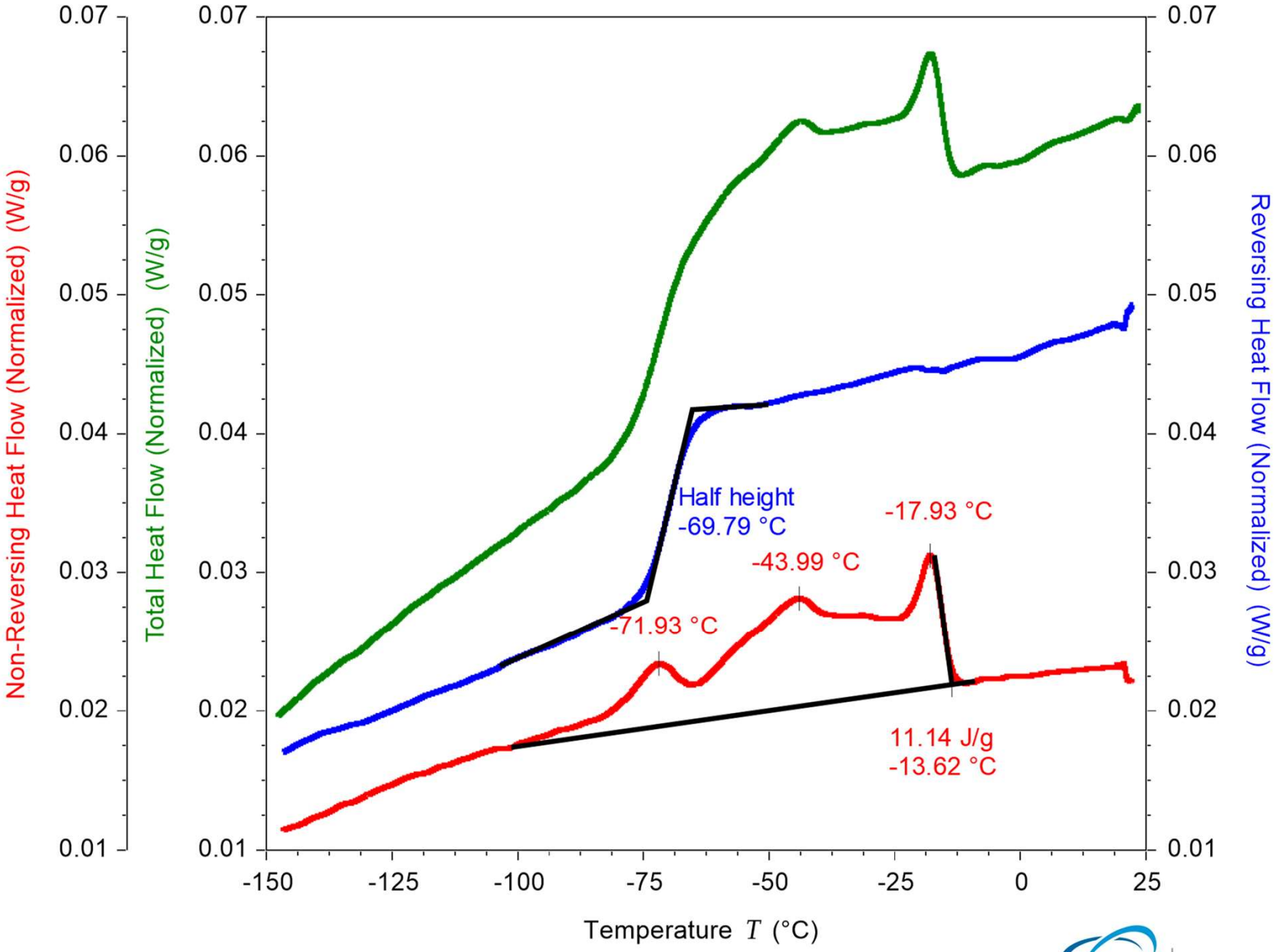


# Modulated® DSC Method

An MDSC Method

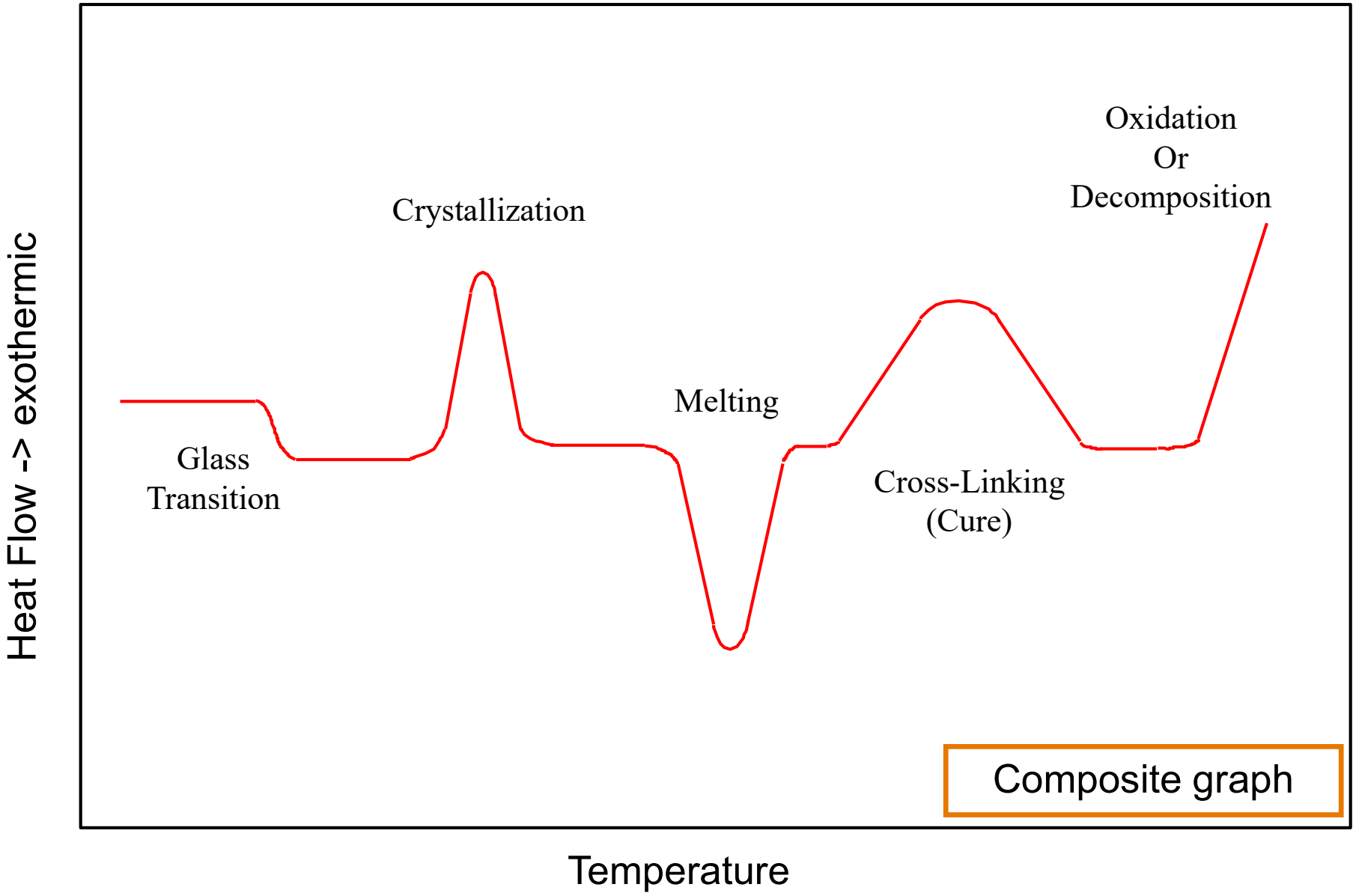
1) Equilibrate at 25°C
2) Modulate ± 0.318°C every 60 seconds
3) Isothermal for 5.00 minutes
4) Data storage: On
5) Ramp 2°C/min. to -90°C
6) Ramp 2°C/min. to 25°C

# MDSC of a Process Oil
# Separation of a Tg from Crystallization



# Applications

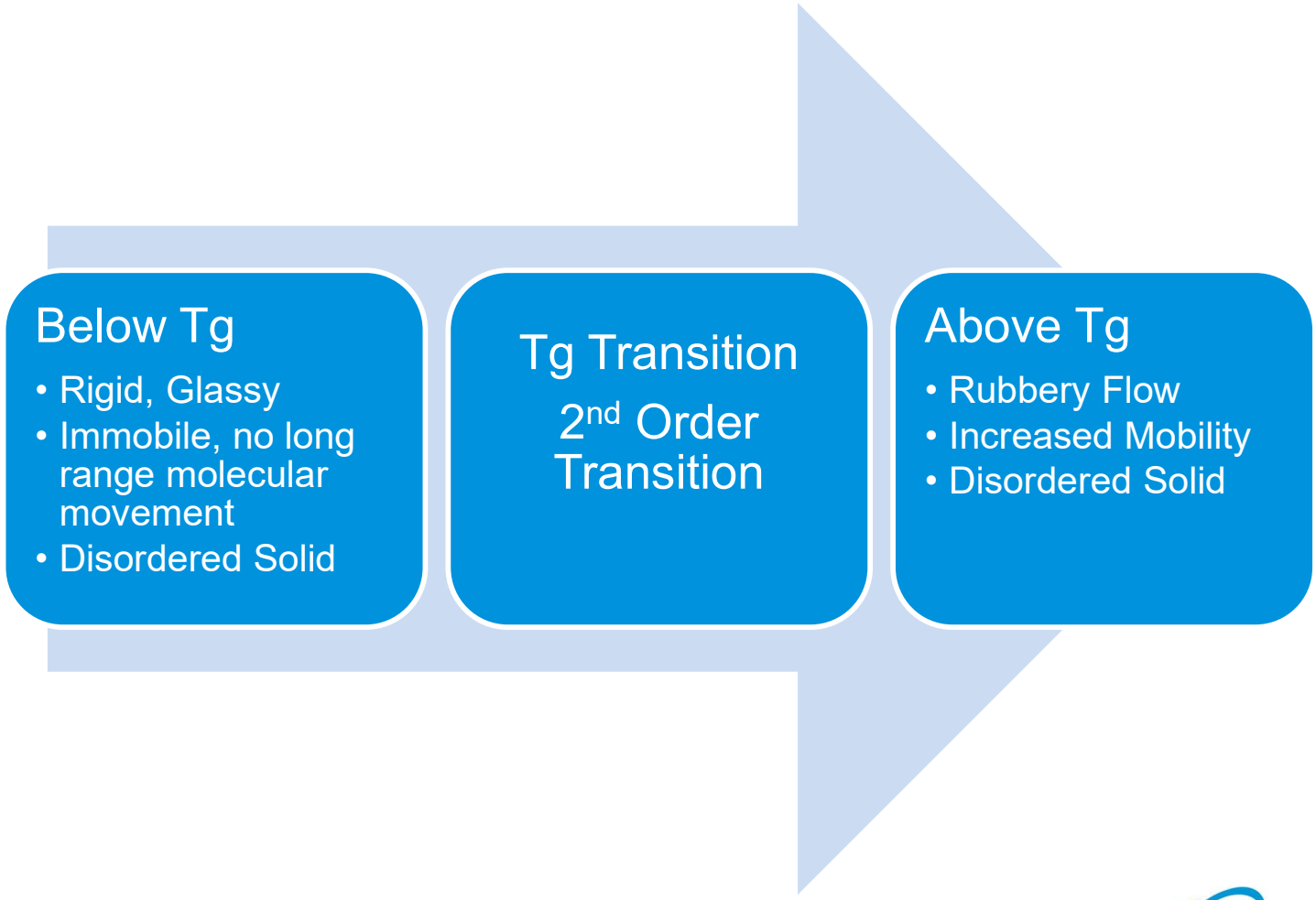
# Typical DSC Transitions



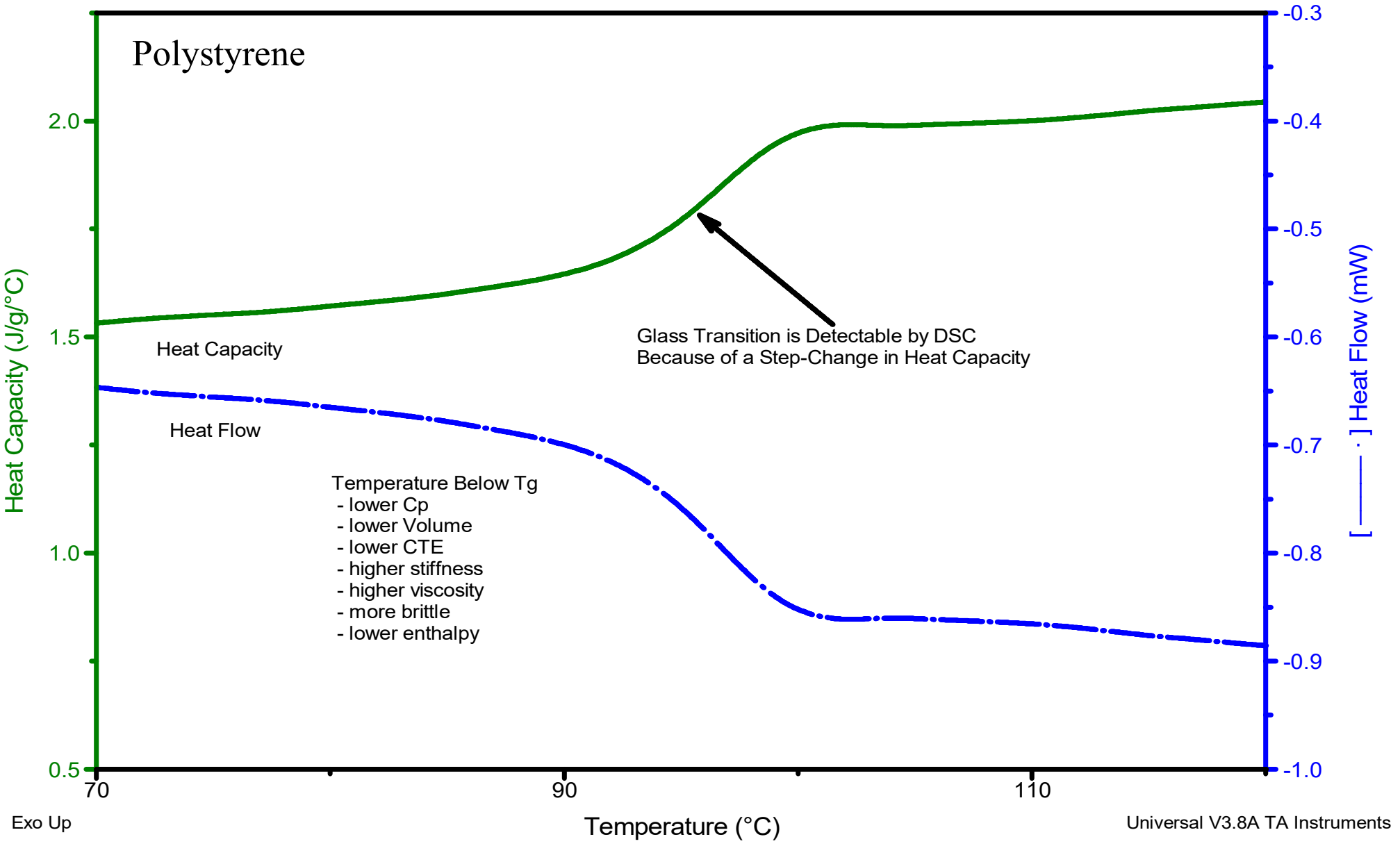
# The Glass Transition Temperature (Tg)

# The Glass Transition (Tg)

- The glass transition is a change in the free volume and molecular mobility in the amorphous phase of a material that results in a step change in heat capacity.



# Heat Flow & Heat Capacity at the Tg

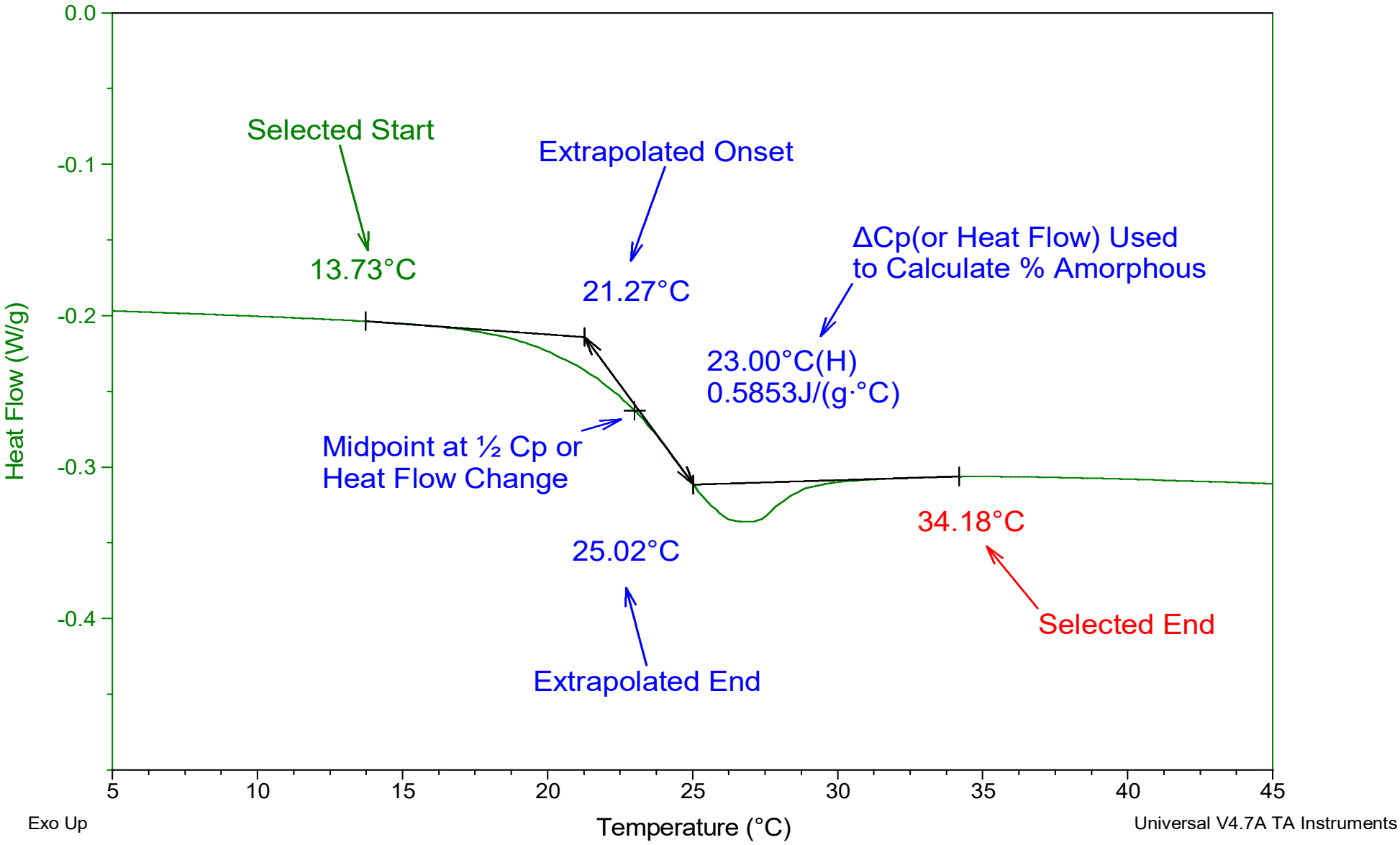


# What Affects the Glass Transition?

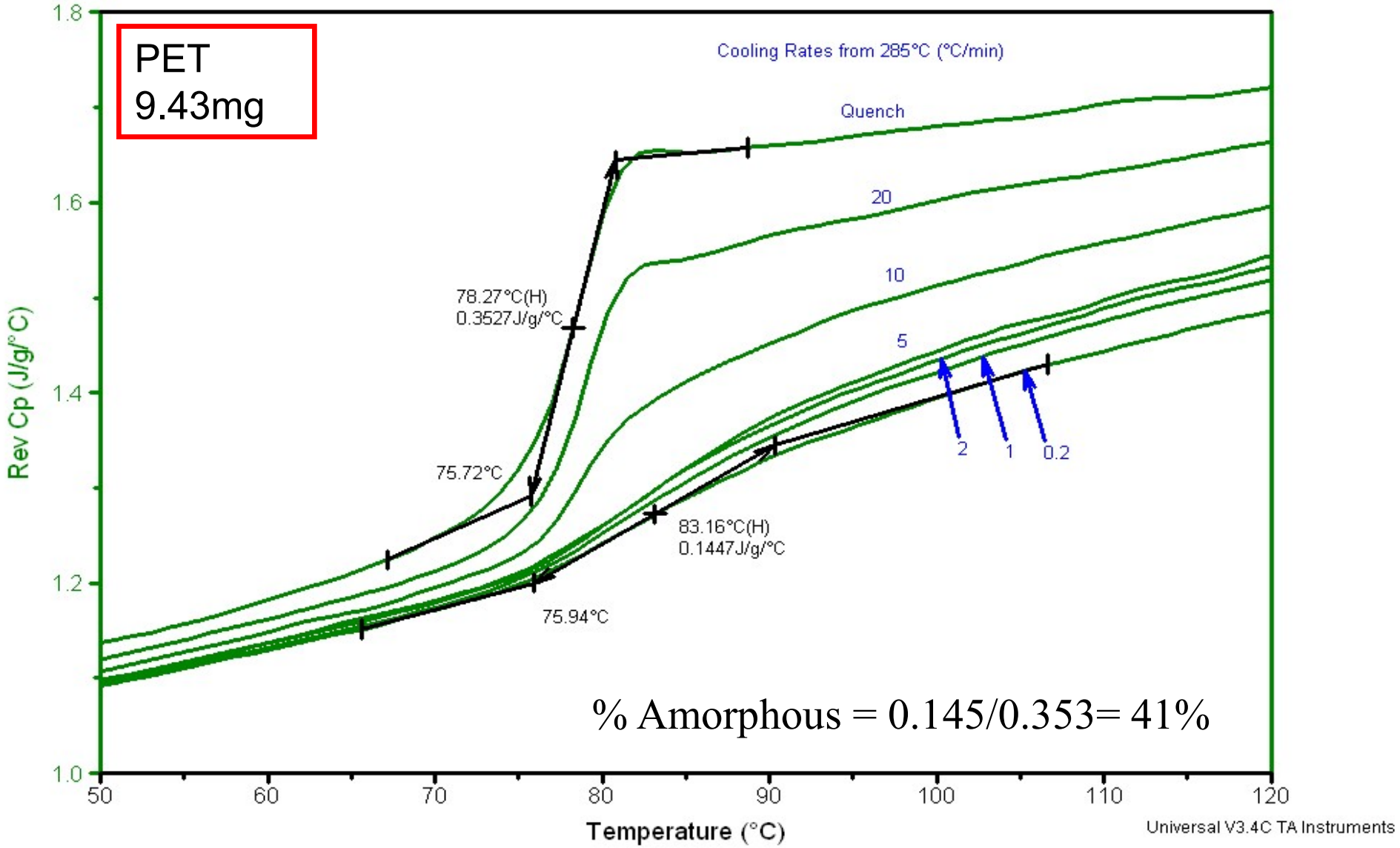
- Heating Rate
- Heating & Cooling
- Aging
- Molecular Weight
- Plasticizer
- Filler
- Crystalline Content
- Copolymers
- Side Chains
- Polymer Backbone
- Hydrogen Bonding

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

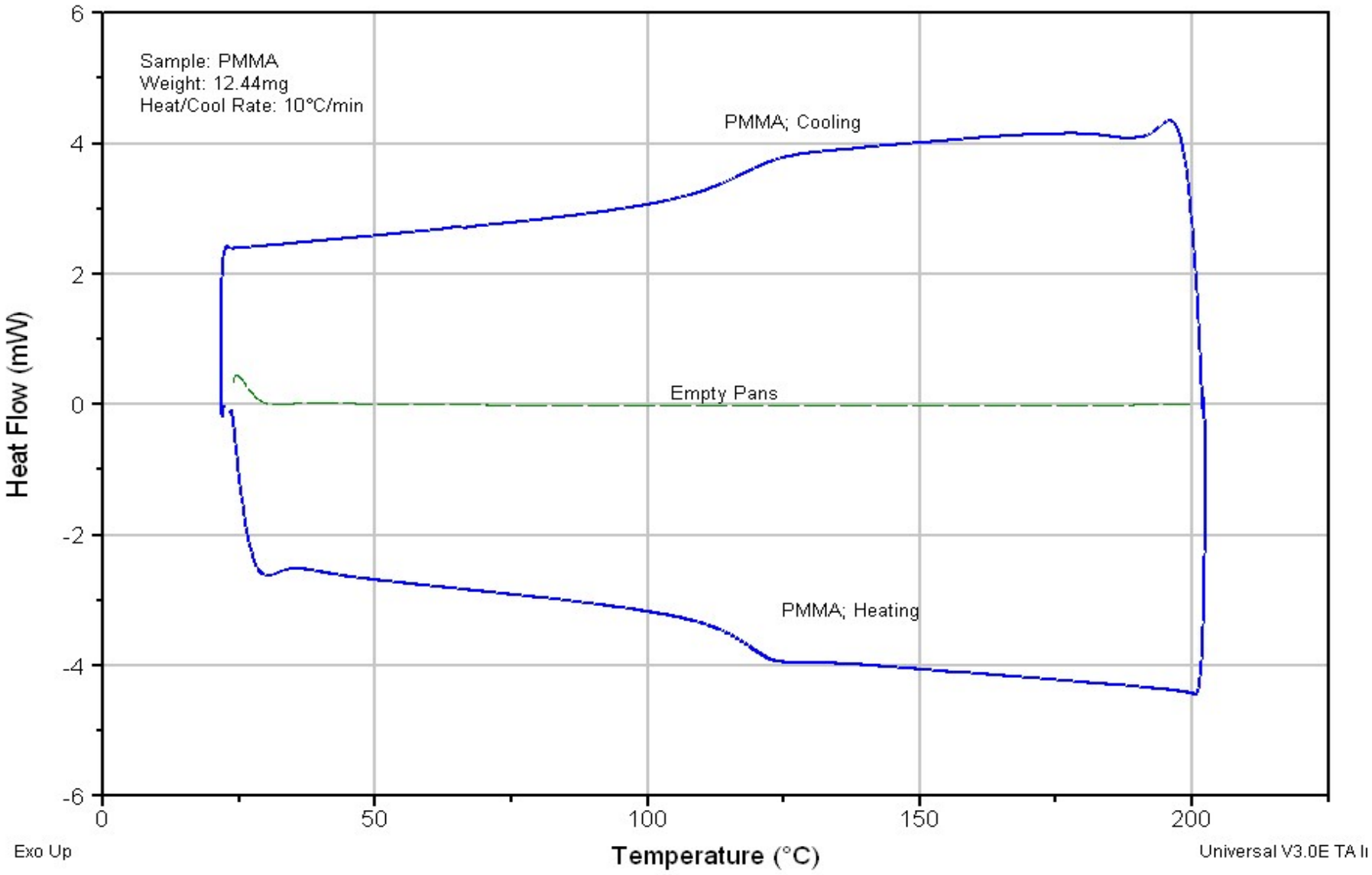
# DSC Tg Analysis – Half-Height



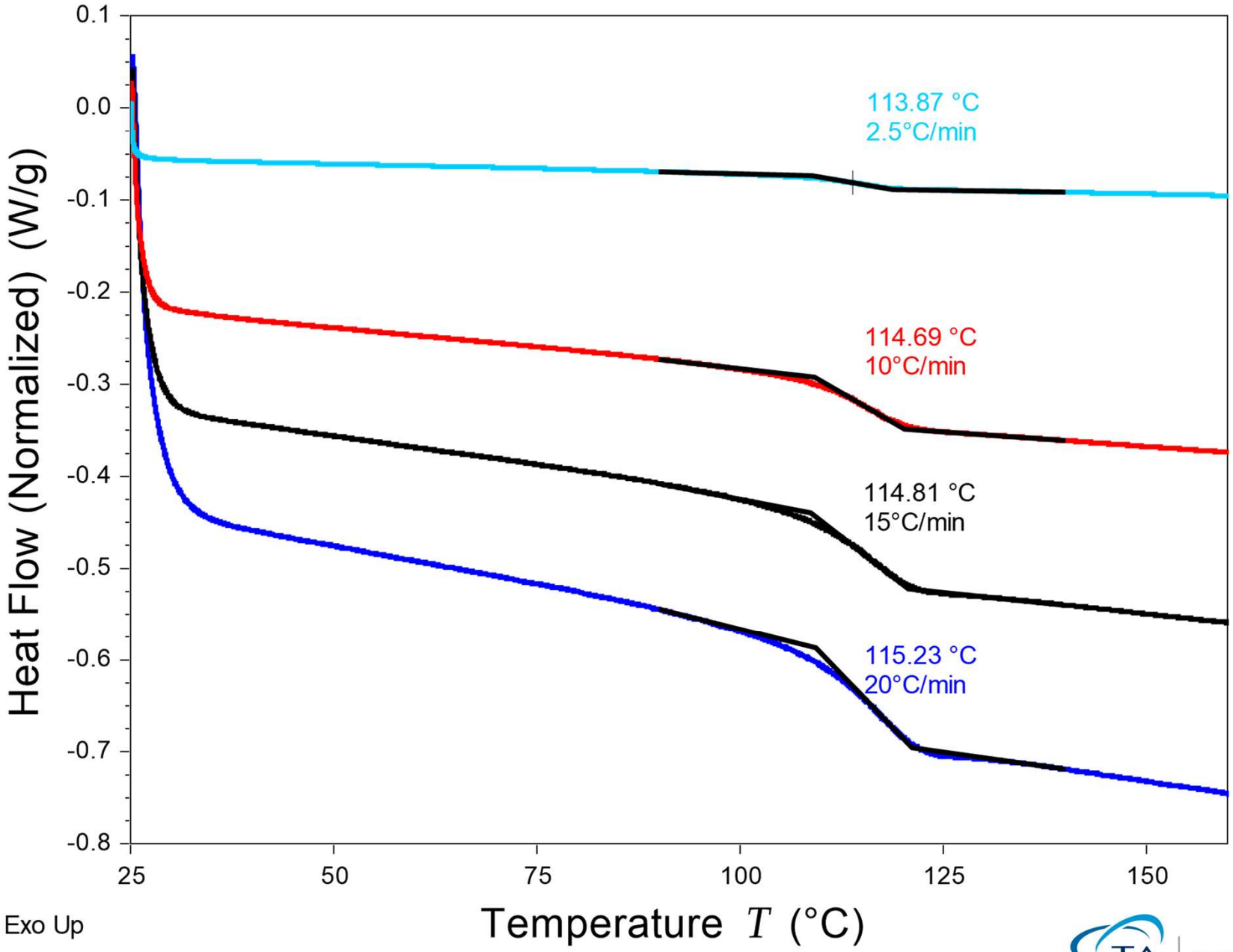
# Step Change in Cp at the Glass Transition



# A Glass Transition is Reversible



# 10mg PMMA Sample at Different Heating Rates



# Glass transition measurements using other techniques

- The Tg can also be measured by other techniques apart from the standard DSC
  - Using a Modulated DSC (MDSC)
  - Dynamic Mechanical Analysis (DMA)

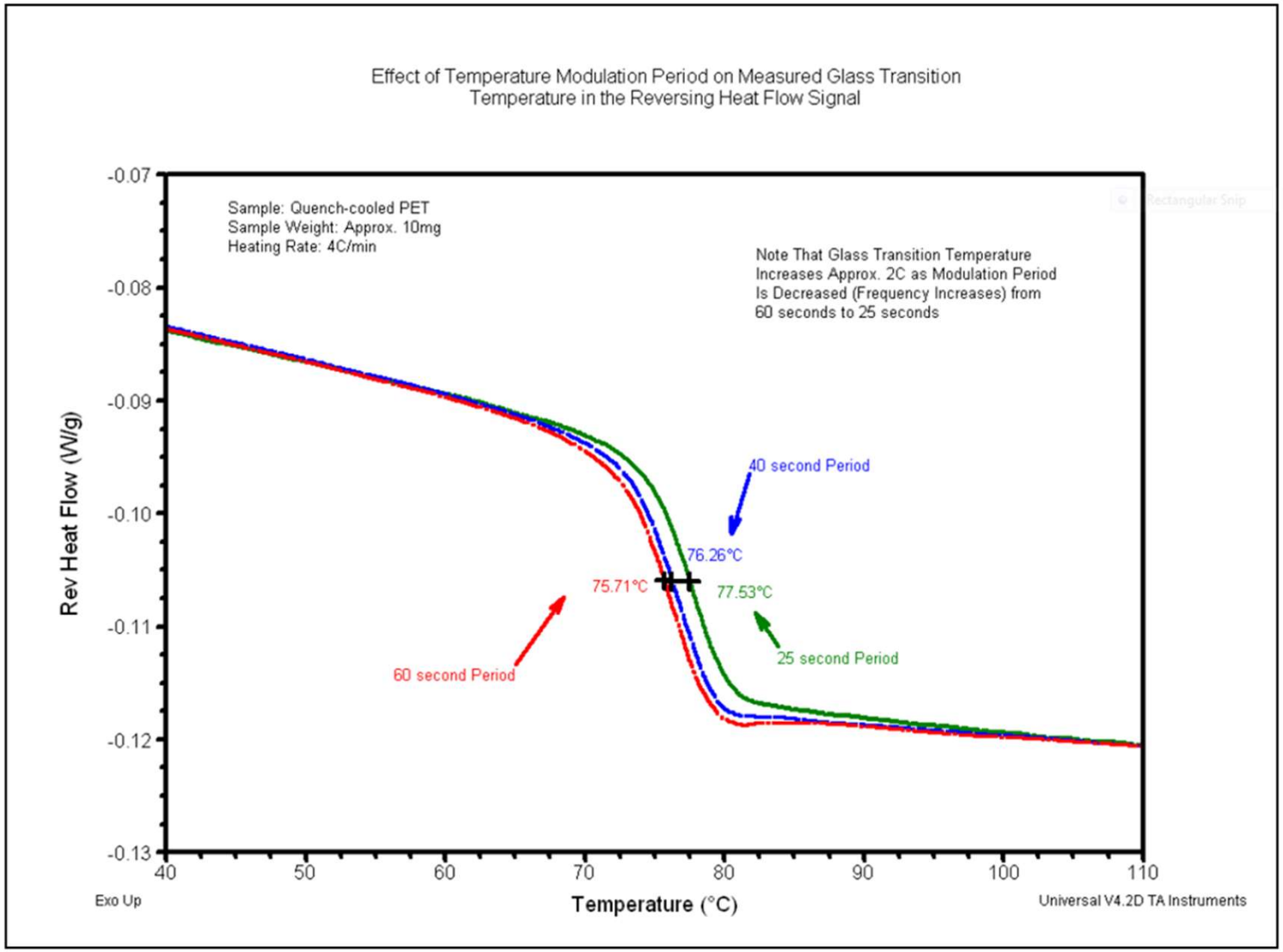
- Sensitivity of the technique to detect a glass transition:-
  - Standard DSC < MDSC < DMA

# The measured value of Tg will depend on the experimental technique as well as the setup…

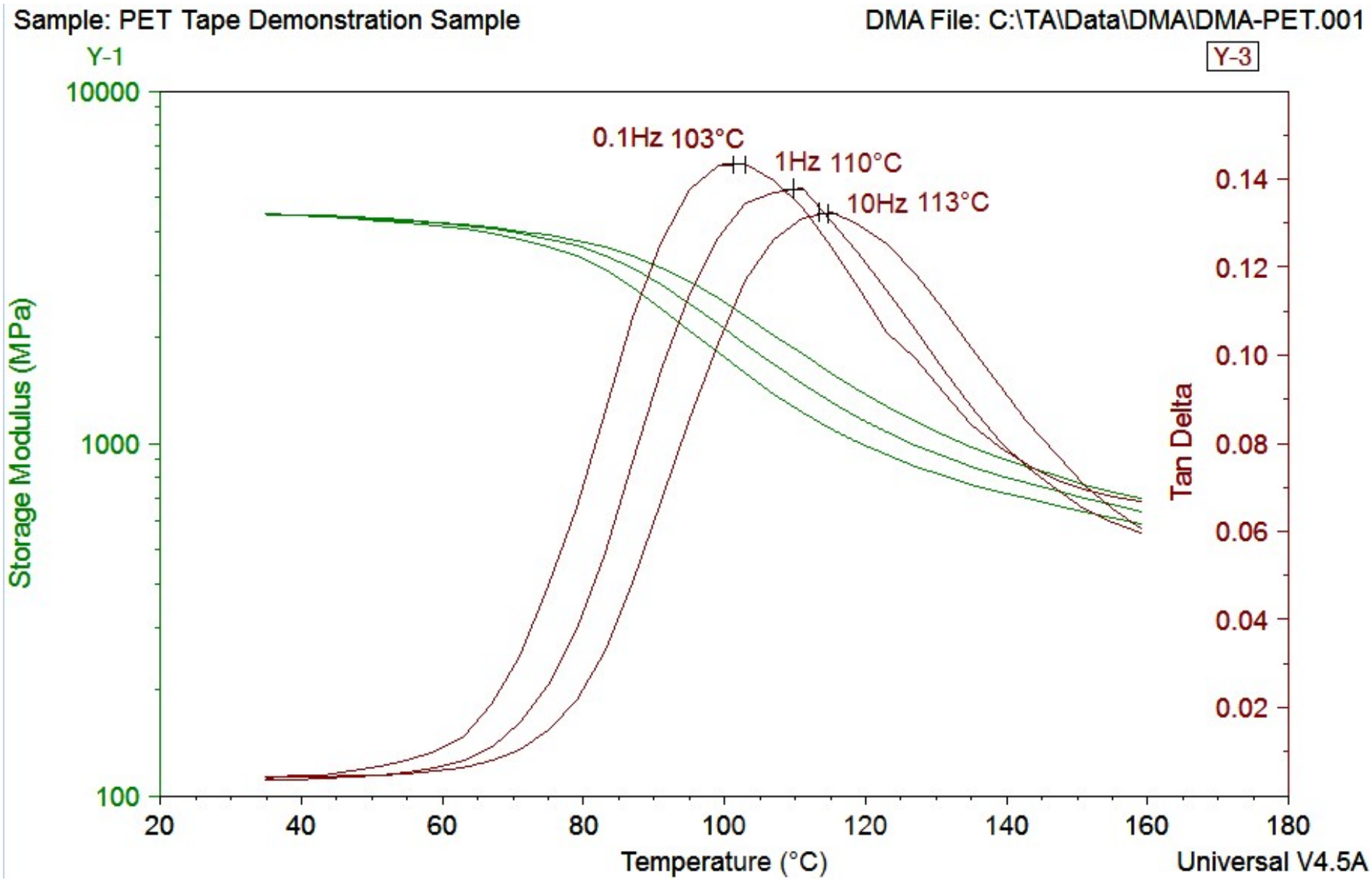
- The molecular motion associated with the glass transition is *time dependent*. Therefore,
  - it takes place over a temperature range
  - is dependent on the test frequency (in case Modulated DSC®, DMA, etc.).

- When reporting Tg, it is necessary to state the test method (DSC, MDSC, DMA, etc.), experimental conditions (heating rate, sample size, etc.) and how Tg was determined

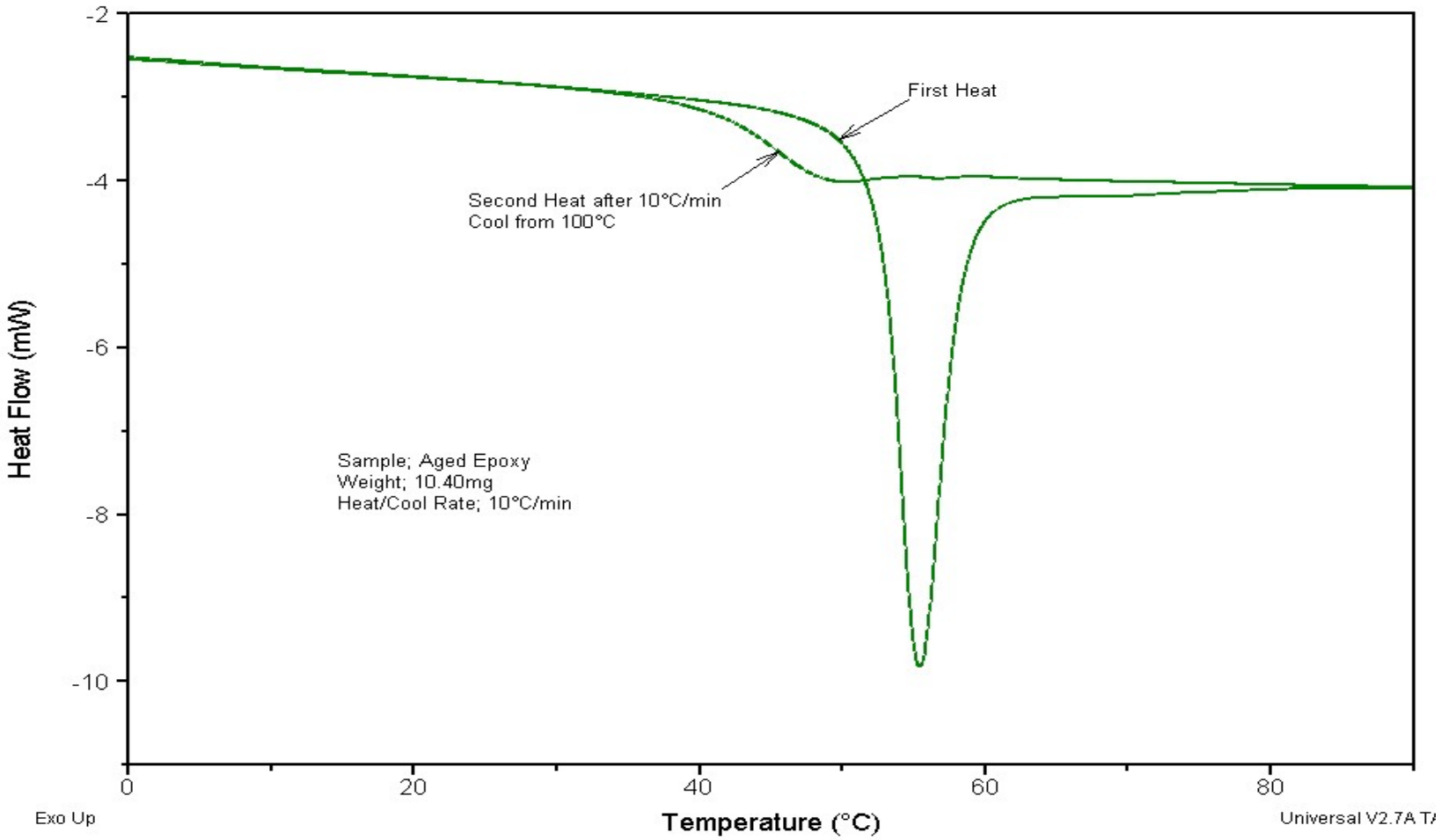
# MDSC: Effect of Frequency on Tg



# DMA: Effect of Frequency on Tg



# Aged Epoxy: The Tg On The First Heat Cycle




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.

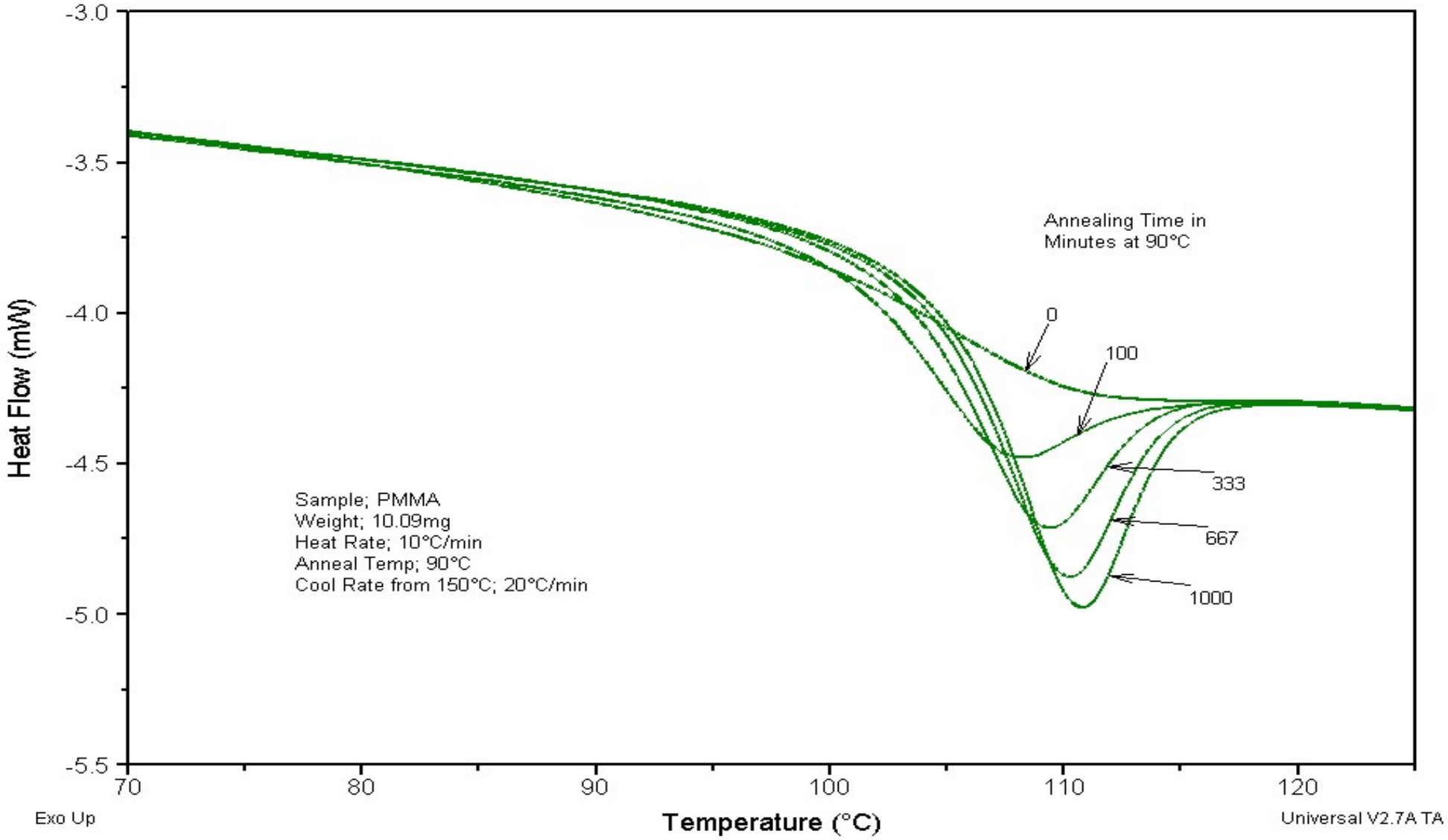
# Enthalpic Recovery

- By heating a sample above the glass transition temperature and then cooling it back to room temperature, the previous thermal history is erased.
  - The second heat typically shows the true properties of the material rather than the material properties with some processing effects
- 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.

# Enthalpic Relaxation and Recovery

- 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 Annealing on the Tg



# 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.

# Glass Transition Summary

- The glass transition is due to the amorphosity of the 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

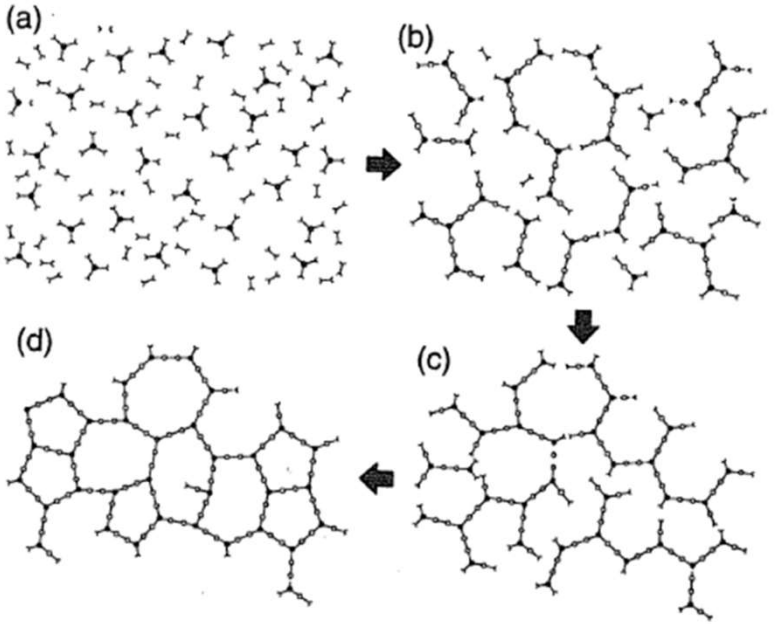
# Thermosets

# Thermosetting Polymers

A “thermoset” is a cross-linked polymer formed by an irreversible exothermic chemical reaction

Thermosetting polymers react (cross-link) irreversibly. A+B will give out heat (exothermic) when they cross-link (cure).

$$A + B \rightarrow C$$




-R. Bruce Prime, *Thermosets*, Thermal Characterization of Polymeric materials

# Commonly used thermoset materials

- Commonly used thermosets
  - Epoxies (a 2 part epoxy adhesive)
  - Phenolics
  - Urea-formaldehyde/Melamine formaldehyde
  - Polyurethanes
  - Bismaleimides
  - Cyanate esters
  - Acrylates

# Typical properties of crosslinking reactions

- Crosslinking reactions are generally exothermic. As the chemical reaction takes place, it is almost always accompanied by a release of heat.
- The reactions can be easily monitored using a DSC.
  - **Heat of reaction**
  - **Residual cure**
  - **Glass transition**
  - **Heat capacity**

- Crosslinking reactions are generally accompanied by a sharp change in the material's mechanical properties.
- Increase in modulus that may be accompanied by shrinkage.
- The reactions can thus be monitored using a Thermo-mechanical Analyzer (TMA)/Dynamic Mechanical Analyzer (DMA)/Rheometer.
  - **Viscosity**
  - **Modulus**
  - **Glass transition**
  - **Dimension change (shrinkage)**

These techniques give useful information about the impact of the polymerization conditions on the end product's thermo-mechanical properties.

# DSC: General considerations for selecting optimum experimental Conditions

- Sample weight: 10–15 mg
- Pan types:
  - Solids – Standard aluminum pan/lid
  - Liquids – Hermetic aluminum pan/lid
- General protocol for studying thermosets:
  - **Determine decomposition temperature using TGA**
  - Heat-Cool-reheat at 10°C/min
  - First Heat is used to measure Tg of starting material, heat of reaction and presence of any reactive functional groups.
  - Second Heat is used to measure the Tg of the fully cured sample and any residual cure from the first heat.

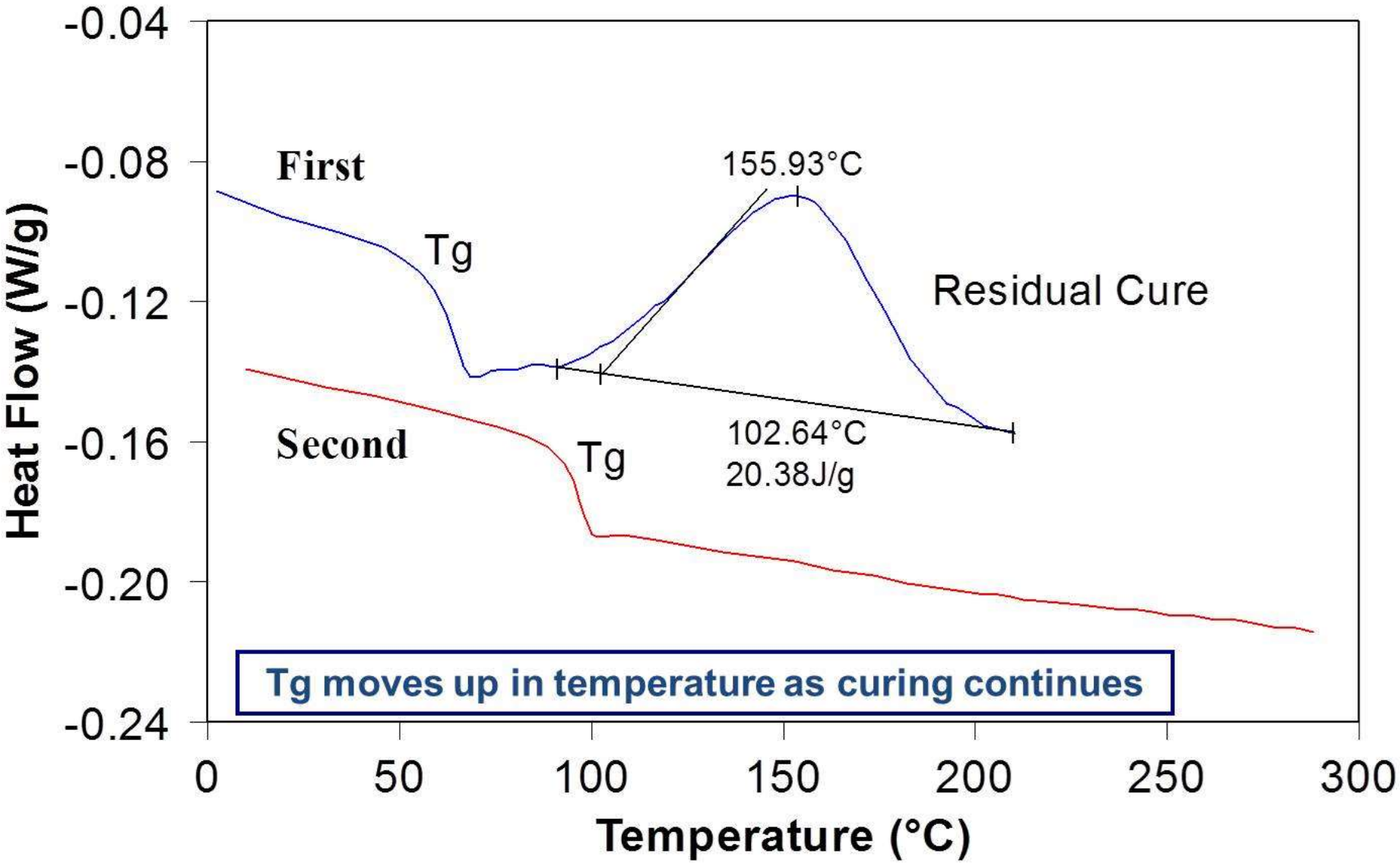
# DSC: General considerations for selecting optimum experimental Conditions

- Sample weight: 10–15 mg
- Pan types:
  - Solids – Standard aluminum pan/lid
  - Liquids – Hermetic aluminum pan/lid
- General protocol for studying thermosets:
  - Determine decomposition temperature using TGA
  - Heat-Cool-reheat at 10°C/min
  - **First Heat** is used to measure Tg of starting material, heat of reaction and presence of any reactive functional groups.
  - Second Heat is used to measure the Tg of the fully cured sample and any residual cure from the first heat.

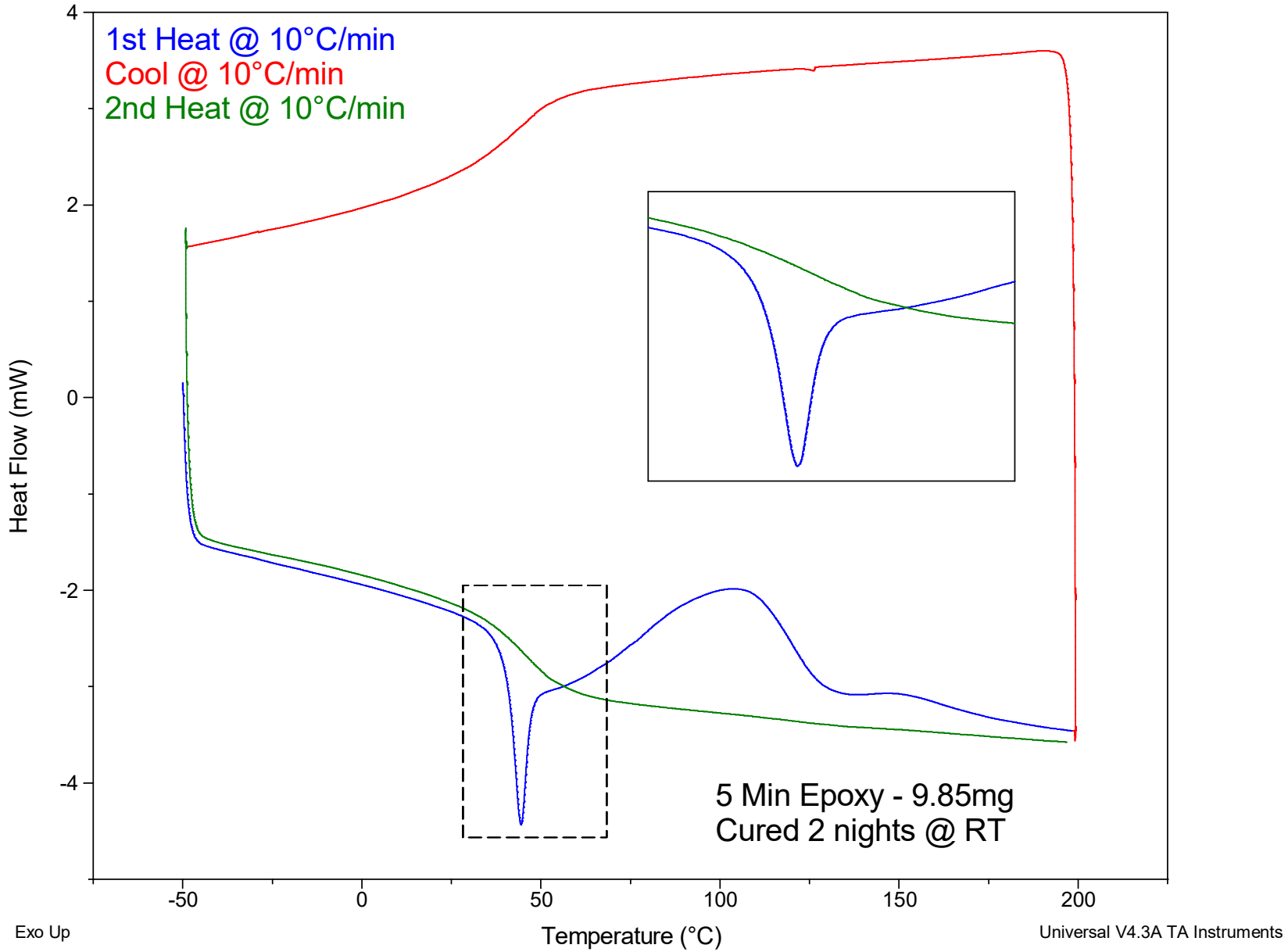
# DSC: General considerations for selecting optimum experimental Conditions

- Sample weight: 10–15 mg
- Pan types:
  - Solids – Standard aluminum pan/lid
  - Liquids – Hermetic aluminum pan/lid
- General protocol for studying thermosets:
  - Determine decomposition temperature using TGA
  - Heat-Cool-reheat at 10°C/min
  - First Heat is used to measure Tg of starting material, heat of reaction and presence of any reactive functional groups.
  - **Second Heat** is used to measure the Tg of the fully cured sample and any residual cure from the first heat.

# Comparison of First and Second Heats



# Epoxy Cured 48 Hours: Heat Cool Heat



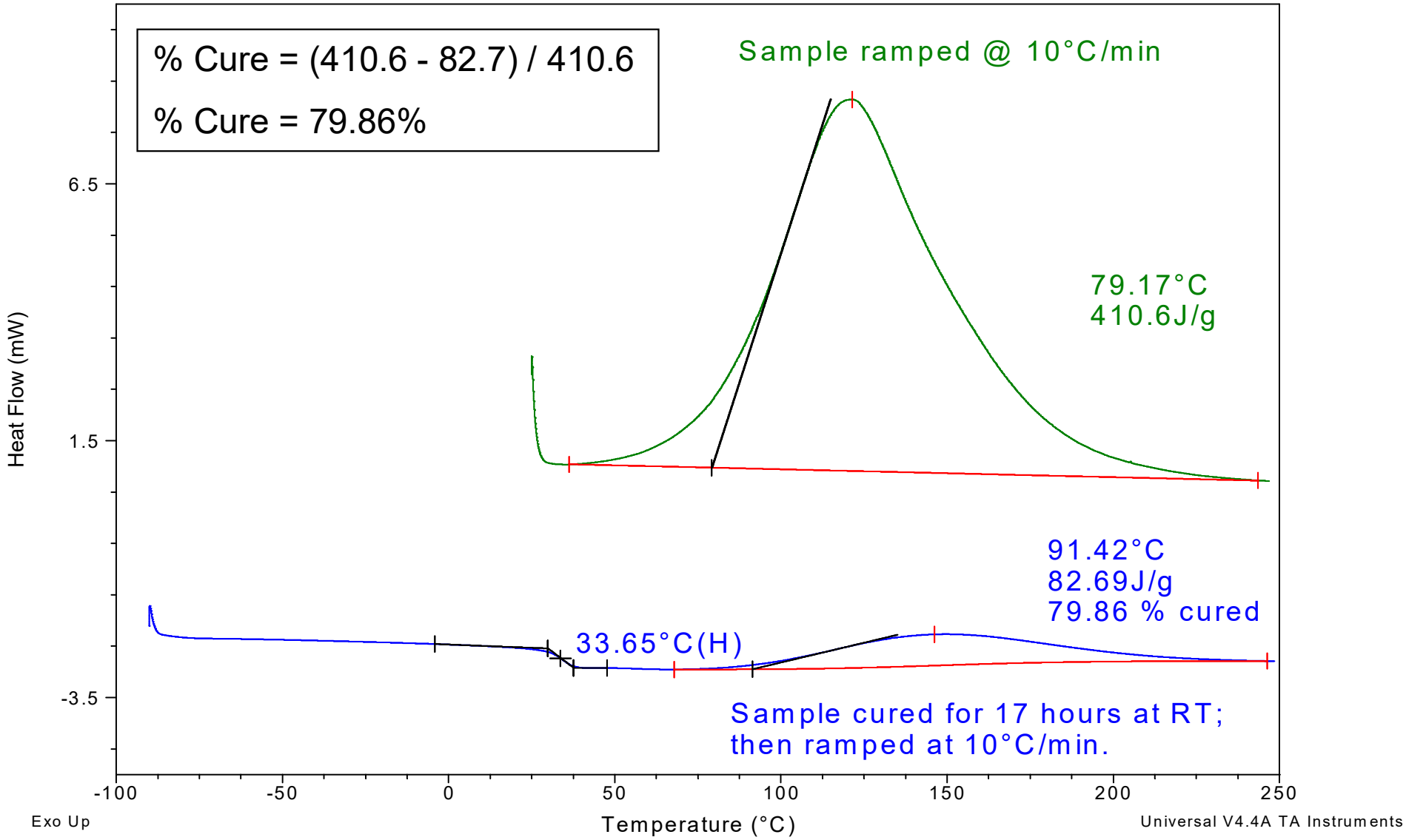
# Percent Cure Calculation by DSC

- Need Heat of Reaction (Enthalpy) of unreacted material curing
  - Typically run uncured material in DSC
- Run cured or partially cured sample in DSC

% Cure = 1 - ($\Delta$H Residual Cure / $\Delta$H Full Cure) * 100

% Uncured = ($\Delta$H Residual Cure / $\Delta$H Full Cure) * 100

# Calculation of % Cure: An Epoxy



# Thank You

The World Leader in Thermal Analysis,
Rheology, and Microcalorimetry