

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



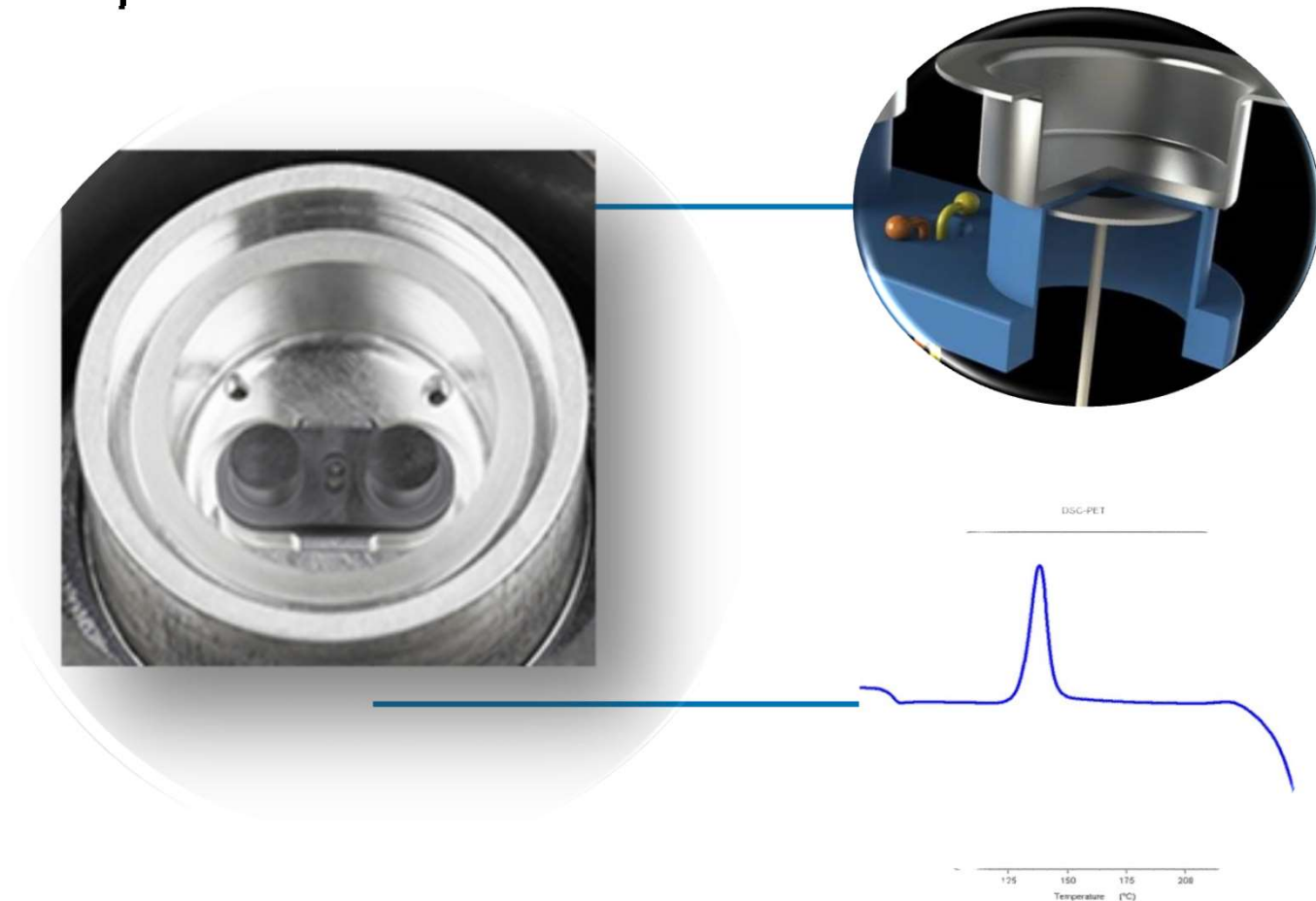
Discovery DSC



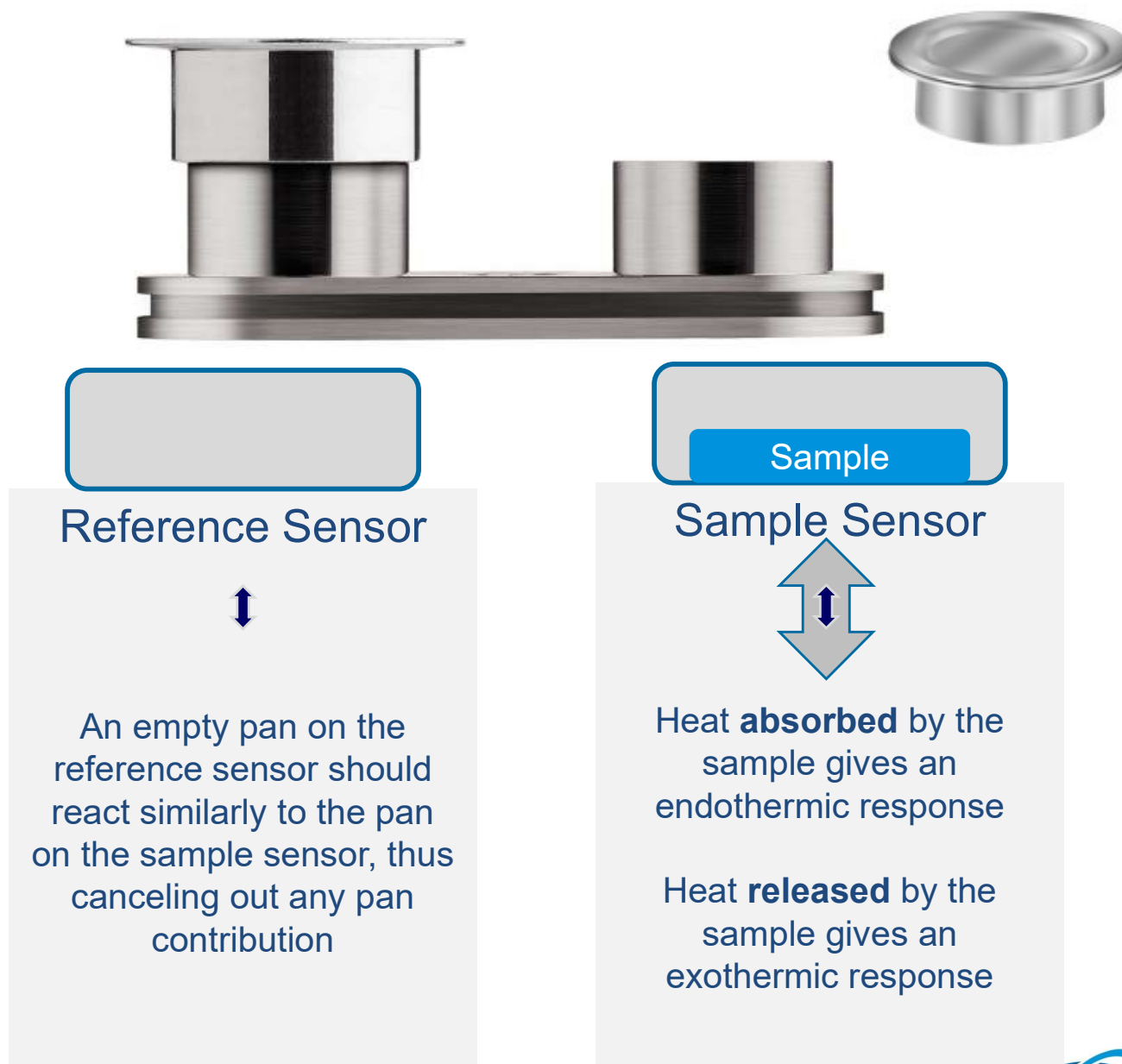
Q2000

What is a Differential Scanning Calorimetry

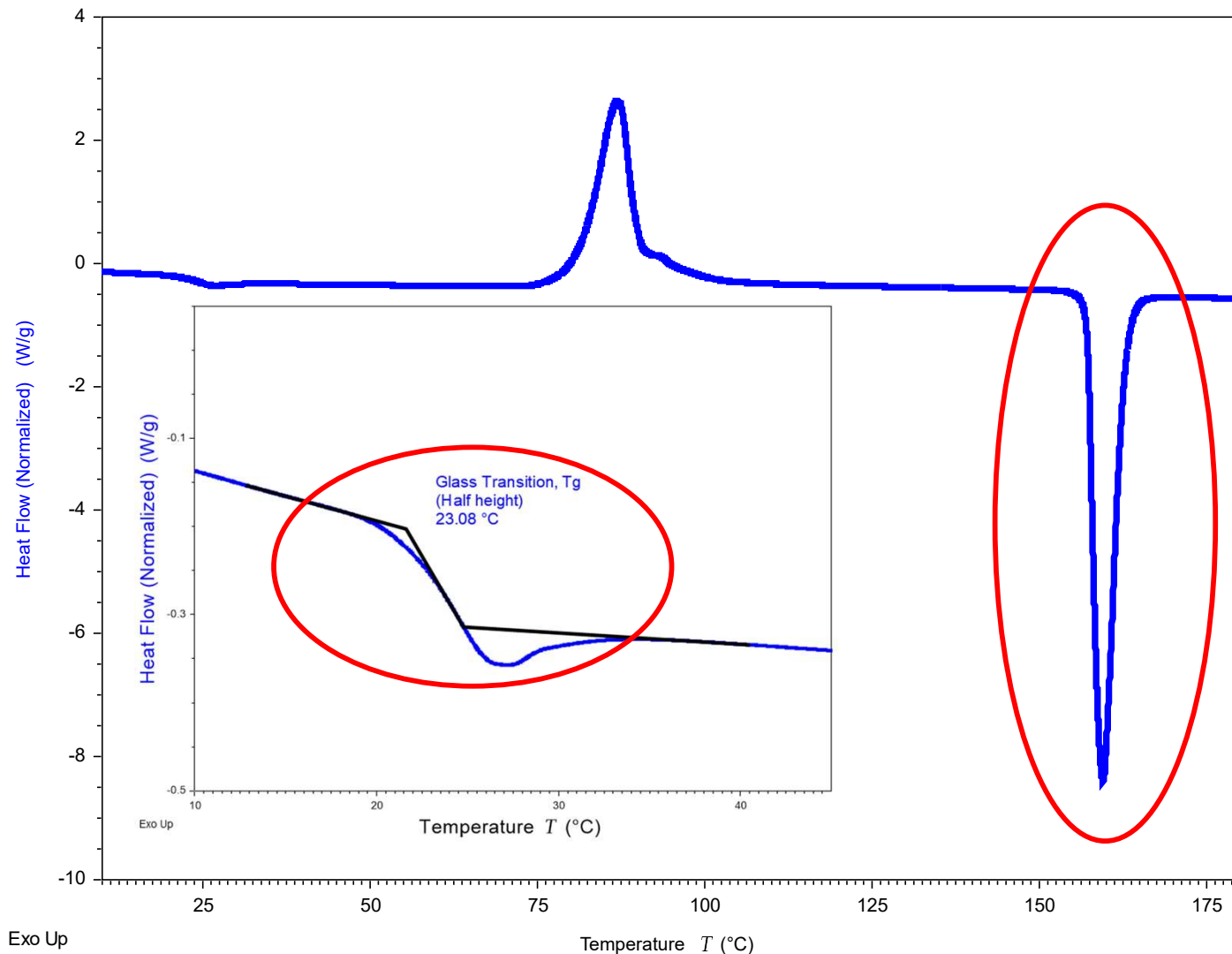
- A DSC measures the difference in Heat Flow Rate between a sample and inert reference as a function of time and temperature



Simple Heat Flux DSC Cell Schematic



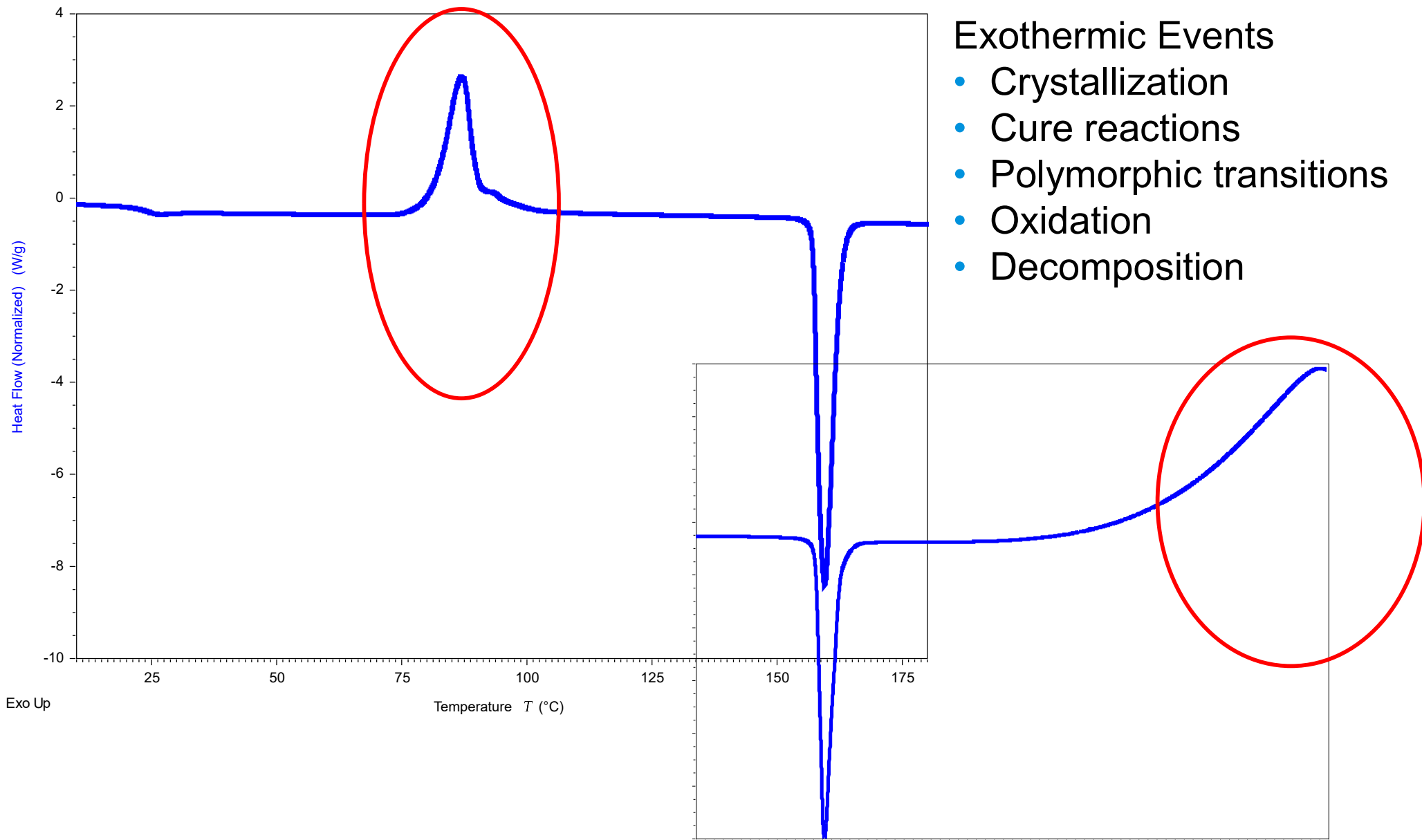
Endothermic Heat Flow – Heat Absorbed by Sample



Endothermic Events

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

Exothermic Heat Flow – Heat Released by Sample



DSC Heat Flow

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

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

$$C_p = \text{Sample Heat Capacity}$$
$$= \text{Sample Specific Heat} \times \text{Sample Weight}$$

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

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

$$f(T, t) = \text{Heat flow that is function of time}$$

at an absolute temperature (kinetic)

DSC Heat Flow

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

Heat
Capacity

Glass
Transition
Some Melting

Kinetic

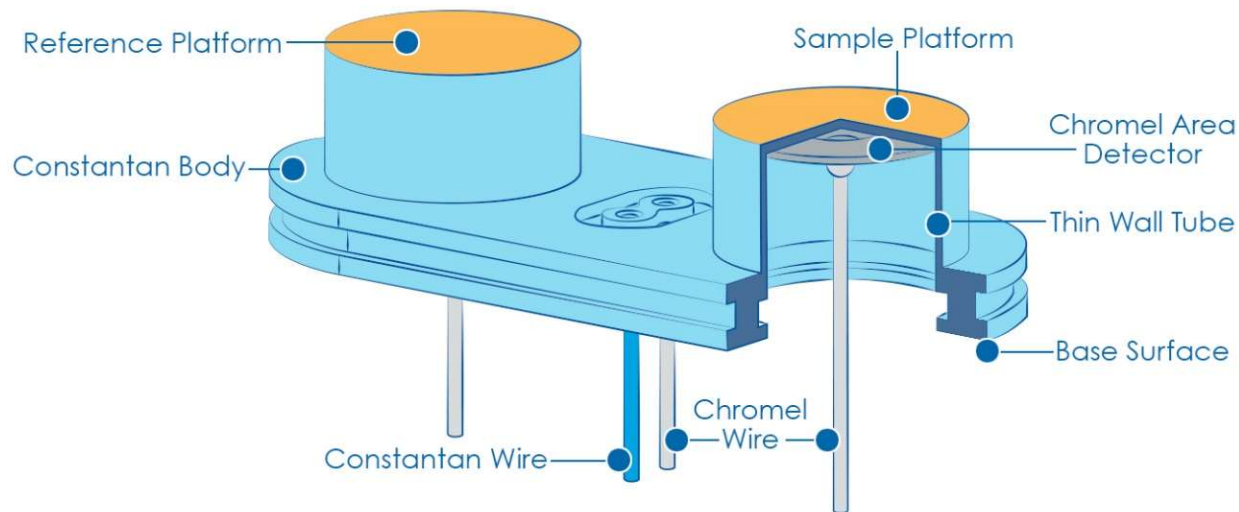
Crystallization
Some melting
Cure reactions
Volatilization
Decomposition
Denaturation

DSC heat flow modes – T1 vs T4 vs T4P mode



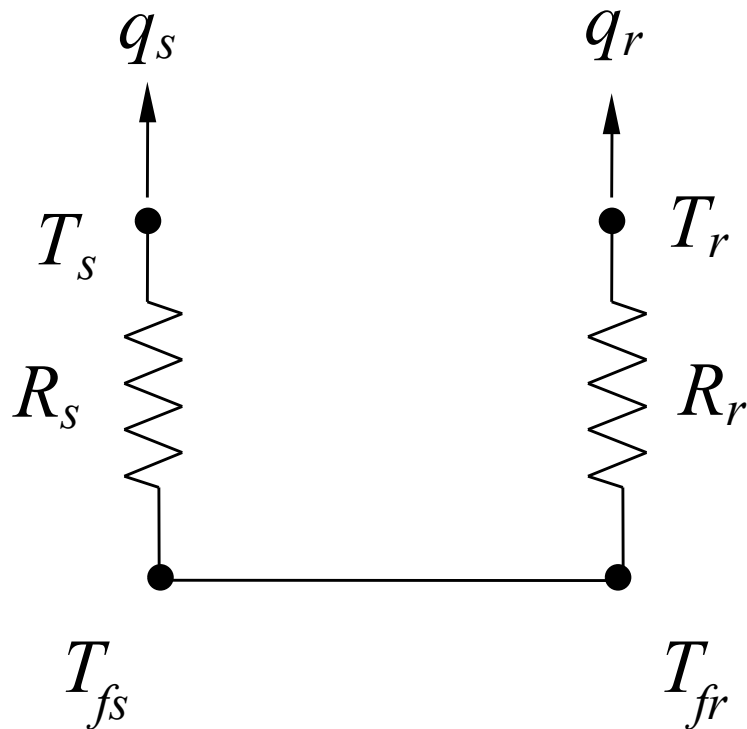
Measurement of Temperature

- 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

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

Conventional DSC Heat
Flow Rate Measurement

$$q = q_s - q_r$$

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

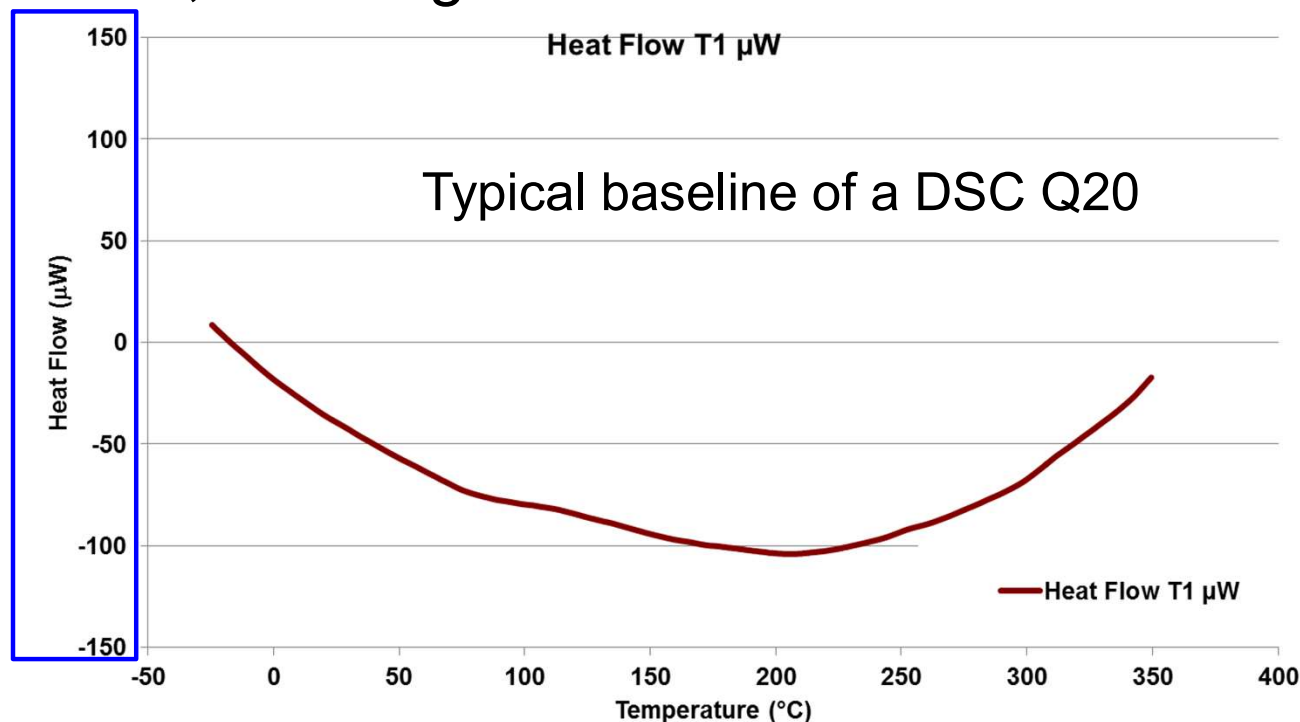
This model assumes that the sample and reference calorimeter thermal resistances are identical and that the furnace temperature is uniform throughout the cell.

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

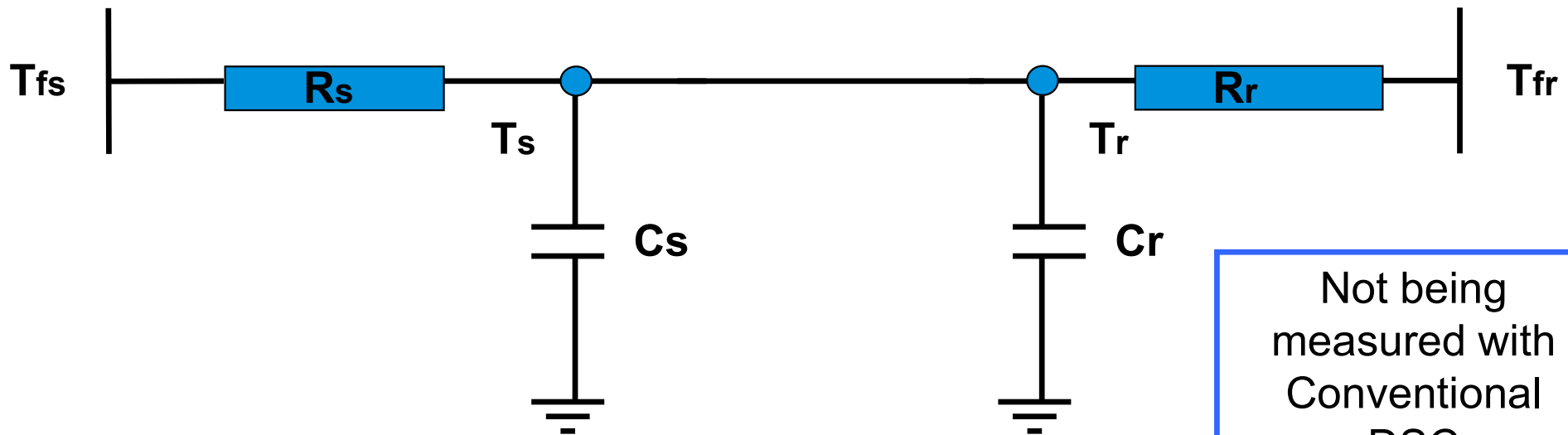
Consequences of the Assumptions

- 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

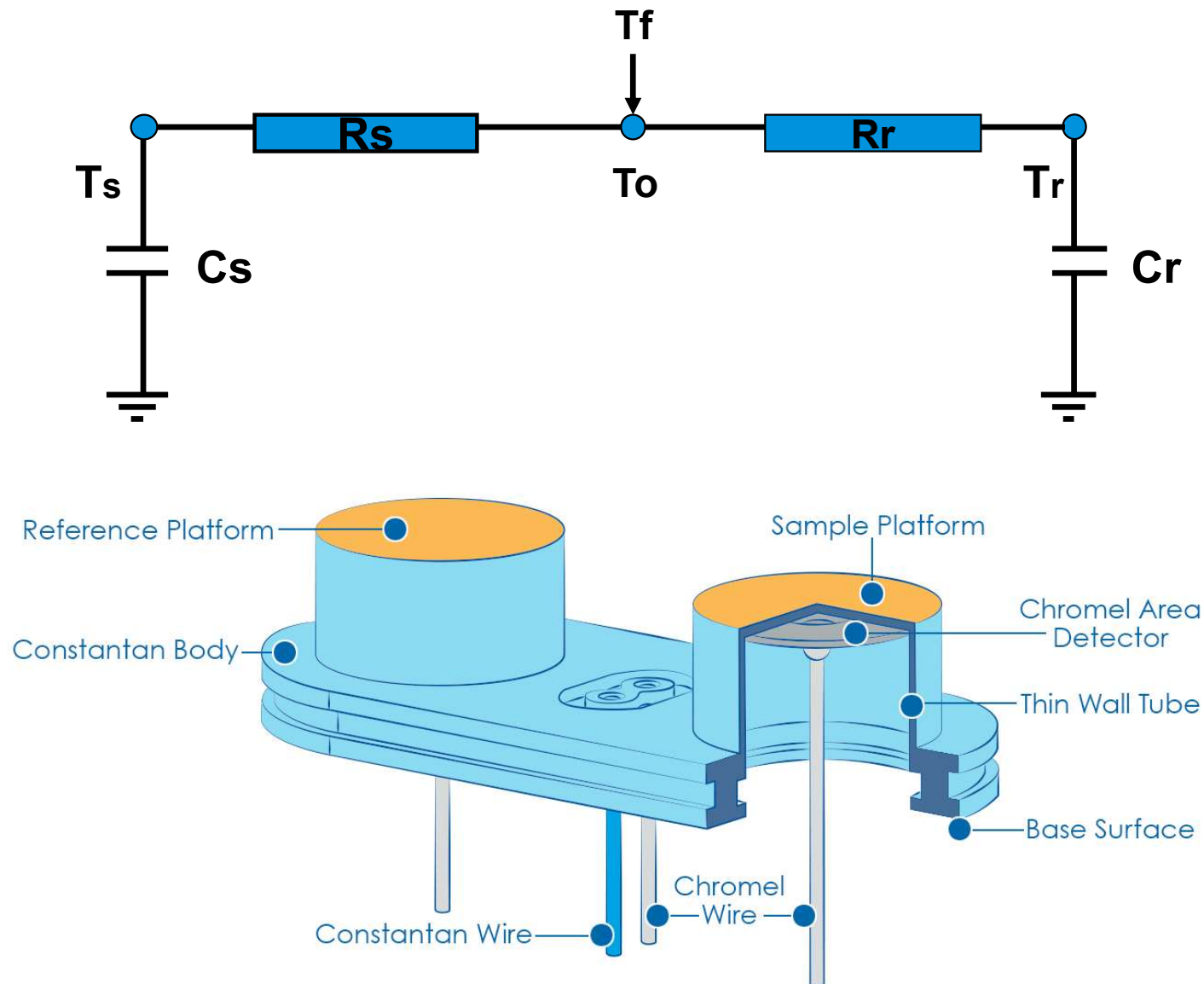


Not being
measured with
Conventional
DSC

$$Q = \frac{T_s - T_r}{R}$$

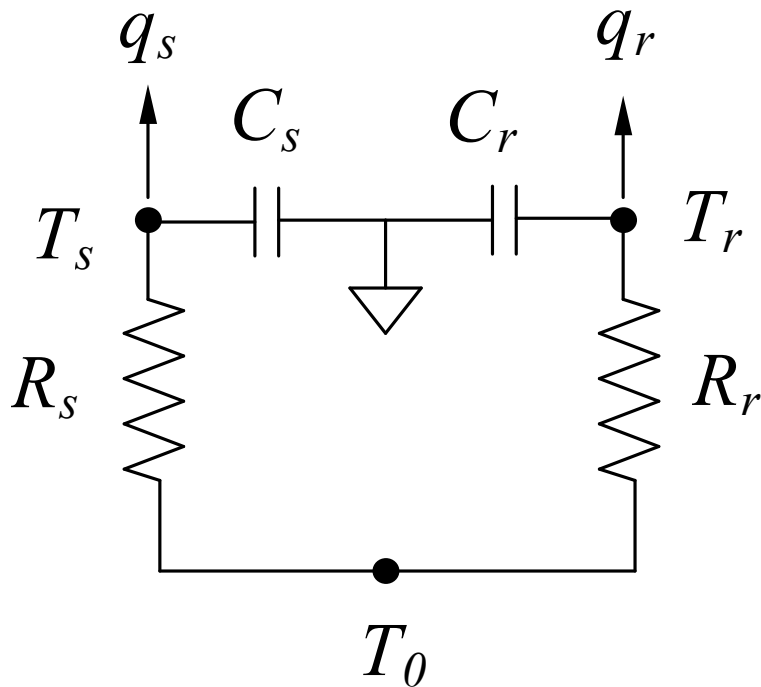
+ $\begin{matrix} \text{A} \\ \uparrow \\ \text{Thermal} \\ \text{Resistance} \\ \text{Imbalance} \end{matrix}$ + $\begin{matrix} \text{B} \\ \uparrow \\ \text{Thermal} \\ \text{Capacitance} \\ \text{Imbalance} \end{matrix}$ + $\begin{matrix} \text{C} \\ \uparrow \\ \text{Heating} \\ \text{Rate} \\ \text{Imbalance} \end{matrix}$

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



Tzero™ Heat Flow Measurement

Heat Flow
Sensor Model



Differential Temperatures

$$\Delta T = T_s - T_r$$

$$\Delta T_0 = T_0 - T_s$$

Heat Flow Rate Equations

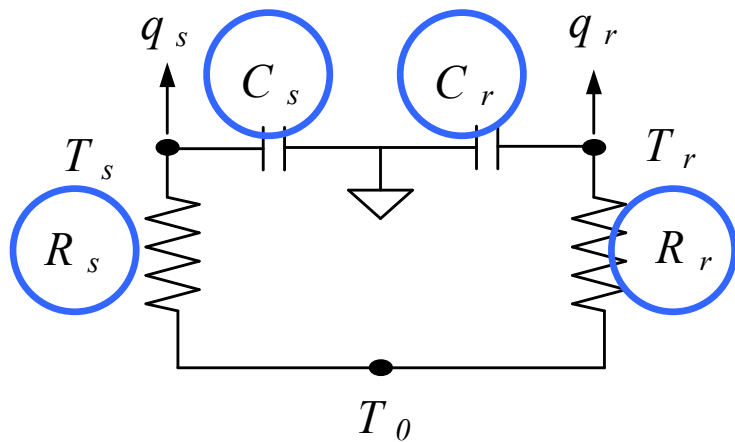
$$q_s = \frac{\Delta T_0}{R_s} - C_s \frac{dT}{dt}$$

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

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

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

Thermal Resistance Imbalance

Heating Rate Difference

Principal DSC Heat Flow

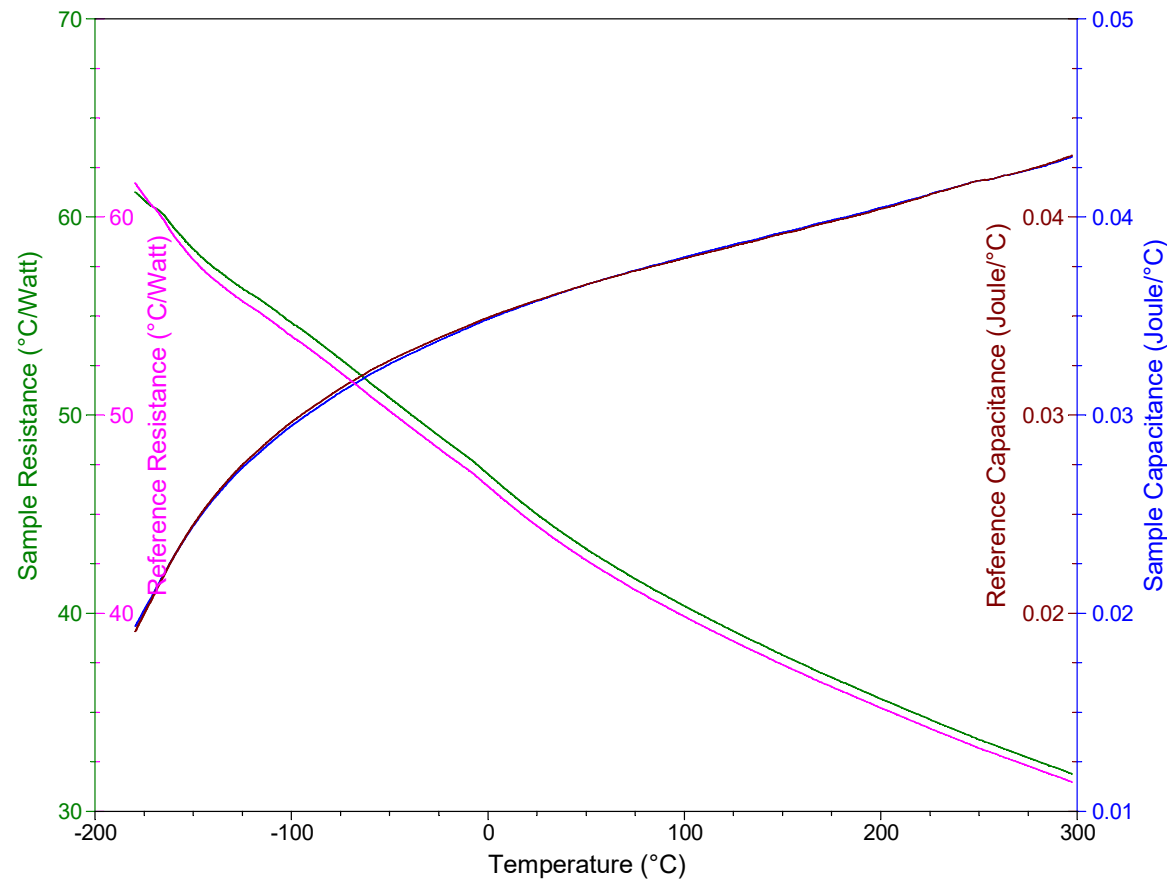
Heat Capacity Imbalance

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

- There is really no user interaction necessary for the analysis of this data, but a qualitative observation of the resulting data is always a good idea
 - The curves should be smooth and continuous, without evidence of noise or artifacts
 - Capacitance values should increase with temperature (with a decreasing slope)
 - Resistance values should decrease with temperature (also with a decreasing slope)
- It is not unusual for there to be a difference between the two sides, although often they are very close to identical
- The software should automatically analyze the data and save it to the instrument
 - Can check the Calibration Report after calibration

Example of Typical Results

Both curves should be smooth, with no steps, spikes or inflection points.
Thermal resistances should always have negative slope that gradually decreases.
Heat capacities should always have positive slope that gradually decreases.

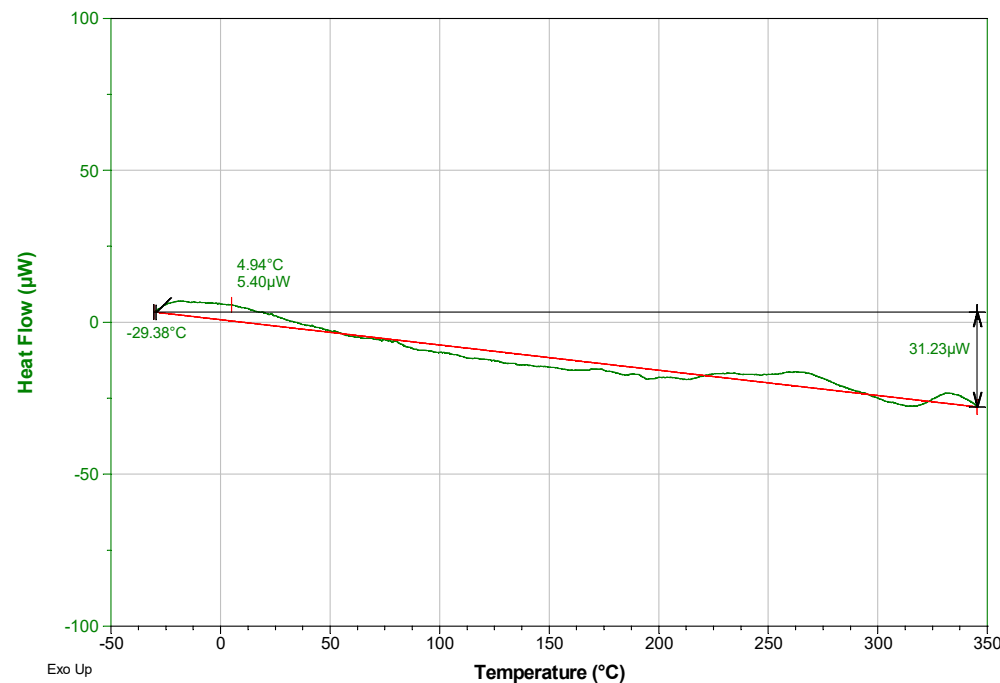
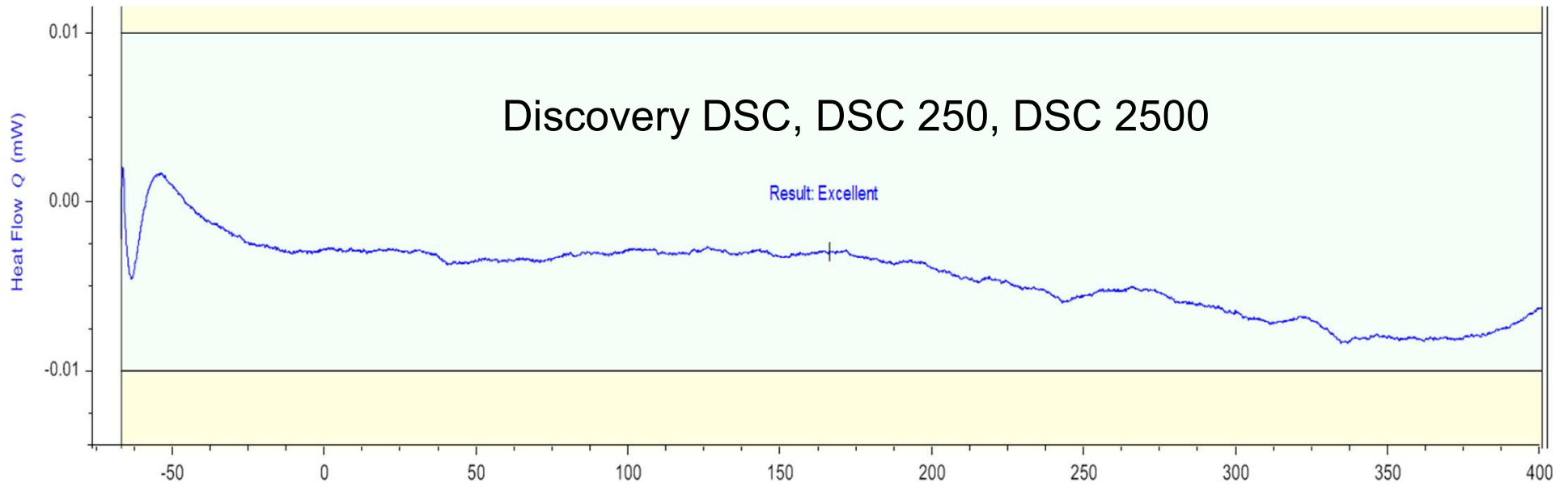


This cell is very well balanced. It is acceptable and usual to have larger differences between sample and reference sensors.

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.

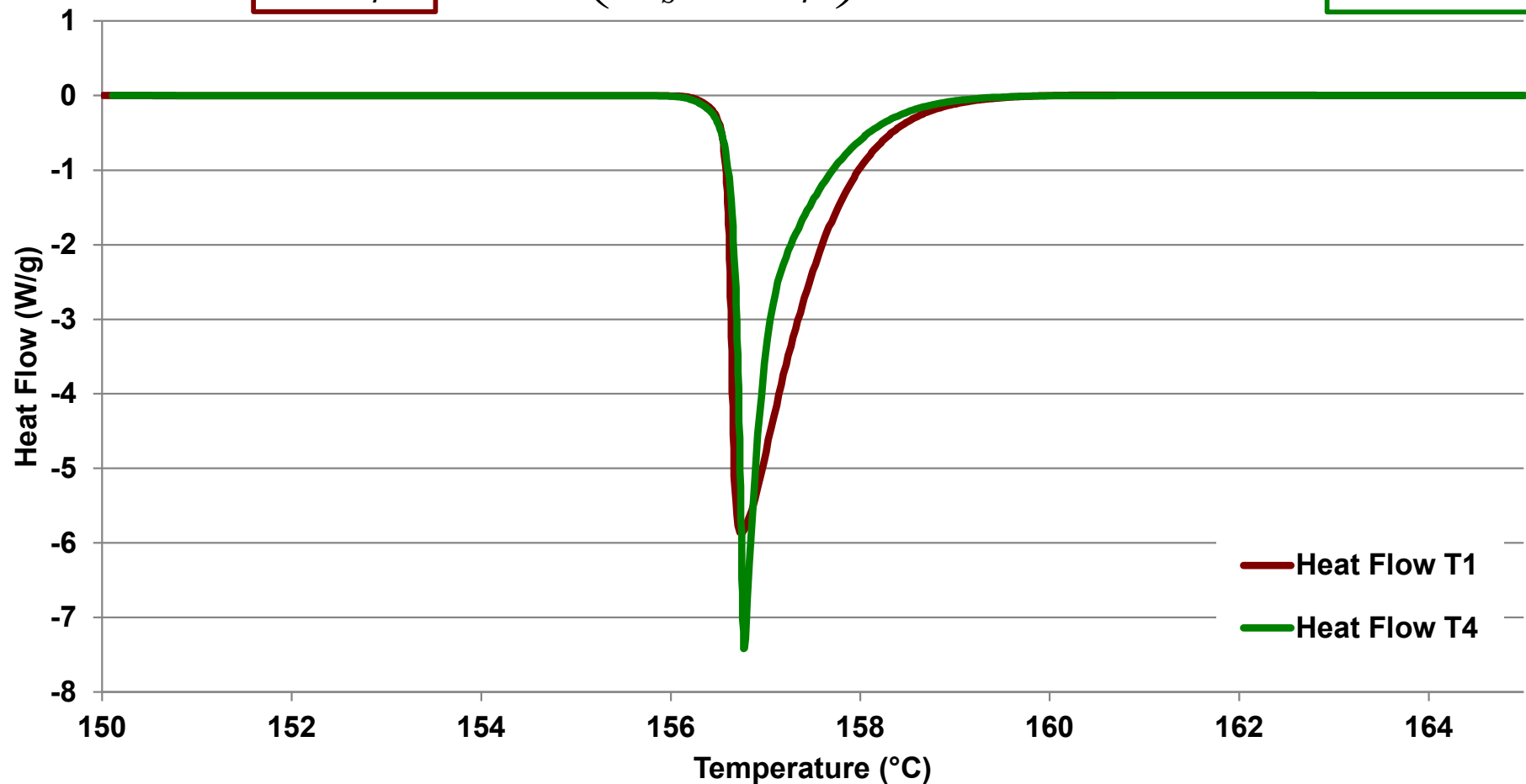
Empty cell baseline using the Tzero™ heat flow equation



DSC Q2000

Tzero Benefit: Improved Peak Resolution

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

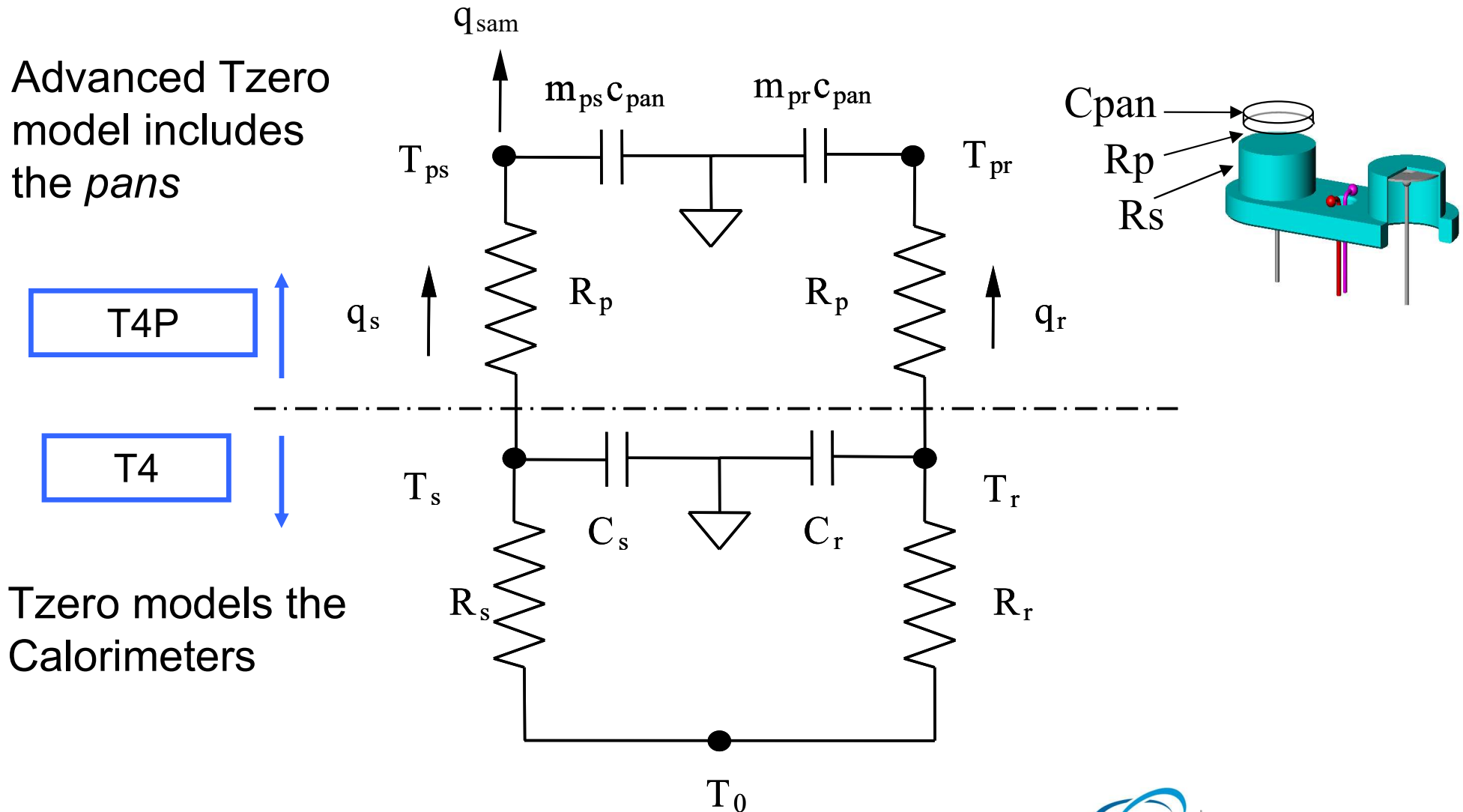


Advanced Tzero Technology (T4P)

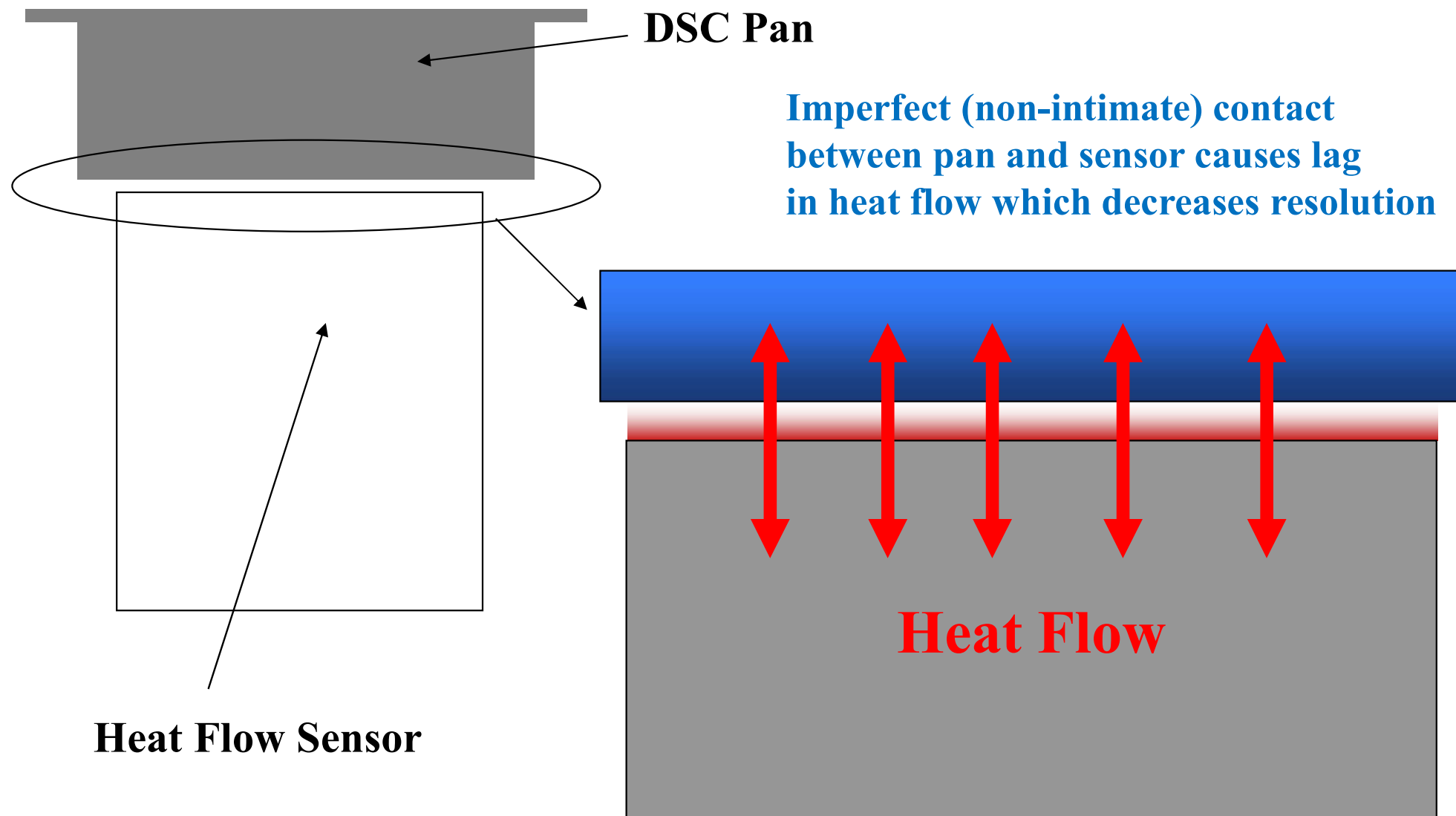
- During transitions and MDSC experiments, the heating rates of the sample pan, sample calorimeter, reference pan and reference calorimeter may be very different.
- Sample pans have thermal resistance and heat capacity; sample and reference pans rarely have the same mass.
- Advanced Tzero includes the 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

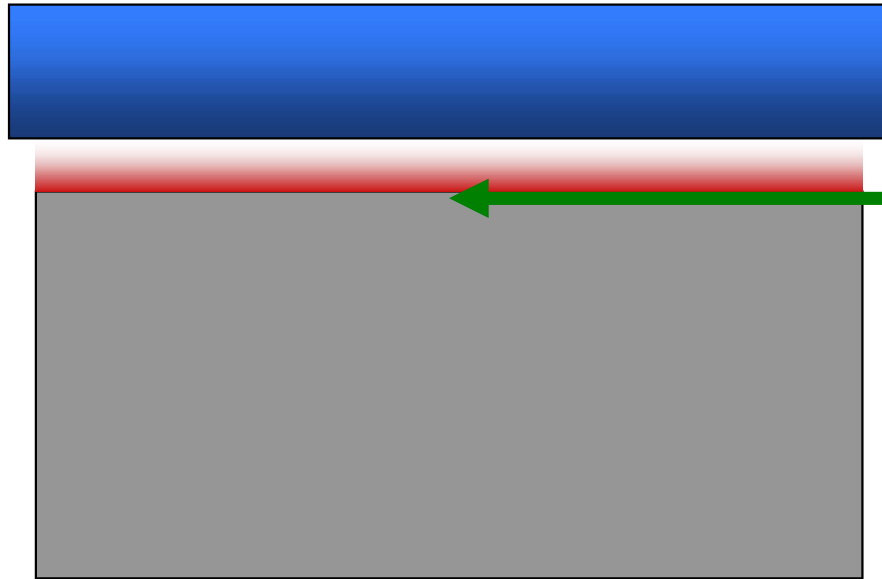
Advanced Tzero is a further refinement of the Tzero model and takes the measurement up to the sample pan, ***one step closer to the actual sample***



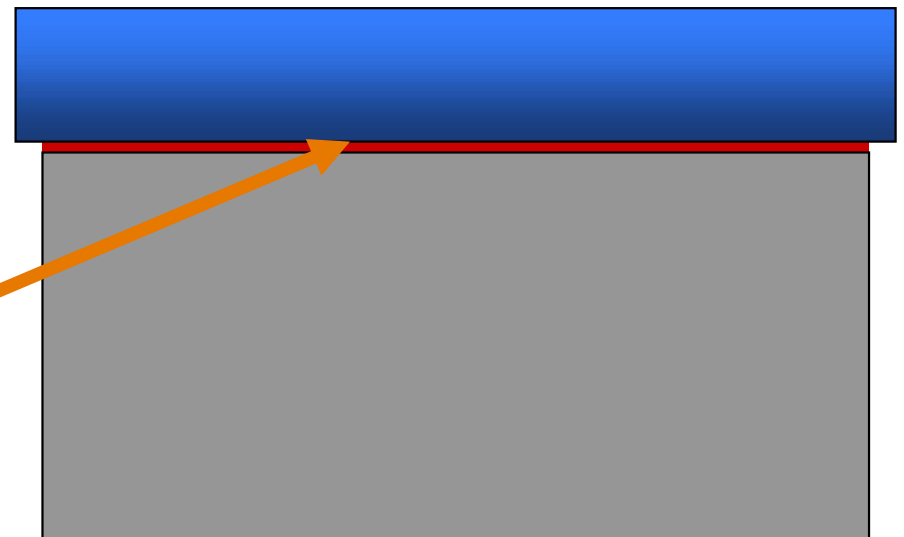
What is Pan Contact Resistance?



Result of Pan Contact Resistance Factor



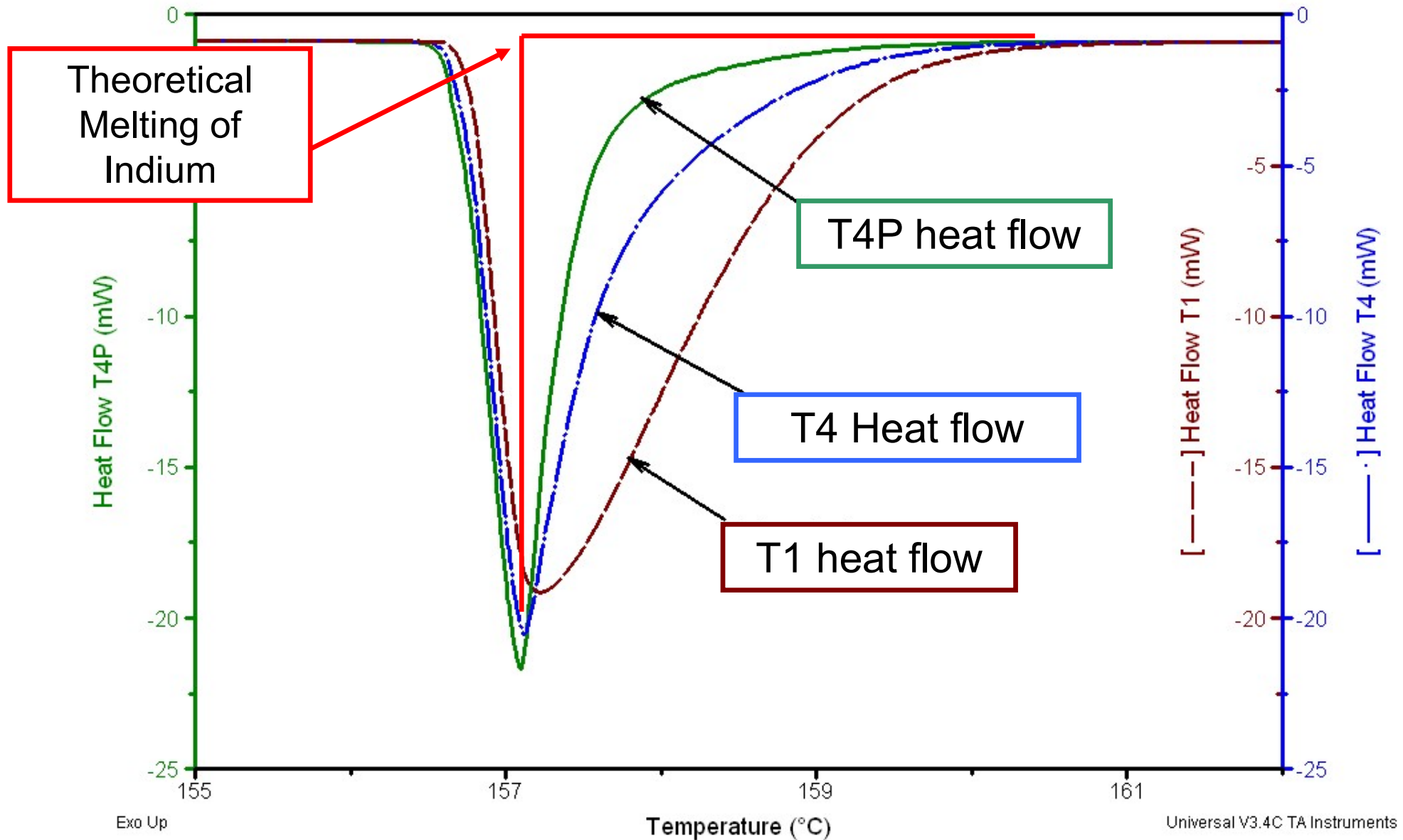
Without pan contact resistance factor, temperature is measured at the sensor



With pan contact resistance factor, temperature is measured at the bottom of the pan, in intimate contact with the sample

Indium with T1, T4 and T4P Heat Flow Signals

Improvements to Sensitivity and Resolution



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.

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

- 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

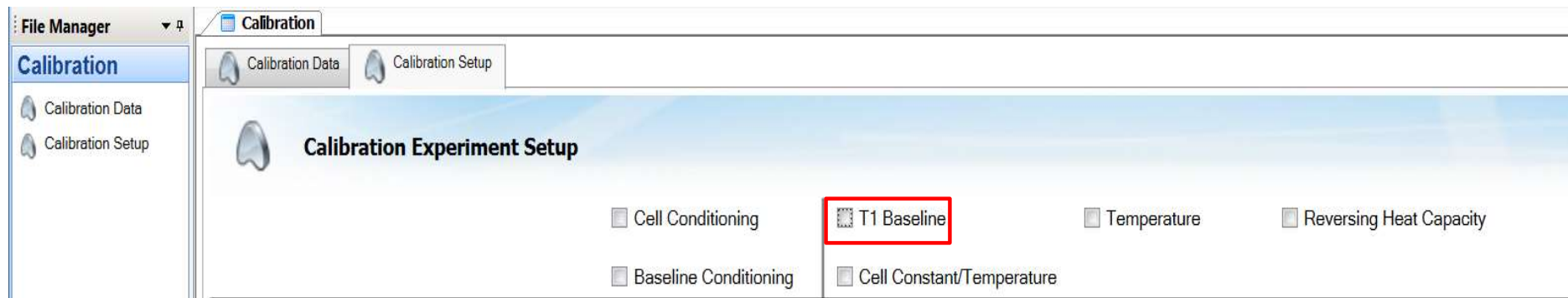
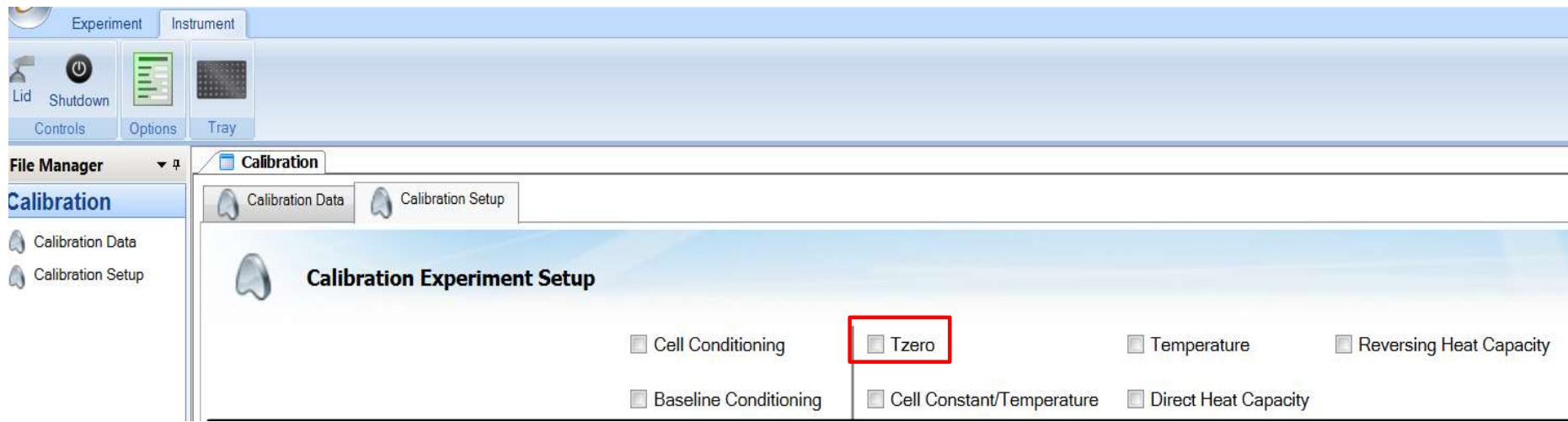
Measurement of
slope and offset

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.

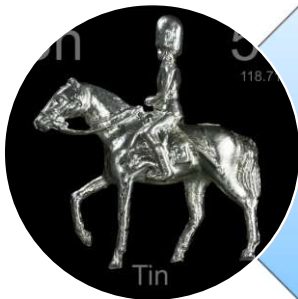
Instrument setup factors affecting calibration

- Purge Gas
 - Re-calibrate baseline/Tzero, temperature and cell constant
 - Thermal conductivity of helium \neq Thermal conductivity of nitrogen/air/oxygen \neq 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



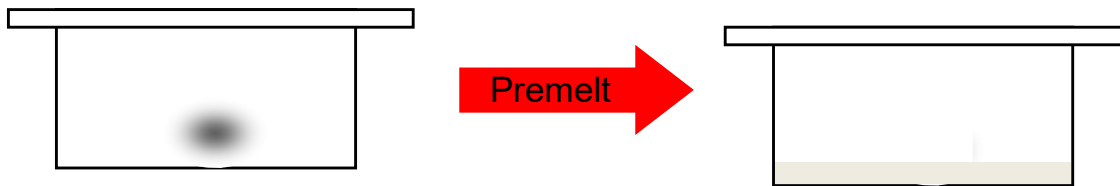
Tin (231.9°C)
Has multiple crystalline forms,
use once – no pre-melt



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



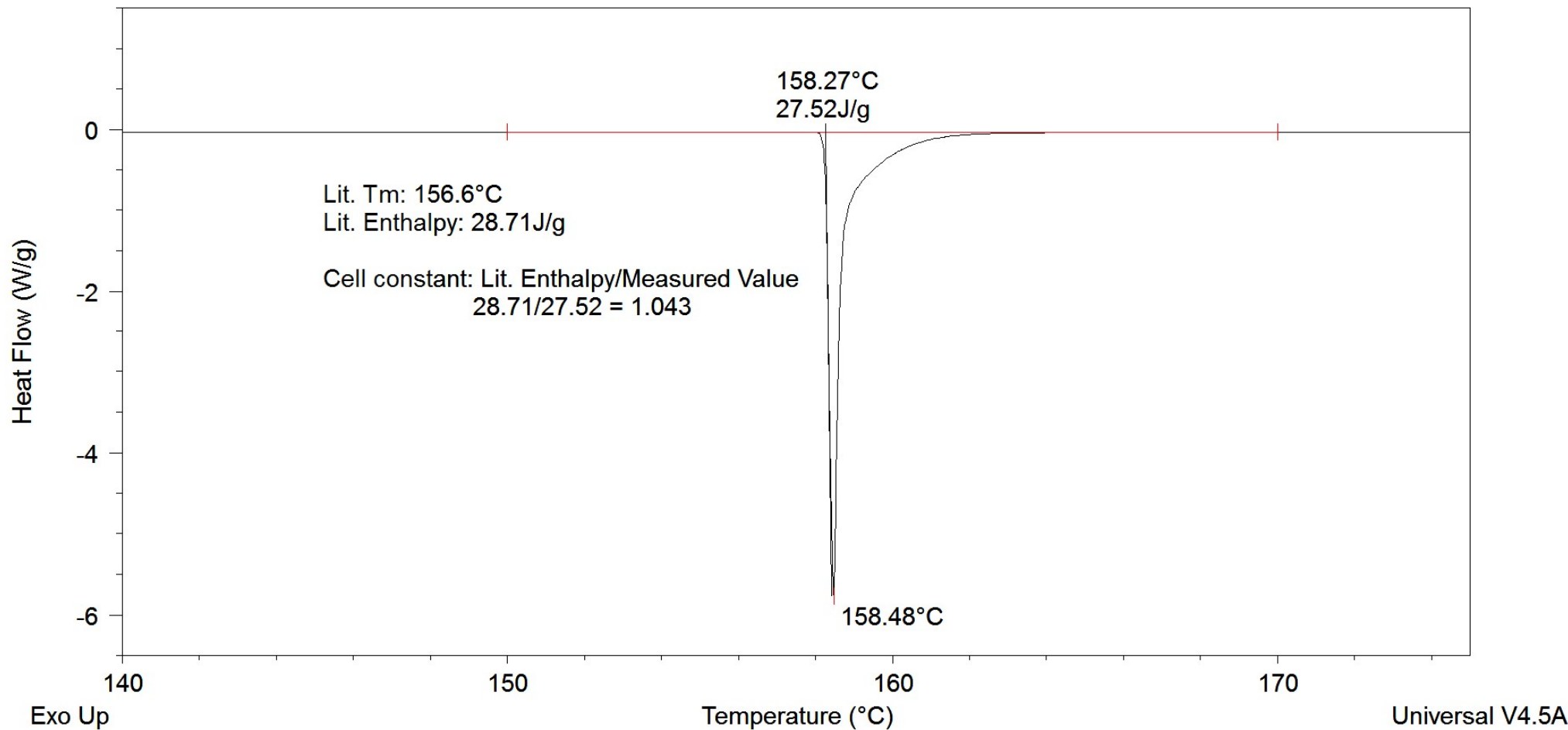
- Verify at least once a month
- Typical values for cell constant:
 - 0.9 to 1.2 (in N₂)
 - Helium will typically give higher values for the cell constant

Verifying Cell Constant & Temperature

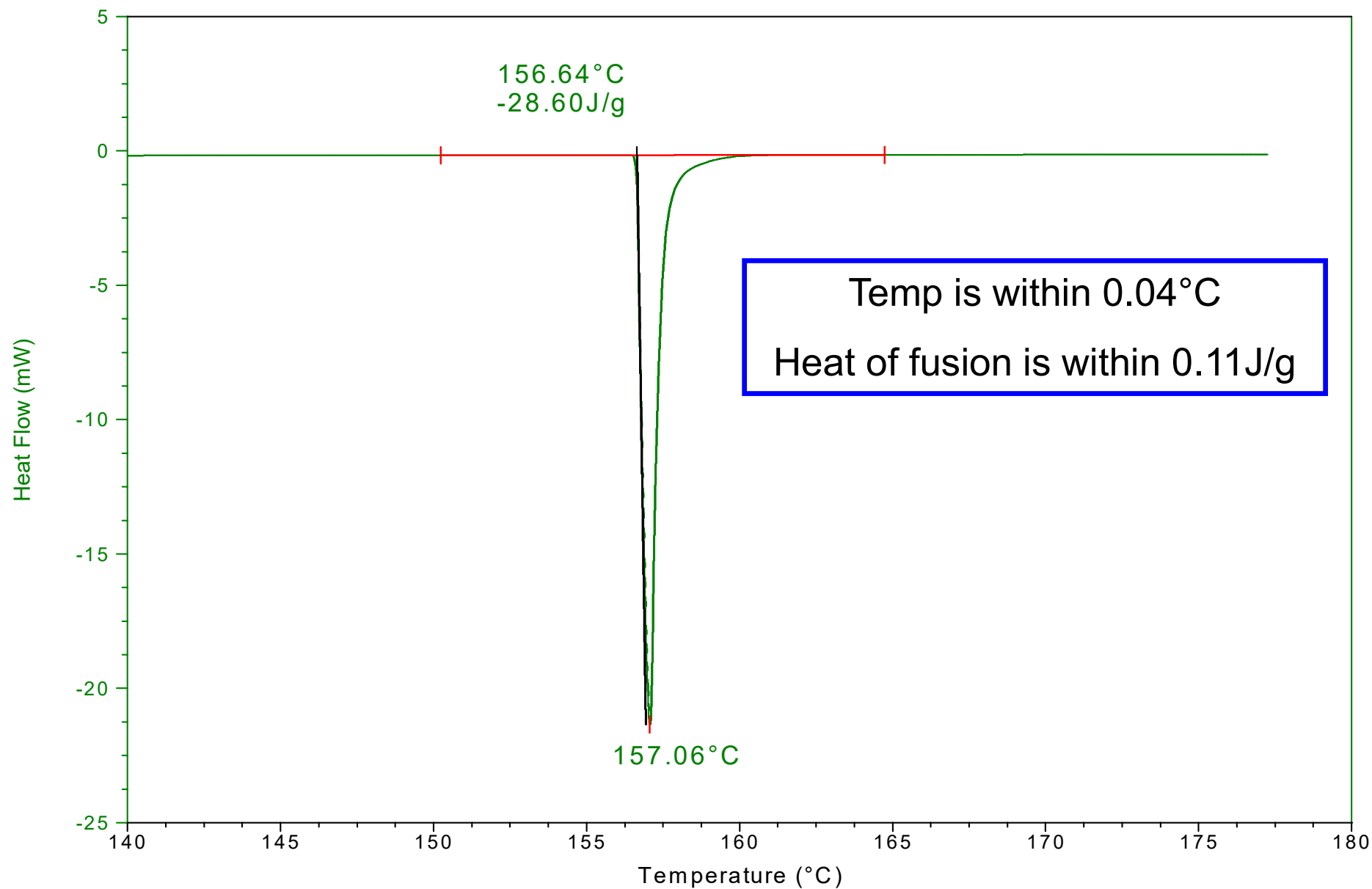
- Run Indium as a sample (i.e. in standard mode not calibration mode)
- Analyze melt and record melt onset & heat of fusion
- Compare to known values
 - Melting of In 156.6°C
 - Heat of Fusion 28.71J/g

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)
T_m = 123°C
- Urea (241.8 J/g)
T_m = 133°C
- **Indium (28.71 J/g)**
T_m = 156.6°C
- Anthracene (161.9 J/g)
T_m = 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

Traceable Calibration Materials

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

Traceable Calibration Materials

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

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

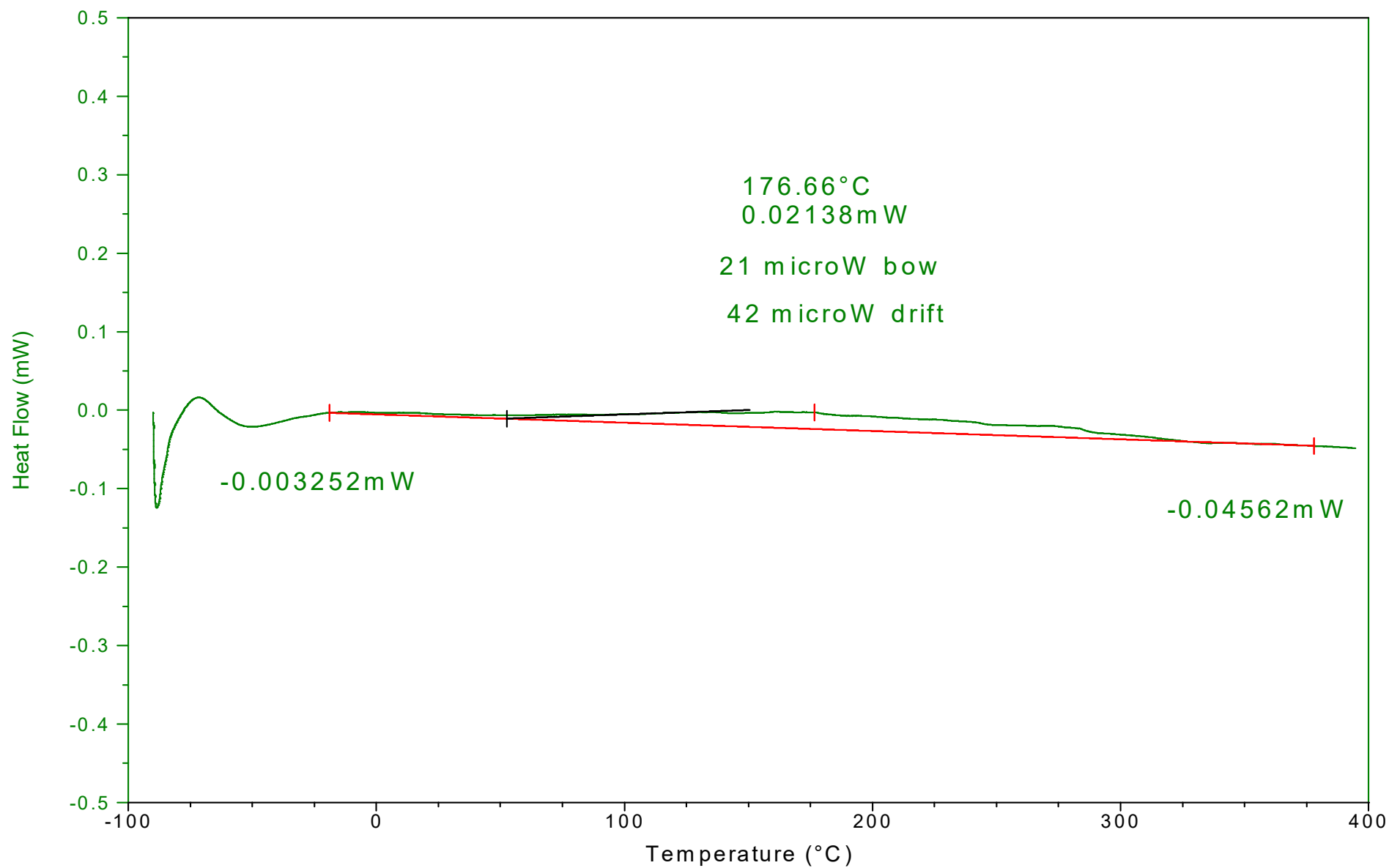
Verifying Baseline

- Run Empty cell (no pans), -90°C to 400°C (w/ RCS) at $20^{\circ}\text{C}/\text{min}$
 - 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

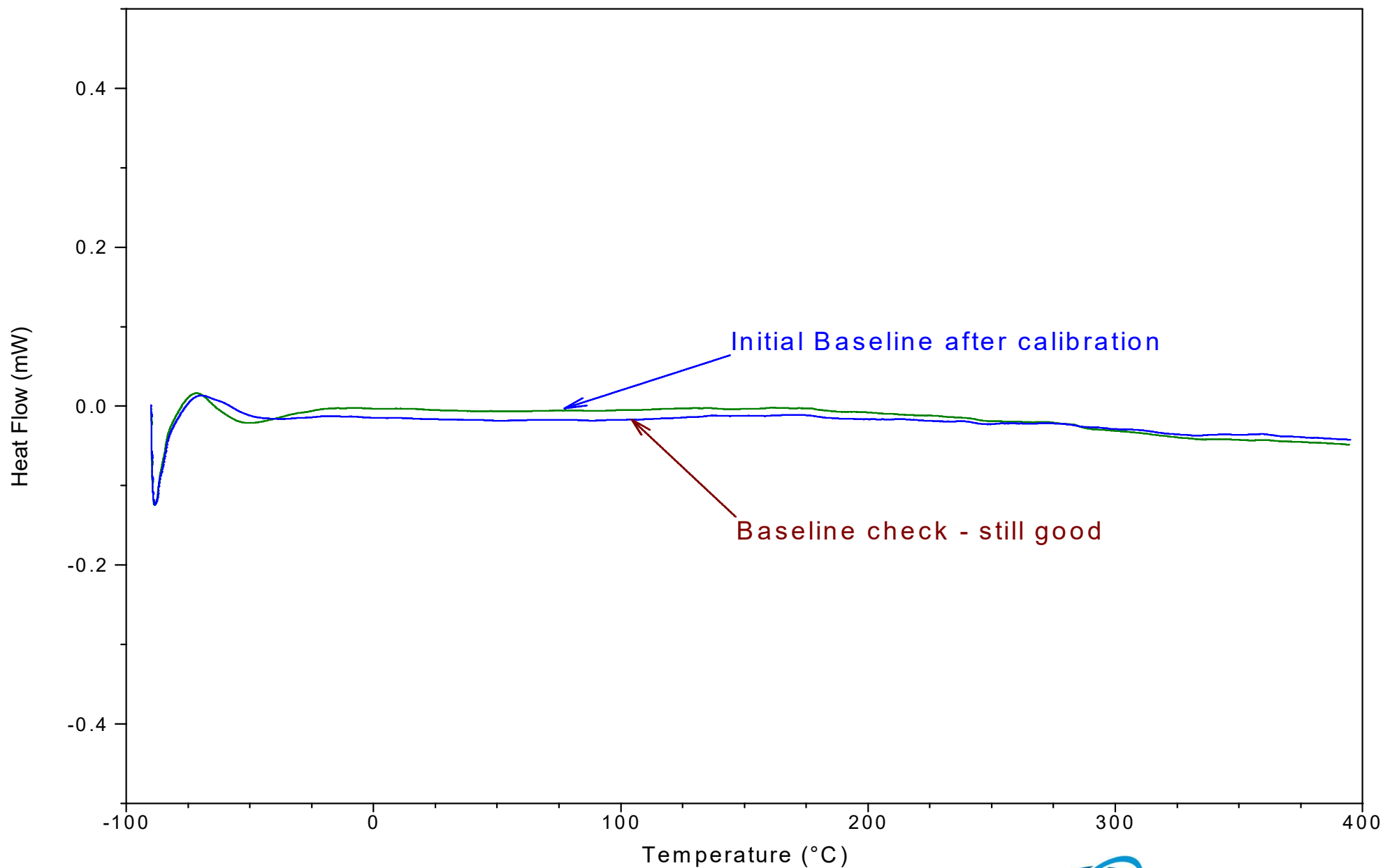
Verifying Baseline

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

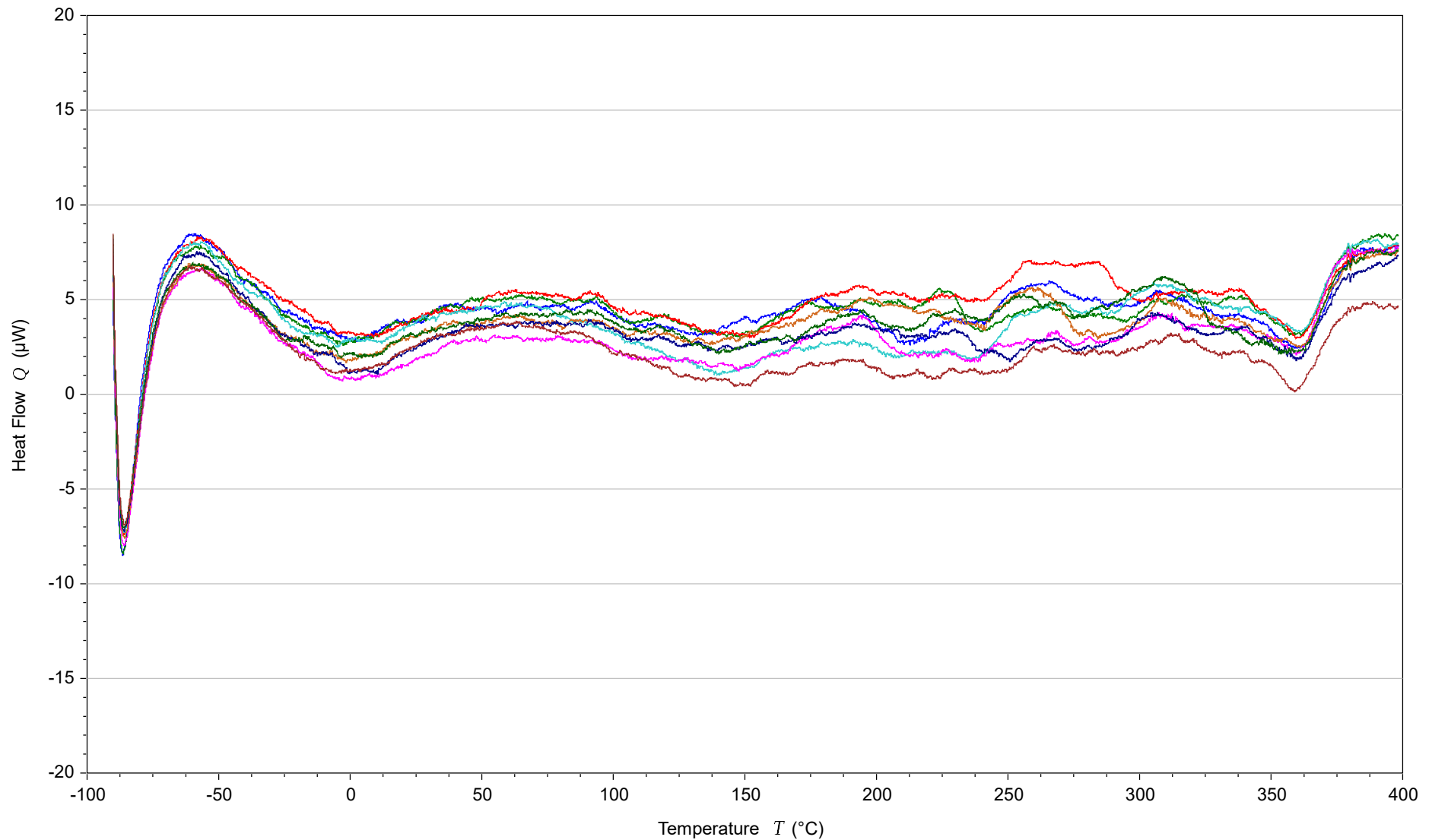
Verifying Baseline



Verifying Baseline



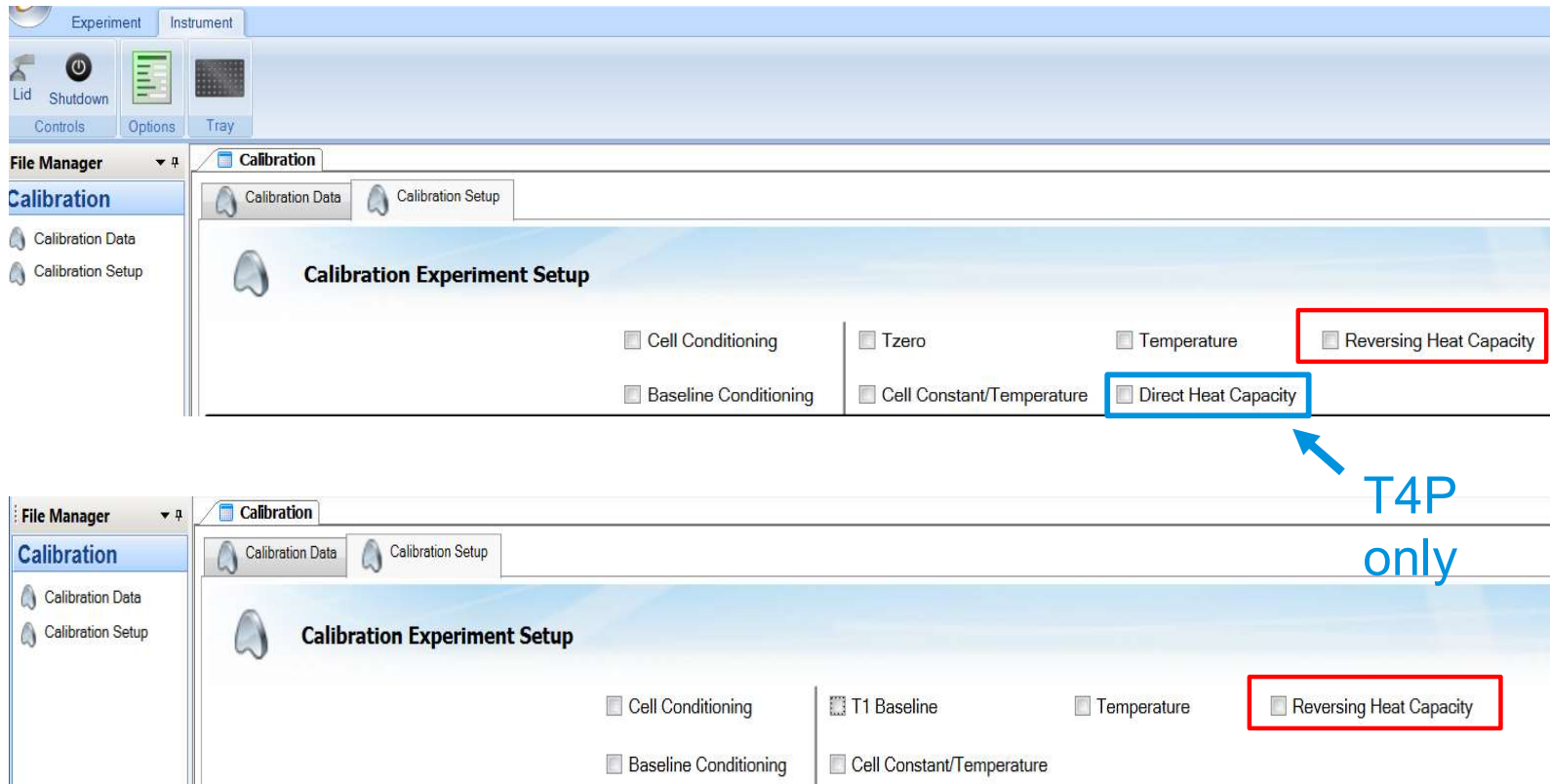
Empty Cell Baseline at 20 deg/min – DSC2500



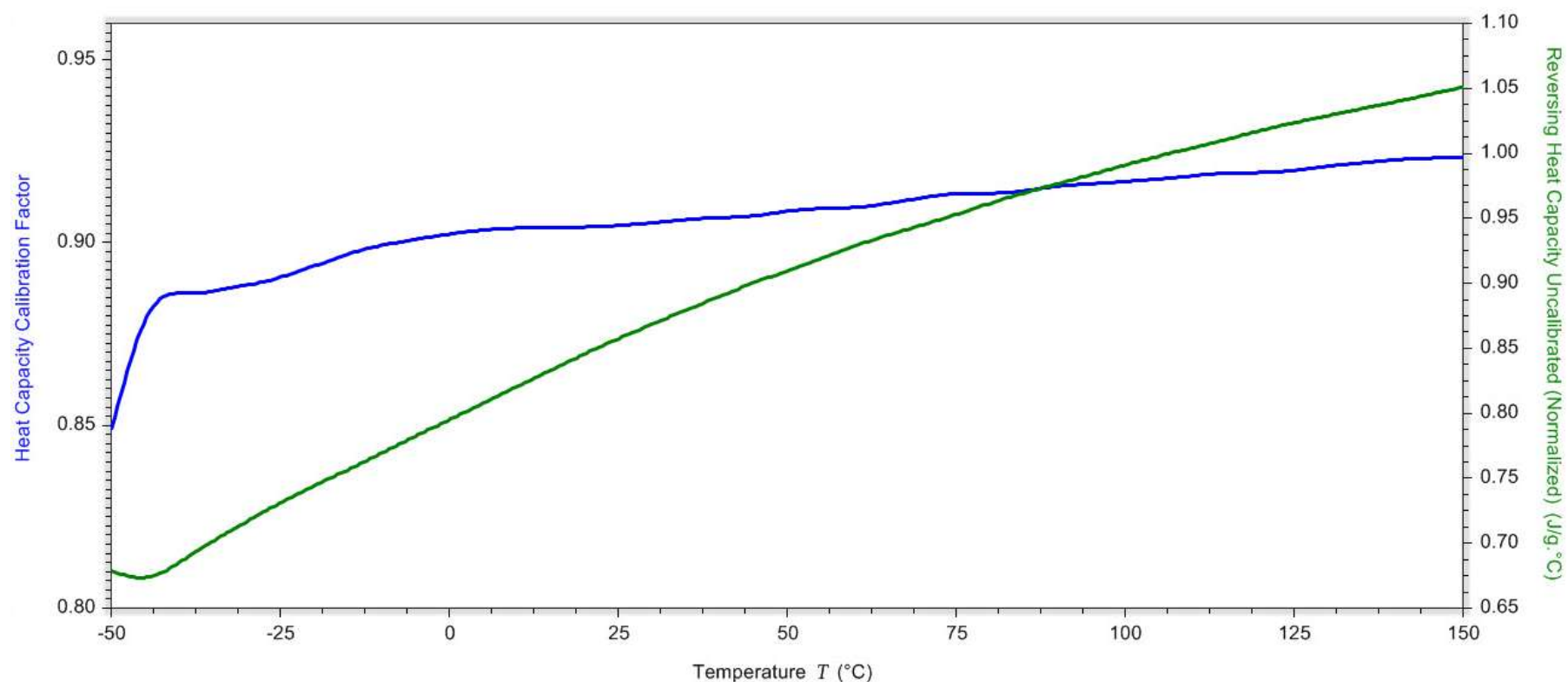
MDSC Calibration – Discovery Series

- 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

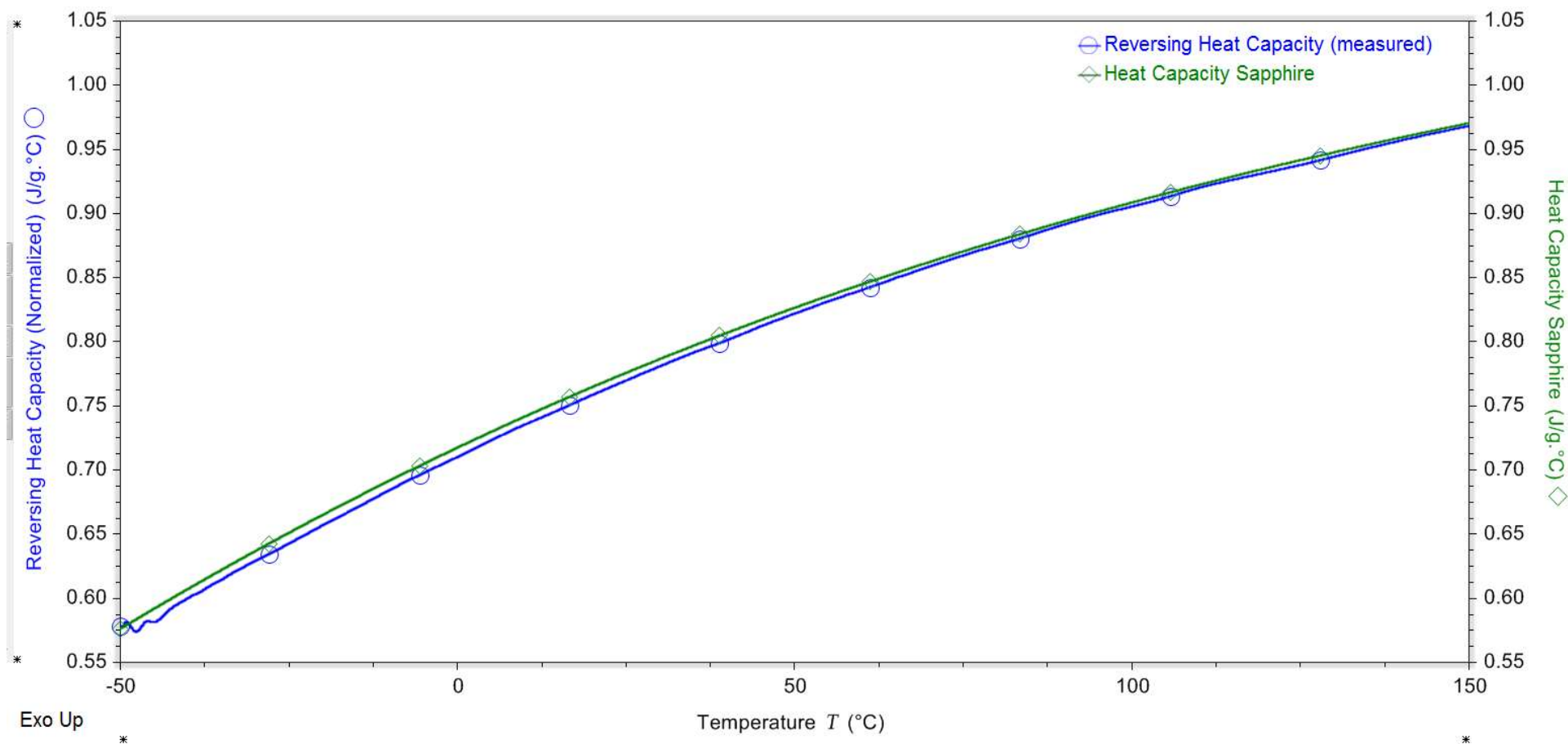


MDSC Cp calibration using TRIOS



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

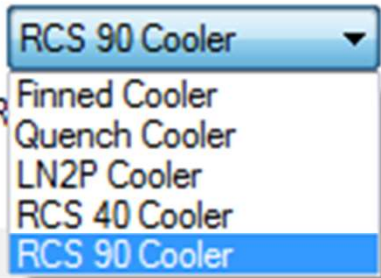
TA Instruments TRIOS

Application
Discovery DSC
Information
General
Cooler
Auto Sampler
Temperature Cal
Heat Capacity

 Cooler Settings

This is used to select the cooler type

Cooler Selection

Cooler Selection 

☒ Activate secondary purge when lid is opened (R

Between Runs

☒ Leave Cooler On

☒ Autofill LN2P if below %

Selecting the purge gas – Discovery DSC

TA Instruments TRIOS

Application
Discovery DSC
Information
General
Cooler
Auto Sampler
Temperature Cal
Heat Capacity

Global Settings

Global Options

Transition Direction: ☐ Exotherm Down ☒ Exotherm Up

Heat Flow Selection: Heat Flow T4P (mW)

Data Sampling Interval: 0.1 s/pt

Lid Type: Standard Temperature Lid

☐ Enable Sequence without Using Autosampler

Gas Connections

Gas 1: Nitrogen

Gas 2: Nitrogen

☒ Stop the experiment when

Instrument Database Backup (Ne 04, 2015)

☒ Backup: Daily Around 1:00 AM Backup Now

Backup Folder: C:\ProgramData\TA Instruments\TRIOS\ThermalDBbackups

☐ Prohibit any scheduled backups on this computer View Log Restore

OK Cancel

Options Exit

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

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.

The screenshot shows the 'General' tab of the Discovery DSC software. The 'Temperature' is 40.01 °C. The 'Flange Temperature' is -82.61 °C. The 'Cooler Selection' is 'RCS 90 Cooler'. The 'Standby' button is highlighted. The 'RCS' button is highlighted. The 'Flow rate' is 50. The 'Gas 1 Nitrogen' section is circled in red.

General	
Temperature:	40.01 °C
Flange Temperature	-82.61 °C
Cooler Selection	RCS 90 Cooler
Standby	40.0 °C
RCS	ON
Gas 1 Nitrogen:	50.0 mL/min
Base purge	263.4 mL/min
Gas 1: Nitrogen	
Flow rate	50

Recommended Purge Gas Flow Rates

Module

Purge Port

All TA DSC's

50 ml/min (N₂) 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

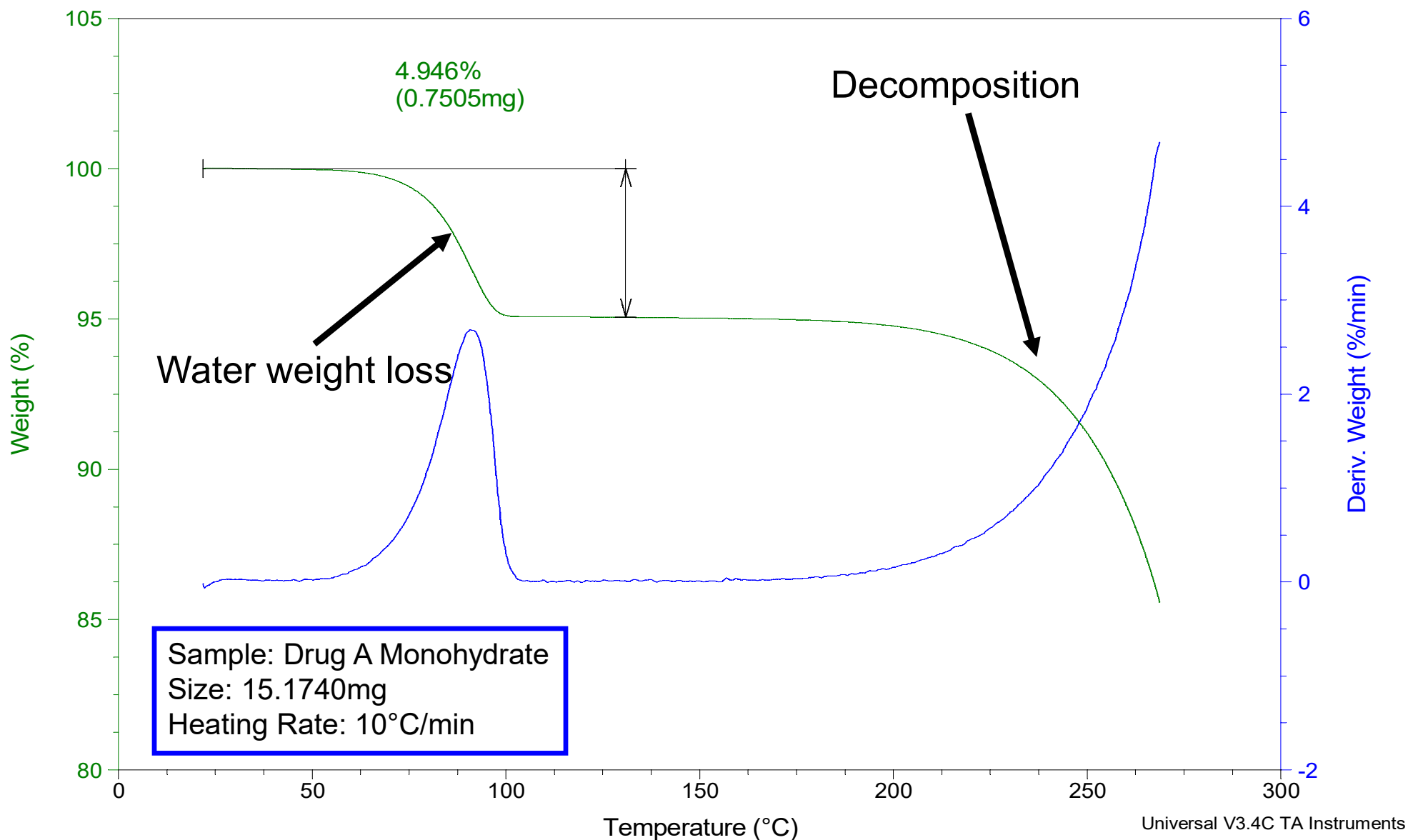
- Thermogravimetric Analysis (TGA) measures weight loss or gain as a function of temperature, time and atmosphere.
- General applications of TGA include:
 - thermal stability
 - residual solvent, out gassing, moisture sorption/desorption
 - filler/fiber content
 - weight loss on cure
- TGA measurements 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

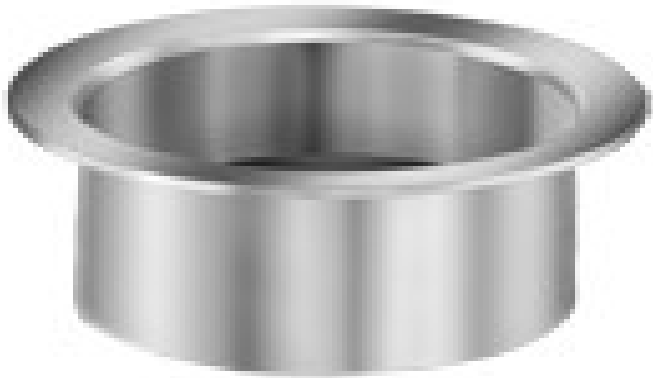


Sample Pans

- 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



- 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.

Tzero Low-Mass Pan



- 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)



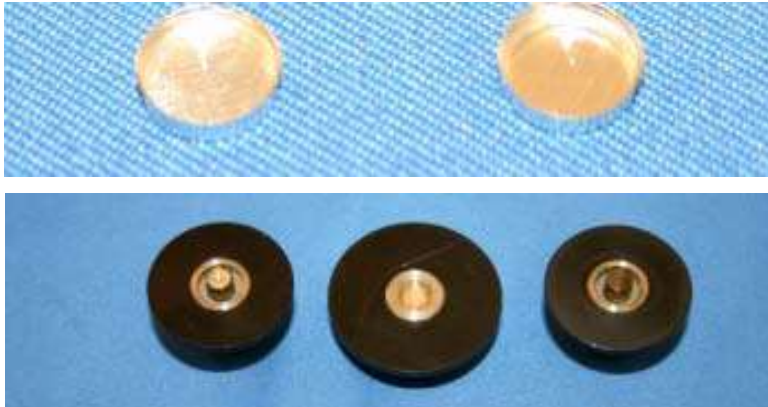
Tzero Press kit includes die sets for:

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).

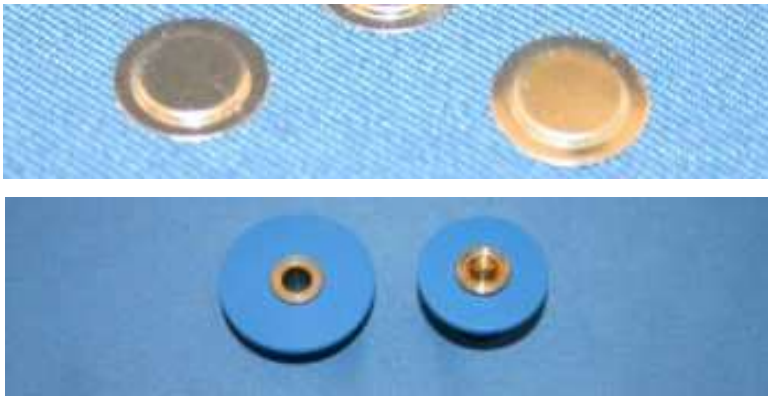
TA Instruments Tzero Pans

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.

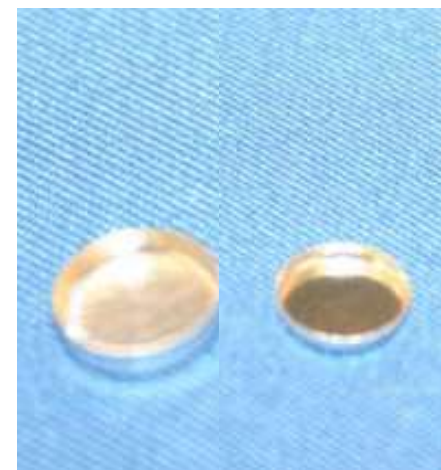
Tzero Hermetic Lid



- 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



Standard Series DSC Pans (Non Hermetic)

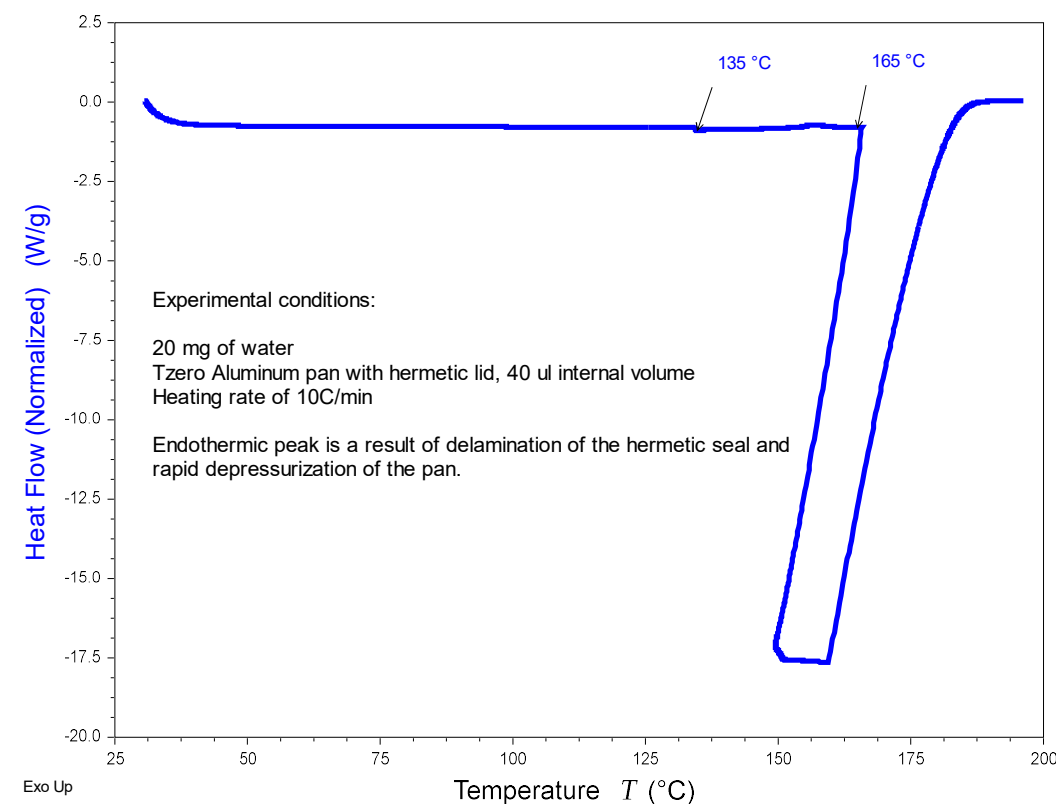
- Standard pans are available in:
 - Aluminum: use up to 600°C maximum
 - Gold (p/n 900866.901 pan, p/n 900868.901 lid): up to 725°C
 - Graphite (p/n 900874.901 pan, p/n 900873.901 lid): up to 725°C (in N₂)
- Standard Pans without lids
 - Platinum (p/n 900578.901): up to 725°C
 - Copper (p/n 900867.901) : up to 725°C (in N₂)

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



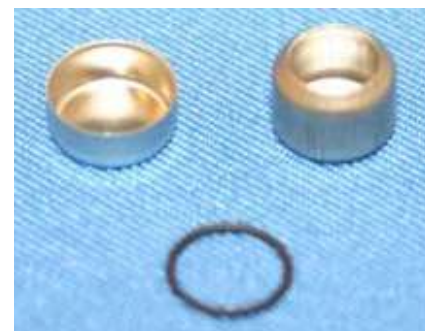
Gold
Hermetic
6 atm



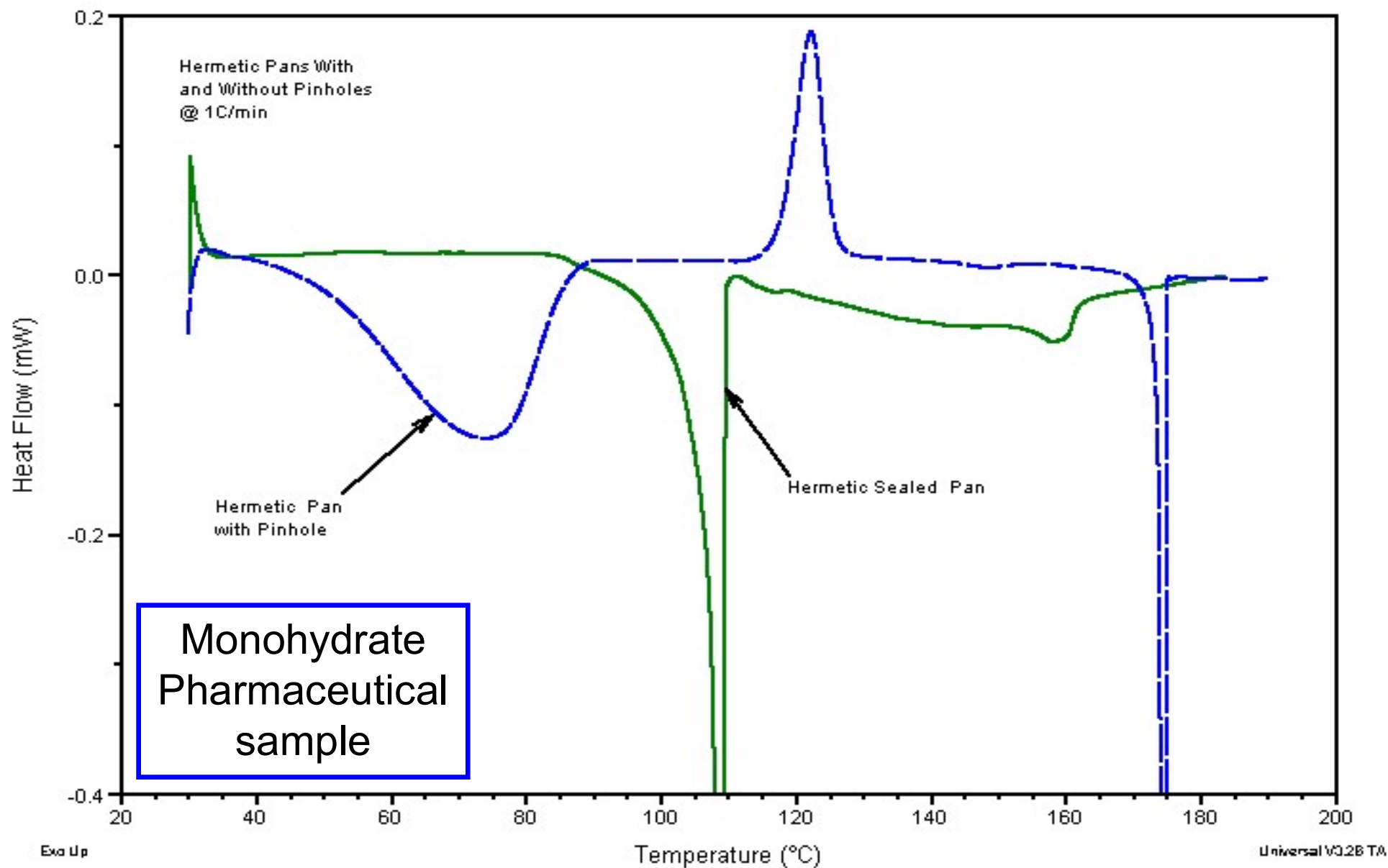
Hermetic Pans (Sealed)

- Hermetic Pans are available in:
 - Aluminum: $<600^{\circ}\text{C}$; <3 atm (300 kPa gage)
 - Alodined Aluminum: $<200^{\circ}\text{C}$; <3 atm (300 kPa gage)
 - Gold: $<725^{\circ}\text{C}$; <6 atm (600 kPa gage)
- Specialized Sealed Pans
 - High Volume: $100\mu\text{L}$; $<250^{\circ}\text{C}$; 600 psig
 - P/N 900825.901
 - High Pressure: $35\mu\text{L}$; $<300^{\circ}\text{C}$; 1450 psig
 - P/N 900808.901

Note: 3 atm is approximately 44 psig



It Can Matter What Pan You Use



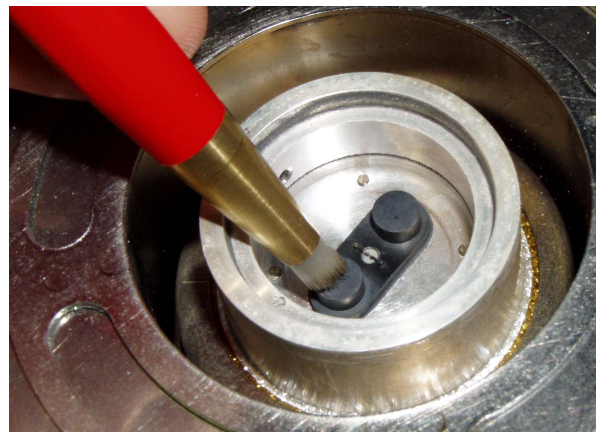
What if Sample Spills out of the Pan?

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

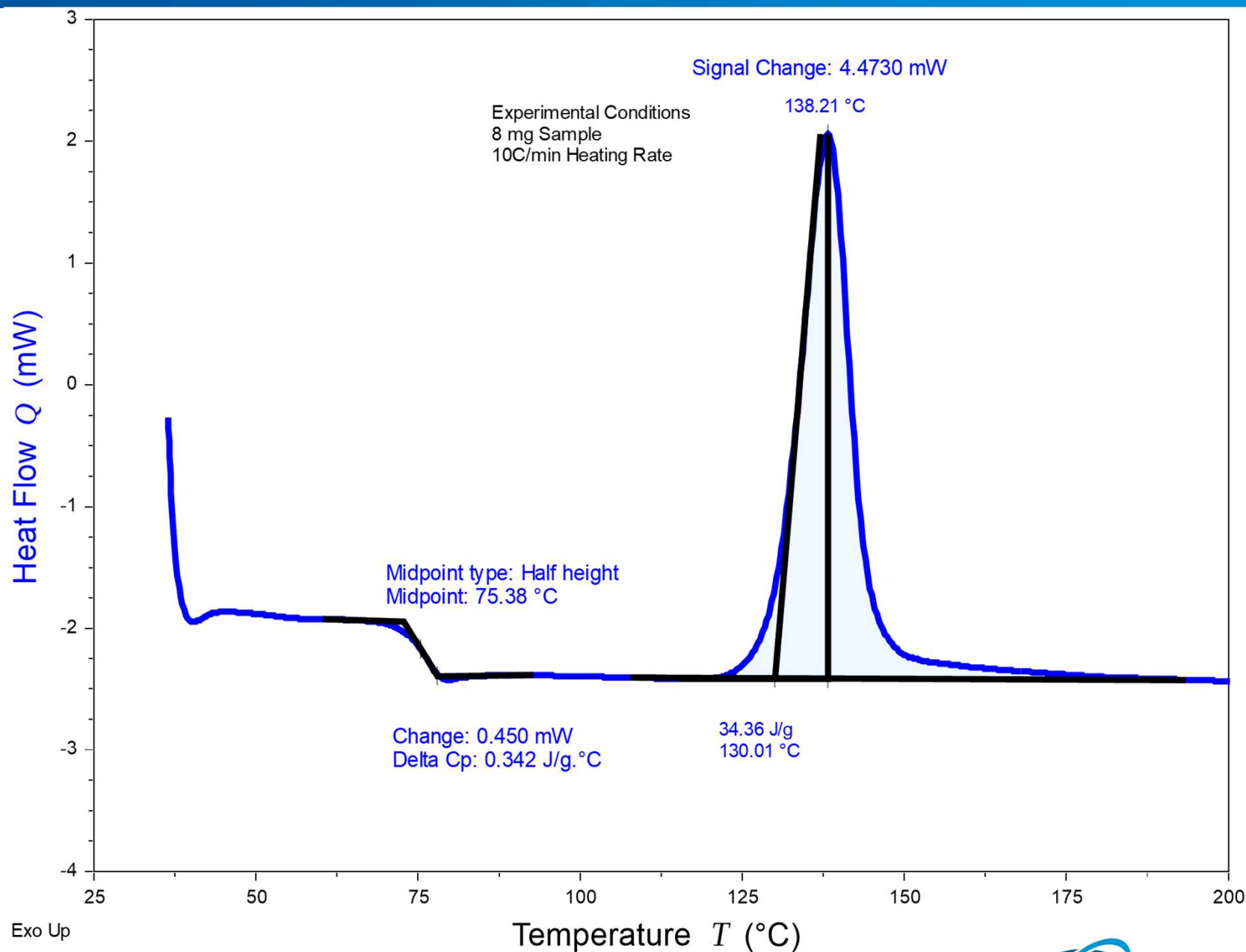
- Bake out
 - Should be used as a last resort if none of the previous steps are effective
 - Involves Air purge and/or an open lid
 - Heat @ 20°C/min to appropriate temp (max of 550°C on Q series, max. 400°C in Discovery)
 - Do NOT hold Isothermal @ the upper temperature
 - Cool back to room temp & brush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

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

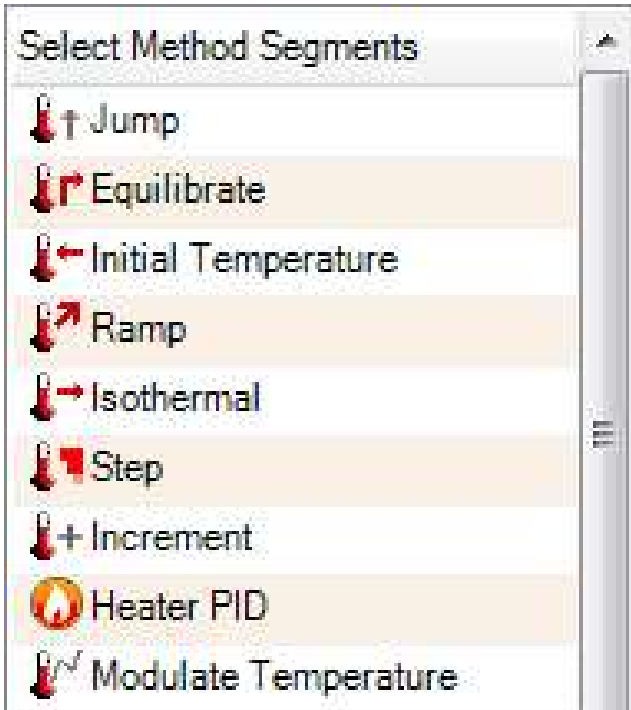
Heat Flow Change During a Transition



Method development



Method Design: DSC Segment List

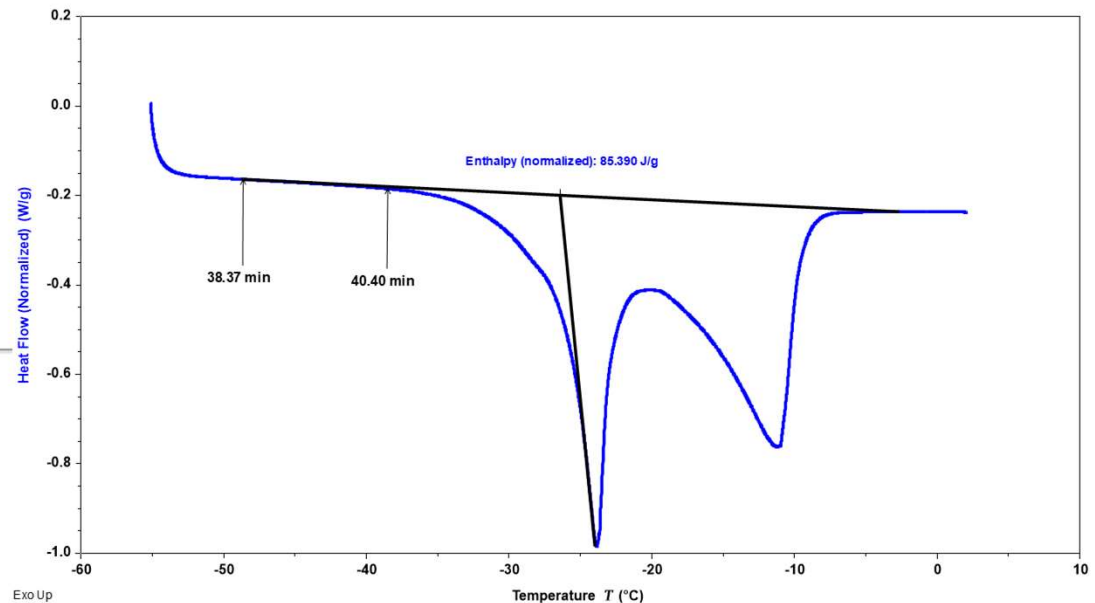
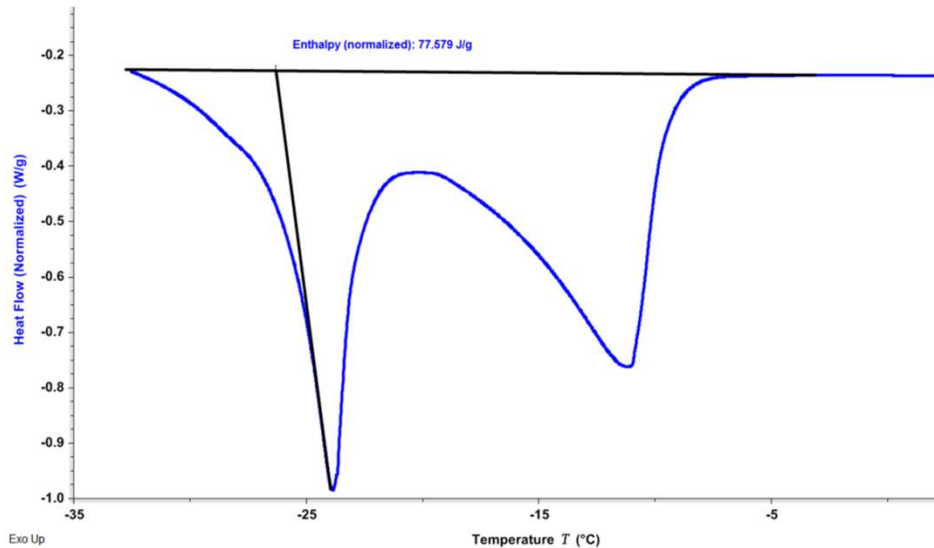


- The Ramp segment heats or cools the sample at a fixed rate until it reaches the specified temperature, producing a linear plot of temperature versus time
- The Equilibrate segment heats or cools the furnace to the defined temperature, stabilizes the furnace at that temperature, then continues to the 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 $10^{\circ}\text{C}/\text{min.}$ to 300°C

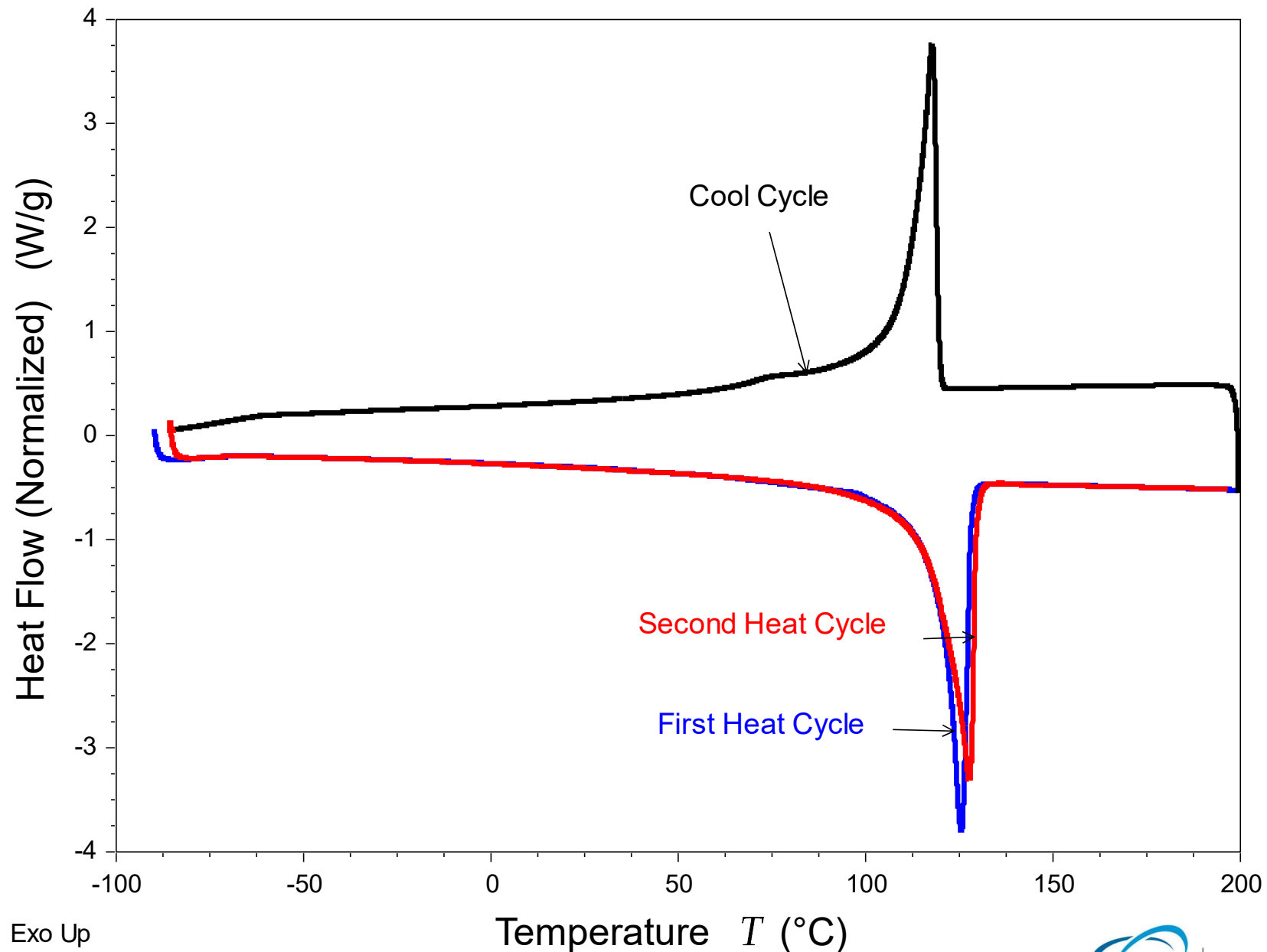
- Typical Cooling Method
 - 1) Equilibrate at 300°C
 - 2) Ramp $10^{\circ}\text{C}/\text{min.}$ to 25°C

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)

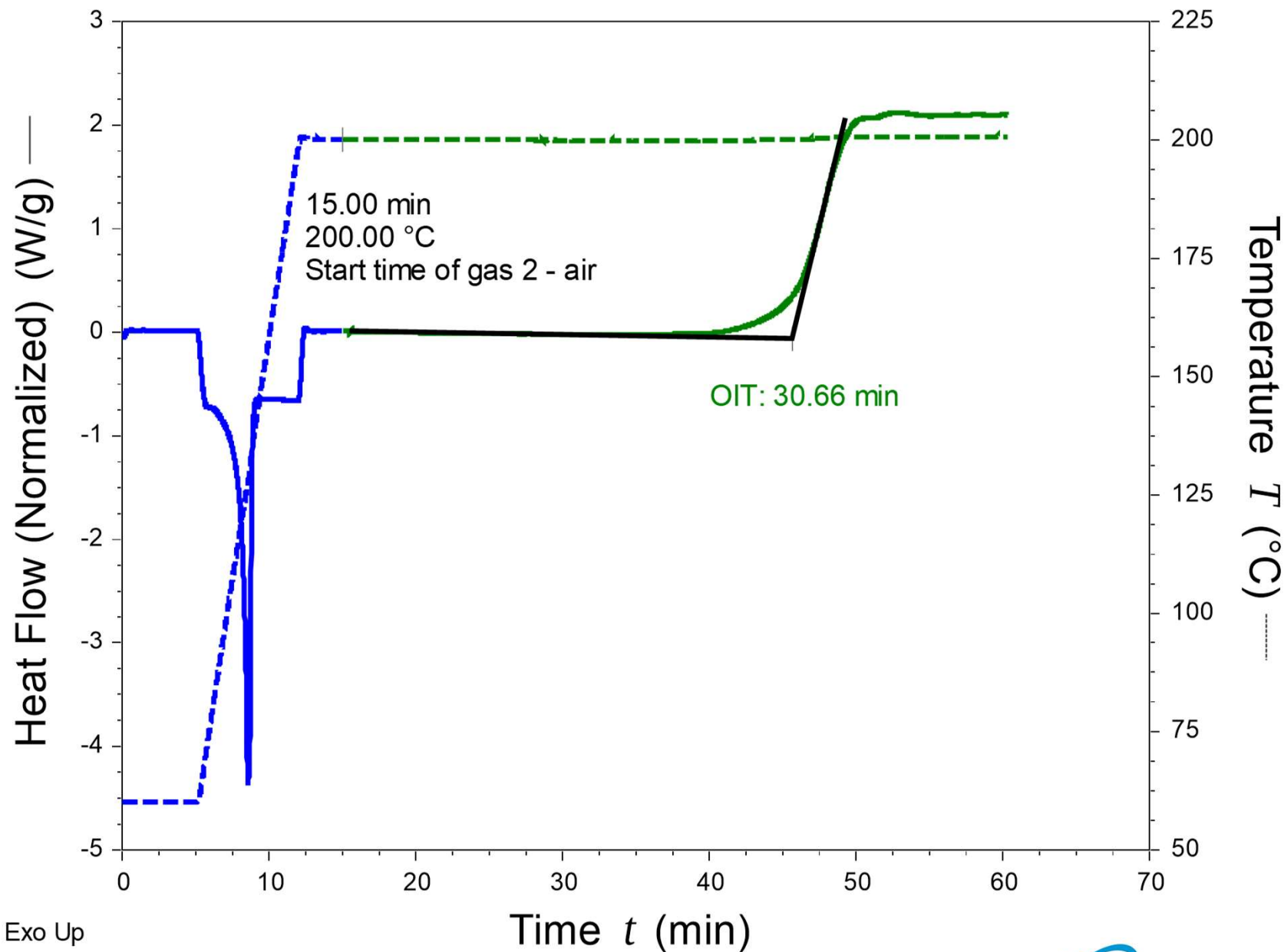


Oxidative Stability (OIT) Method

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



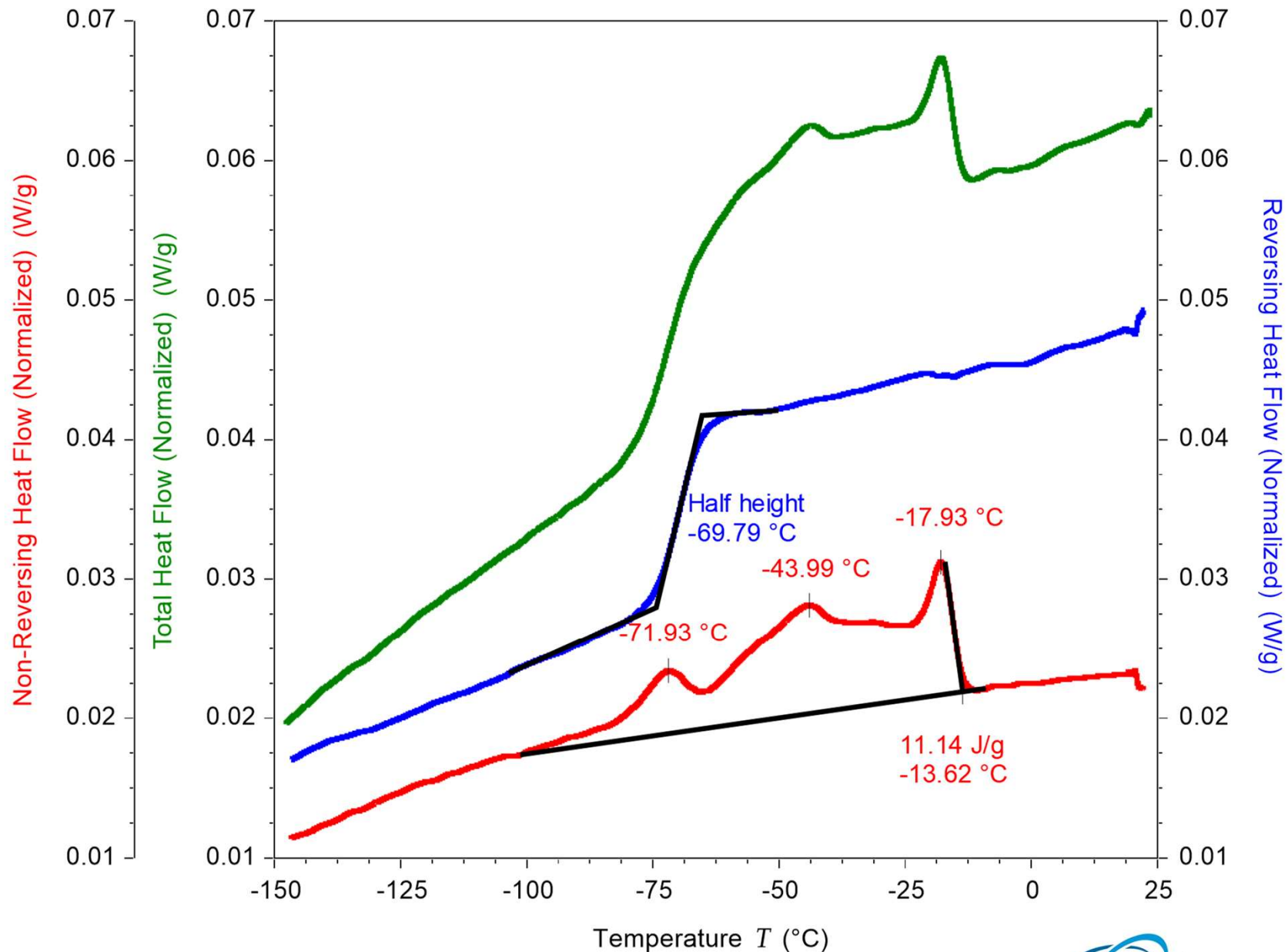
Modulated® DSC Method

An MDSC Method

- 1) Equilibrate at 25°C
- 2) Modulate $\pm 0.318^{\circ}\text{C}$ every 60 seconds
- 3) Isothermal for 5.00 minutes
- 4) Data storage: On
- 5) Ramp $2^{\circ}\text{C}/\text{min.}$ to -90°C
- 6) Ramp $2^{\circ}\text{C}/\text{min.}$ to 25°C

MDSC of a Process Oil

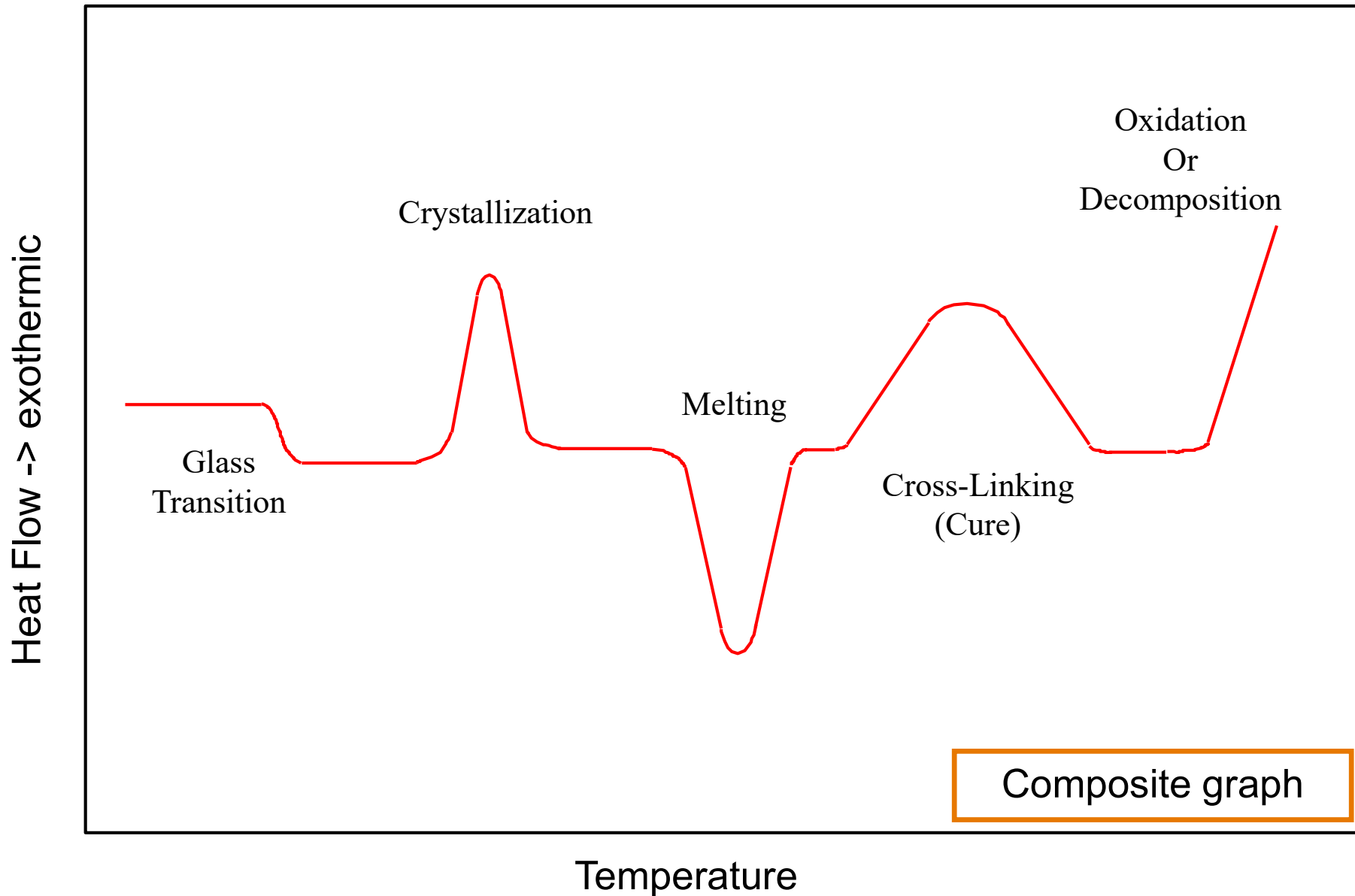
Separation of a Tg from Crystallization



Applications



Typical DSC Transitions

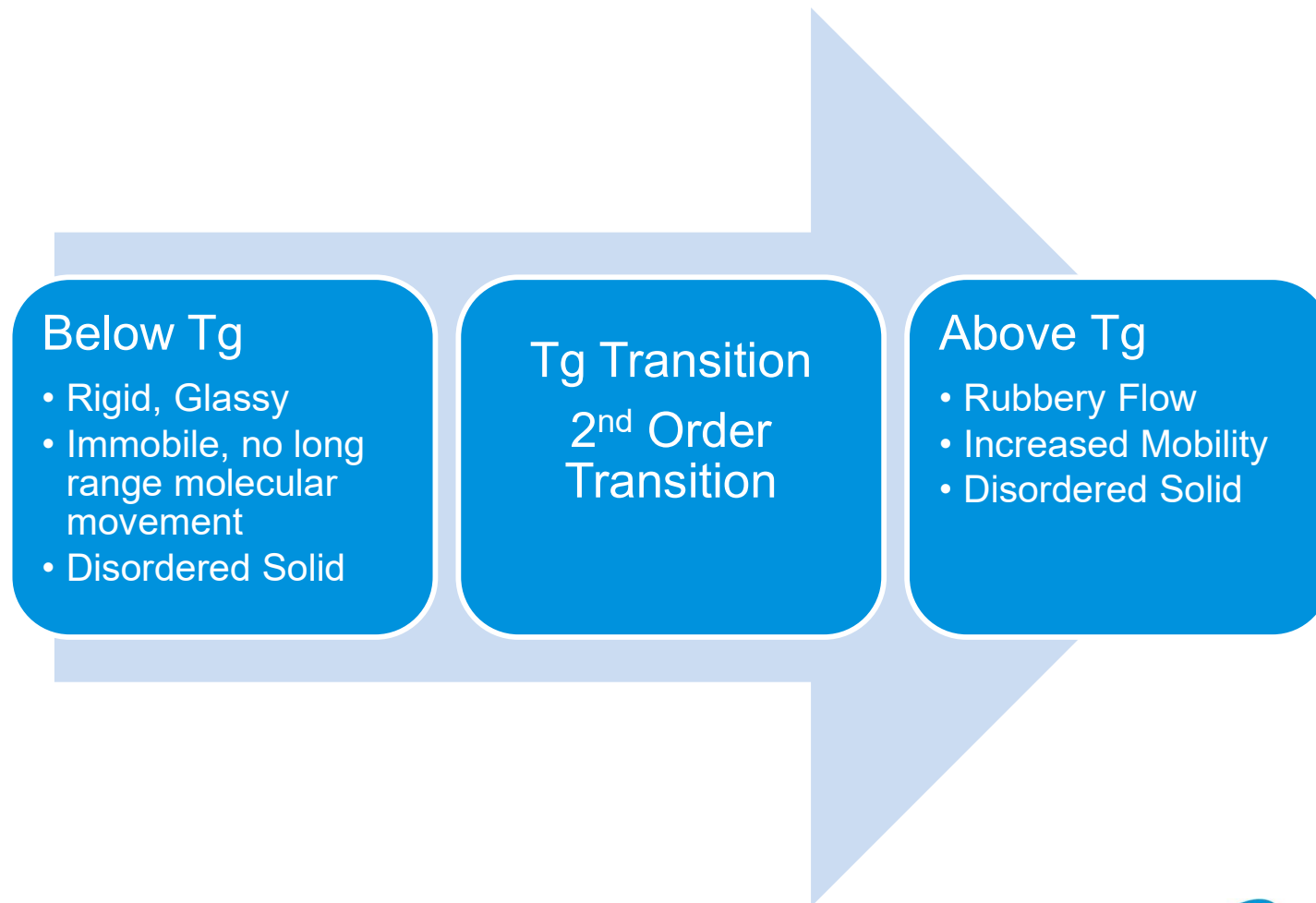


The Glass Transition Temperature (T_g)

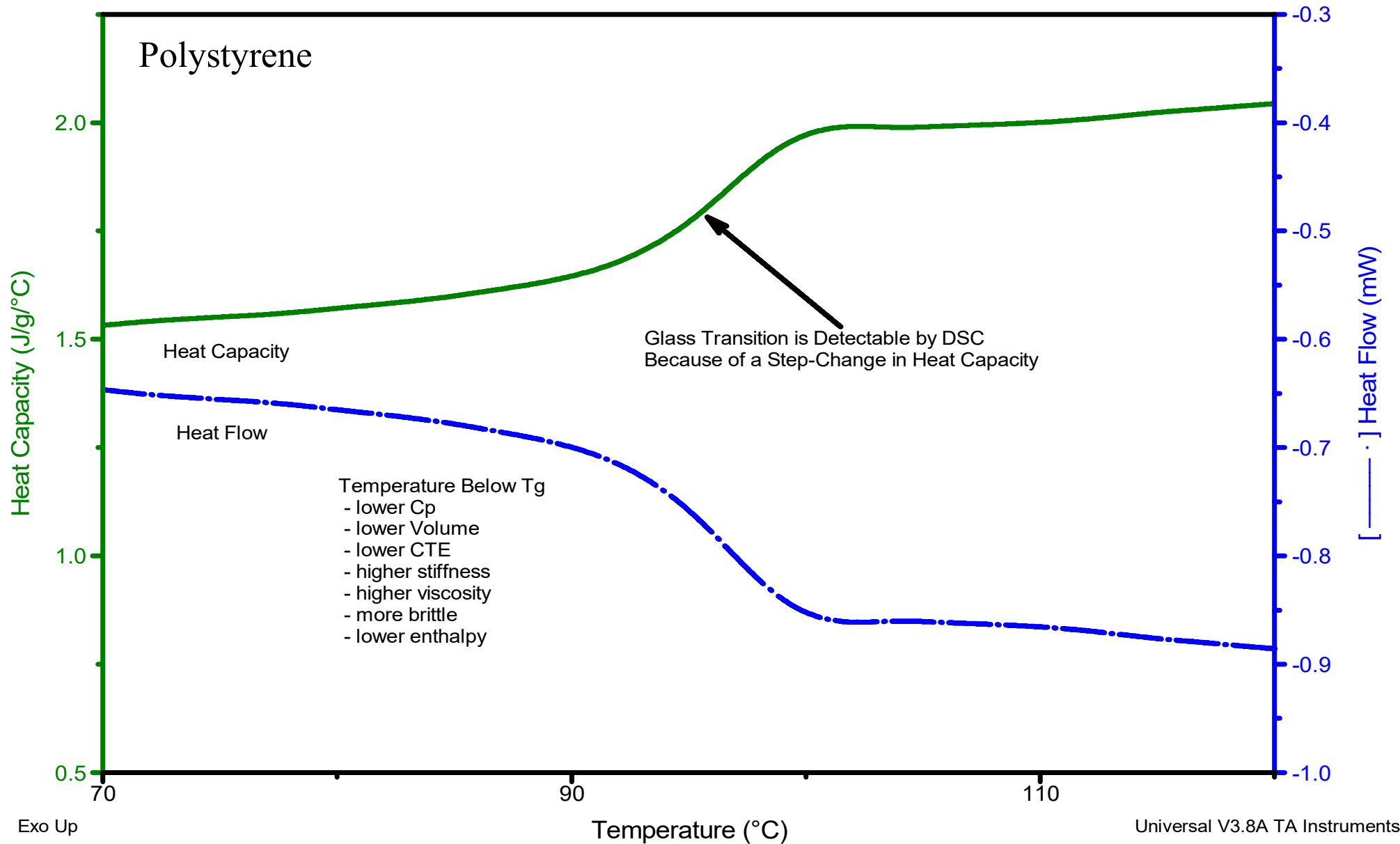


The Glass Transition (T_g)

- 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 T_g

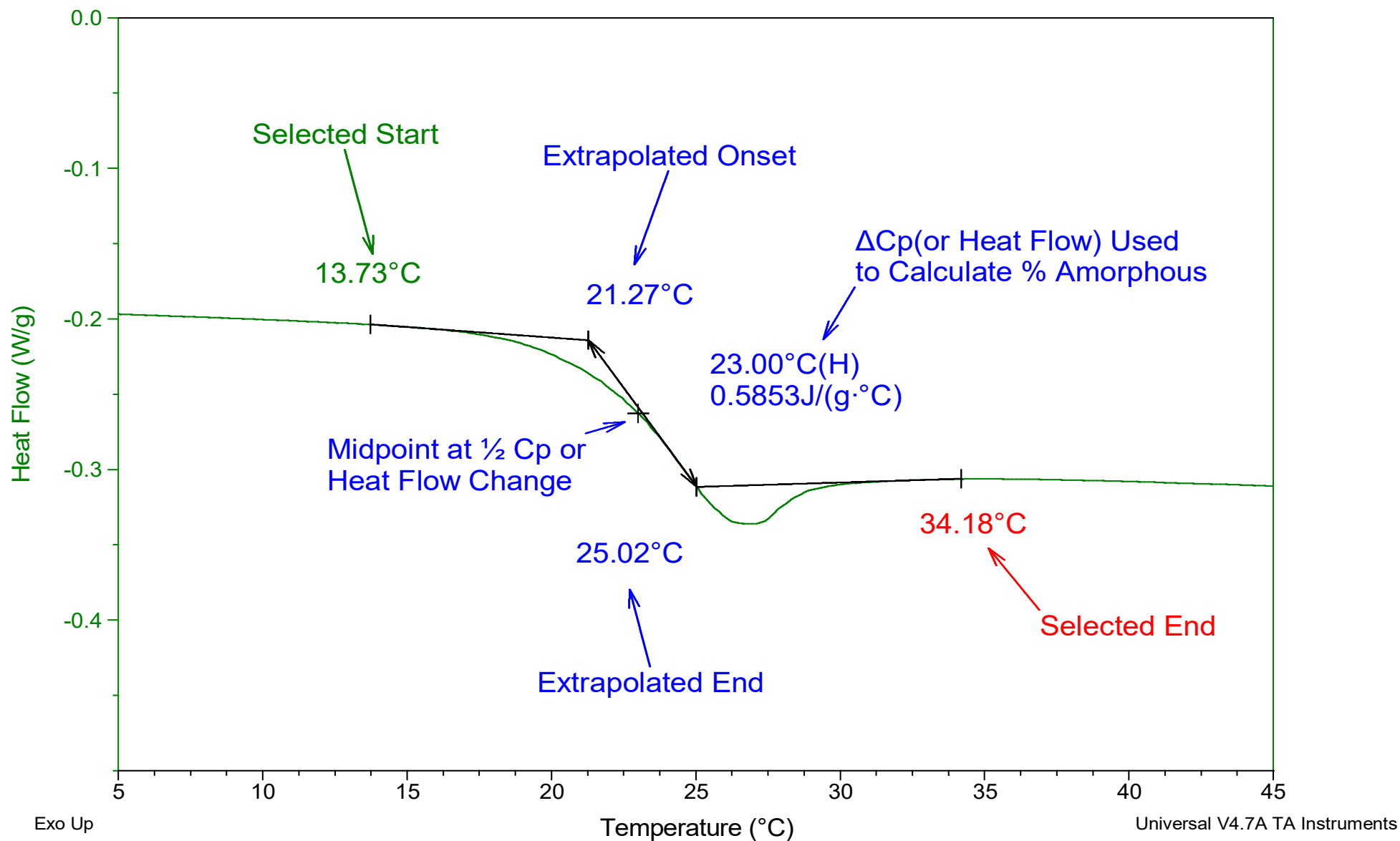


What Affects the Glass Transition?

- 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

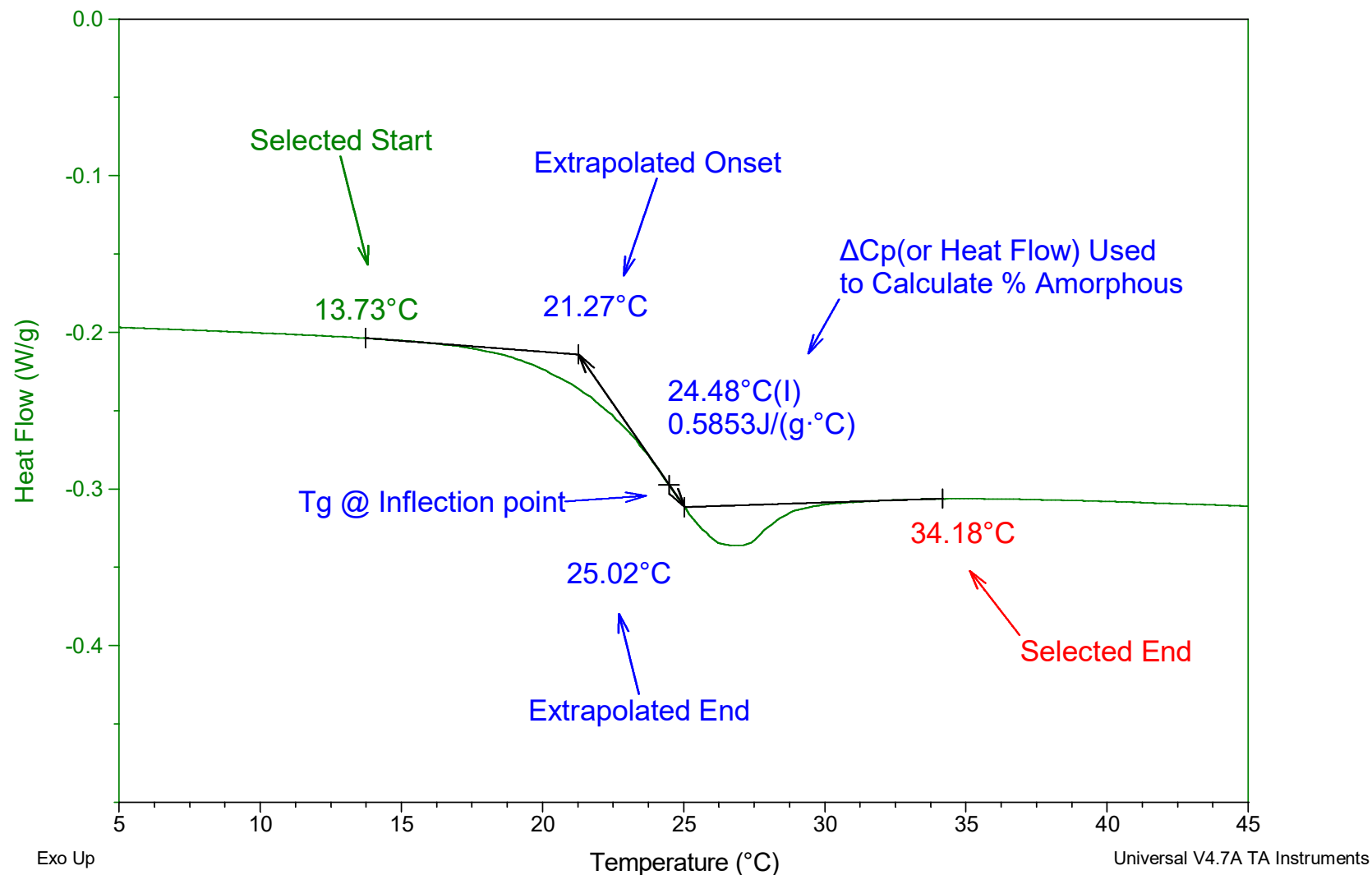


DSC Tg Analysis – Inflection

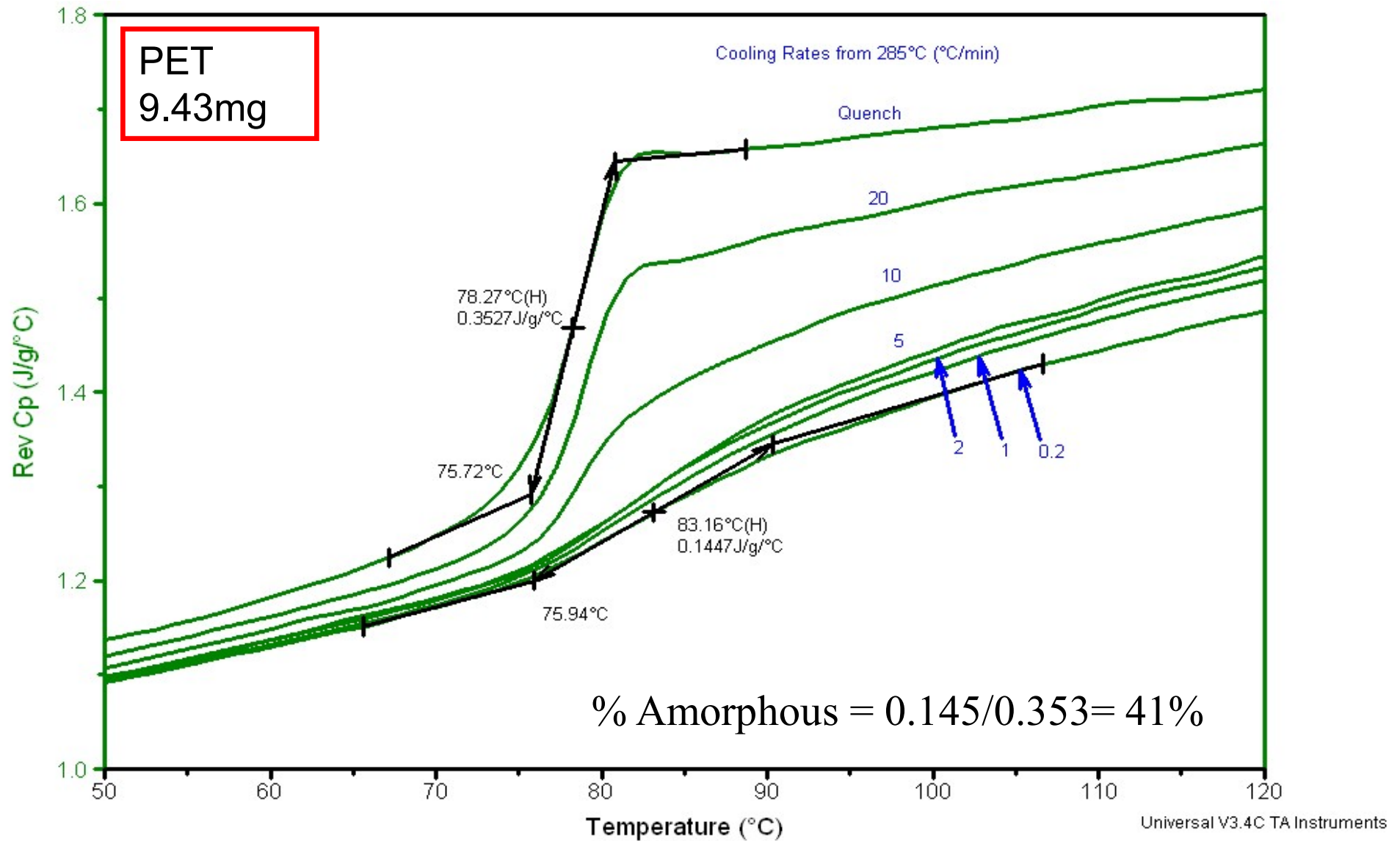
Sample: Acetaminophen - Tylenol Caplet
Size: 8.7100 mg
Method: Heat/Cool/Heat

DSC

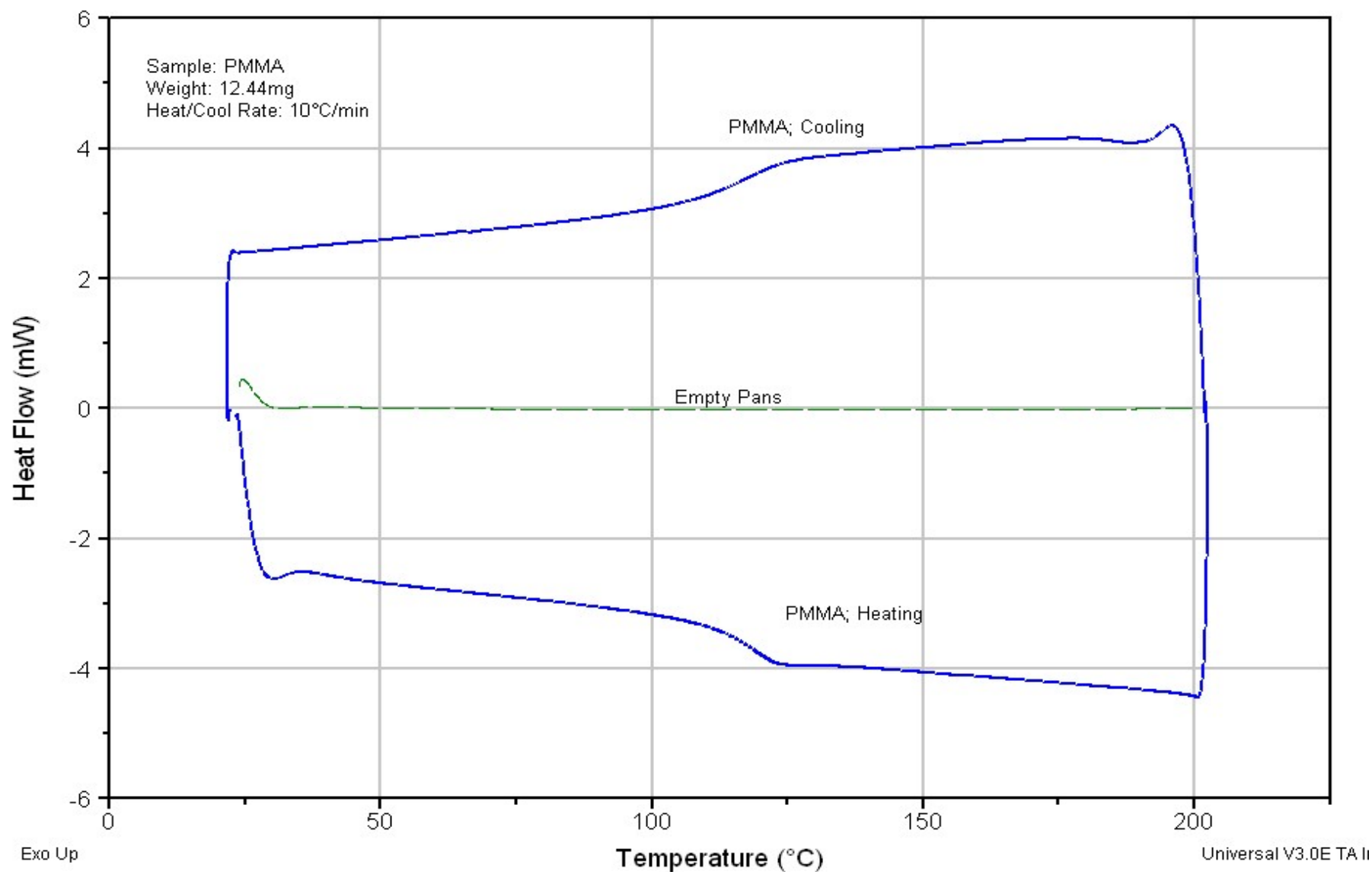
File: Q2000-ACETAMINOPHEN-TYLCAP-022412.00
Operator: Waguespack
Run Date: 24-Feb-2012 07:37
Instrument: DSC Q2000 V24.10 Build 122



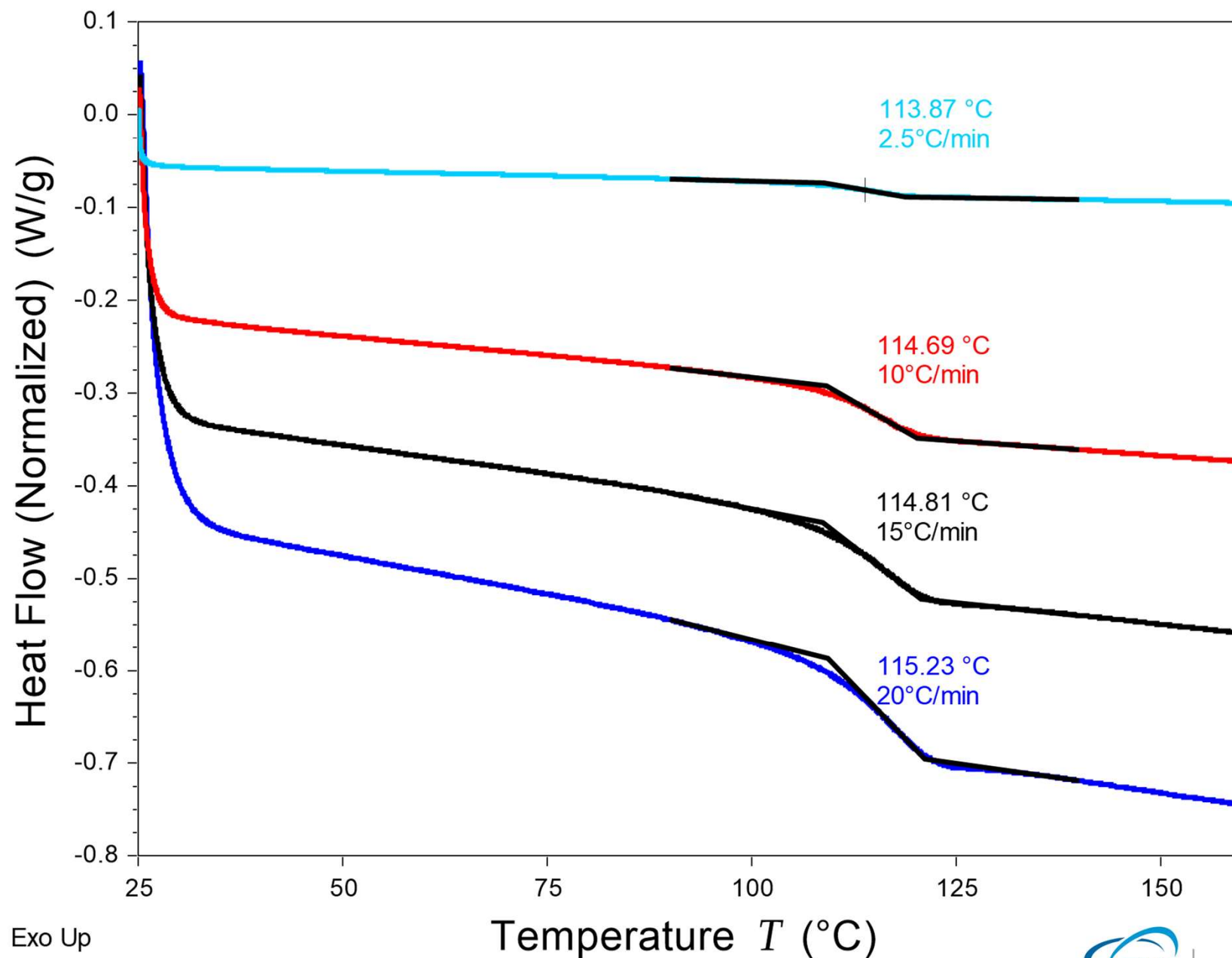
Step Change in Cp at the Glass Transition



A Glass Transition is Reversible



10mg PMMA Sample at Different Heating Rates



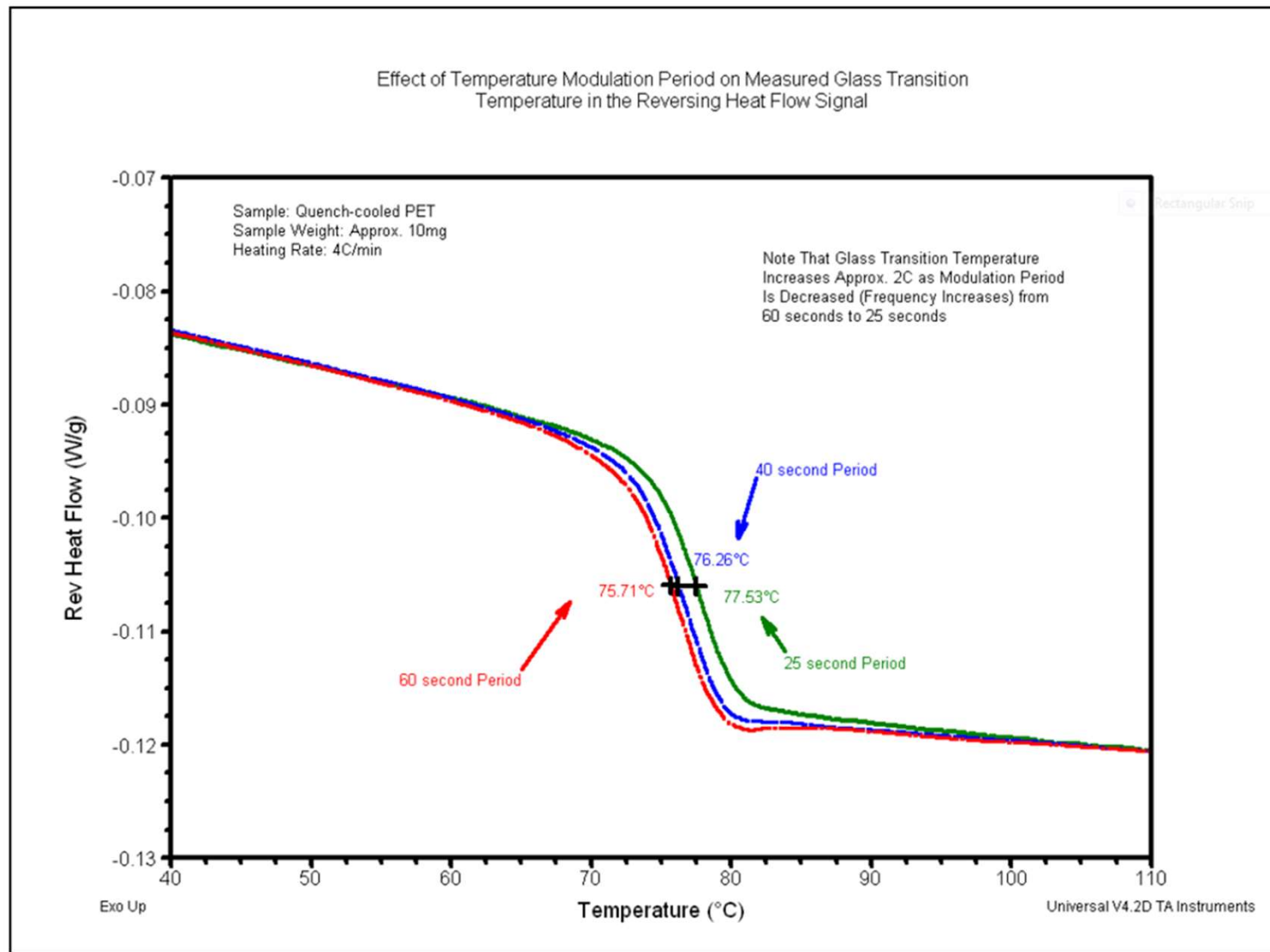
Glass transition measurements using other techniques

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

MDSC: Effect of Frequency on T_g

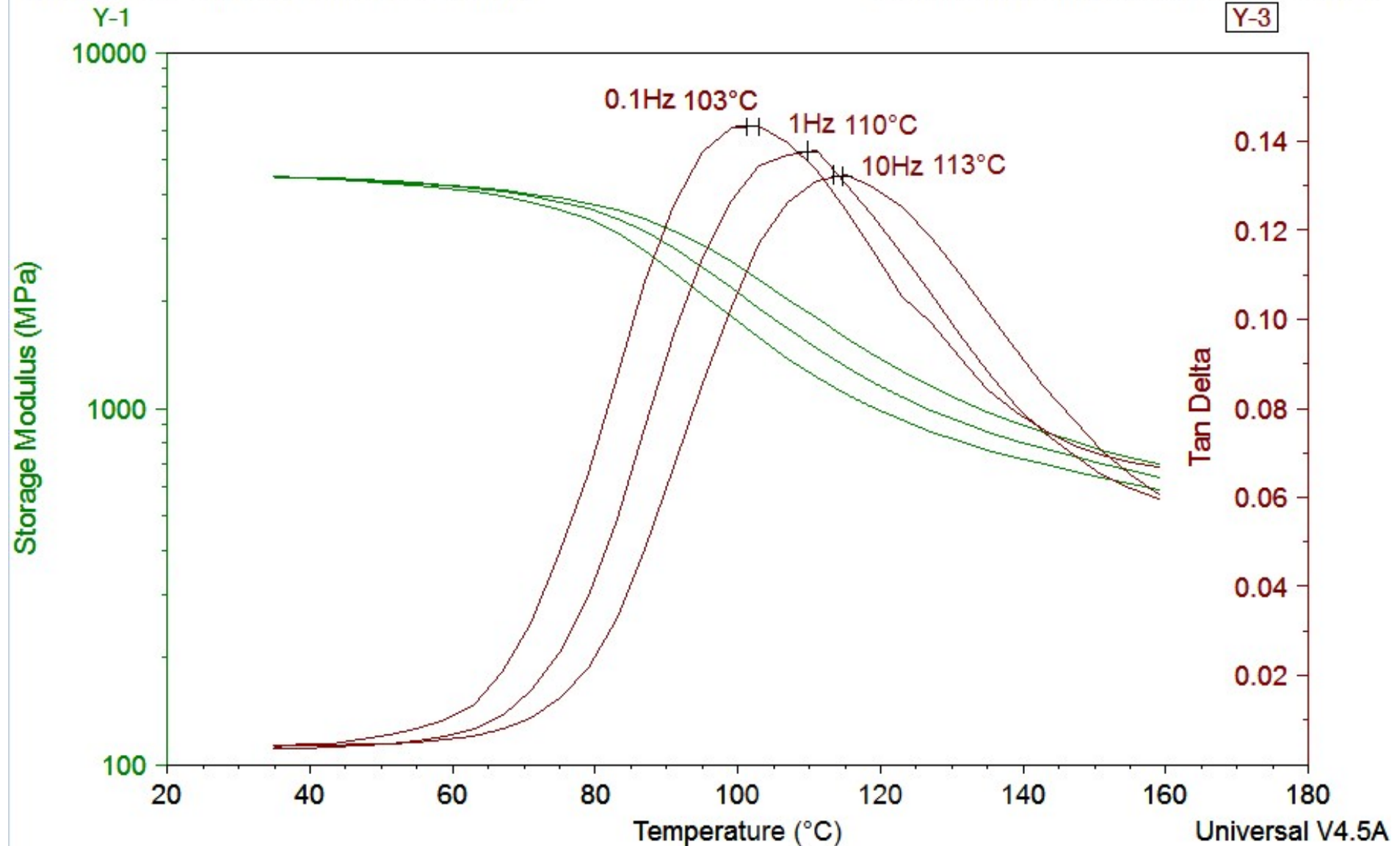


DMA: Effect of Frequency on Tg

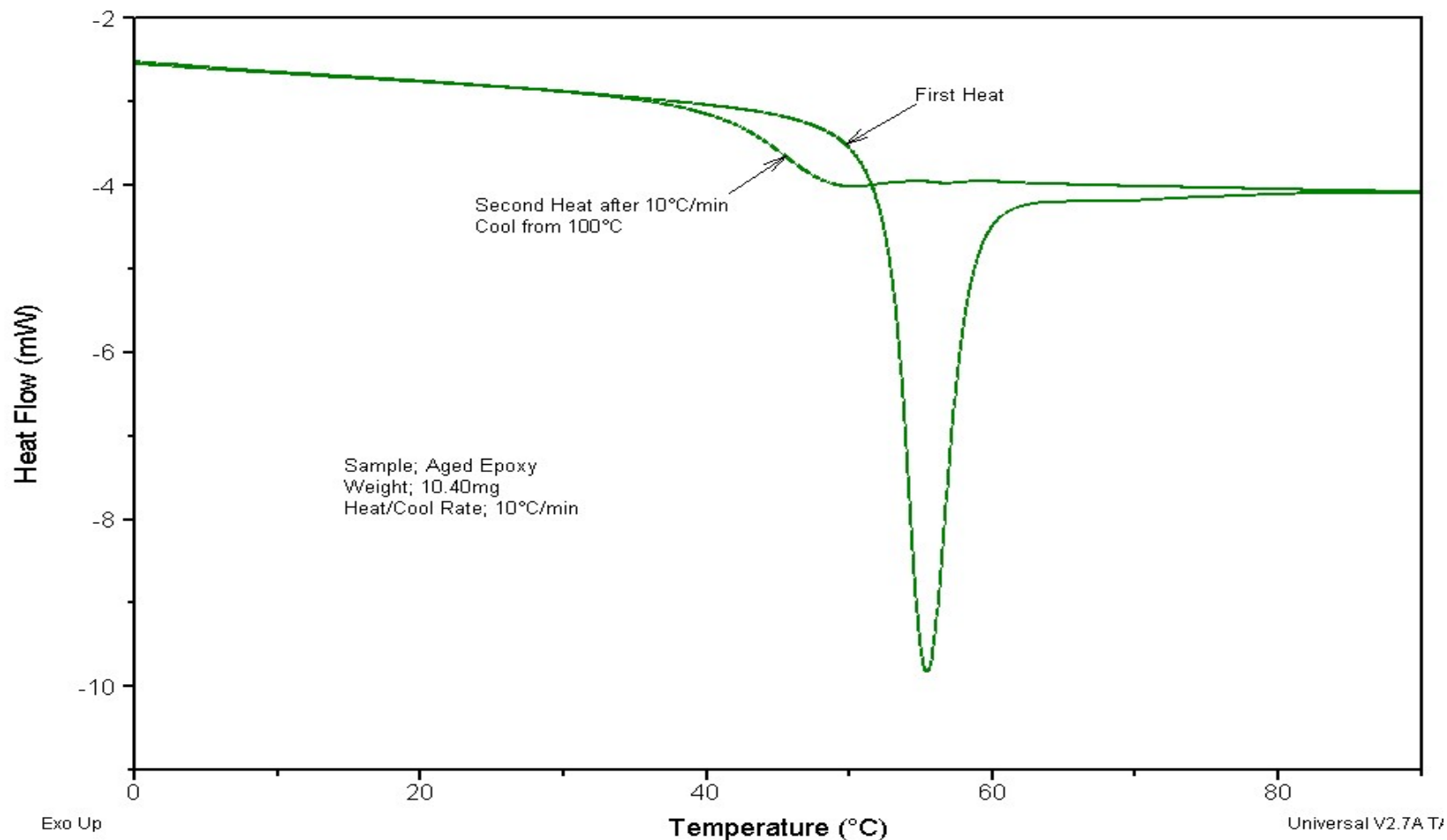
Sample: PET Tape Demonstration Sample

DMA File: C:\TA\Data\DMA\DMA-PET.001

Y-3



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.

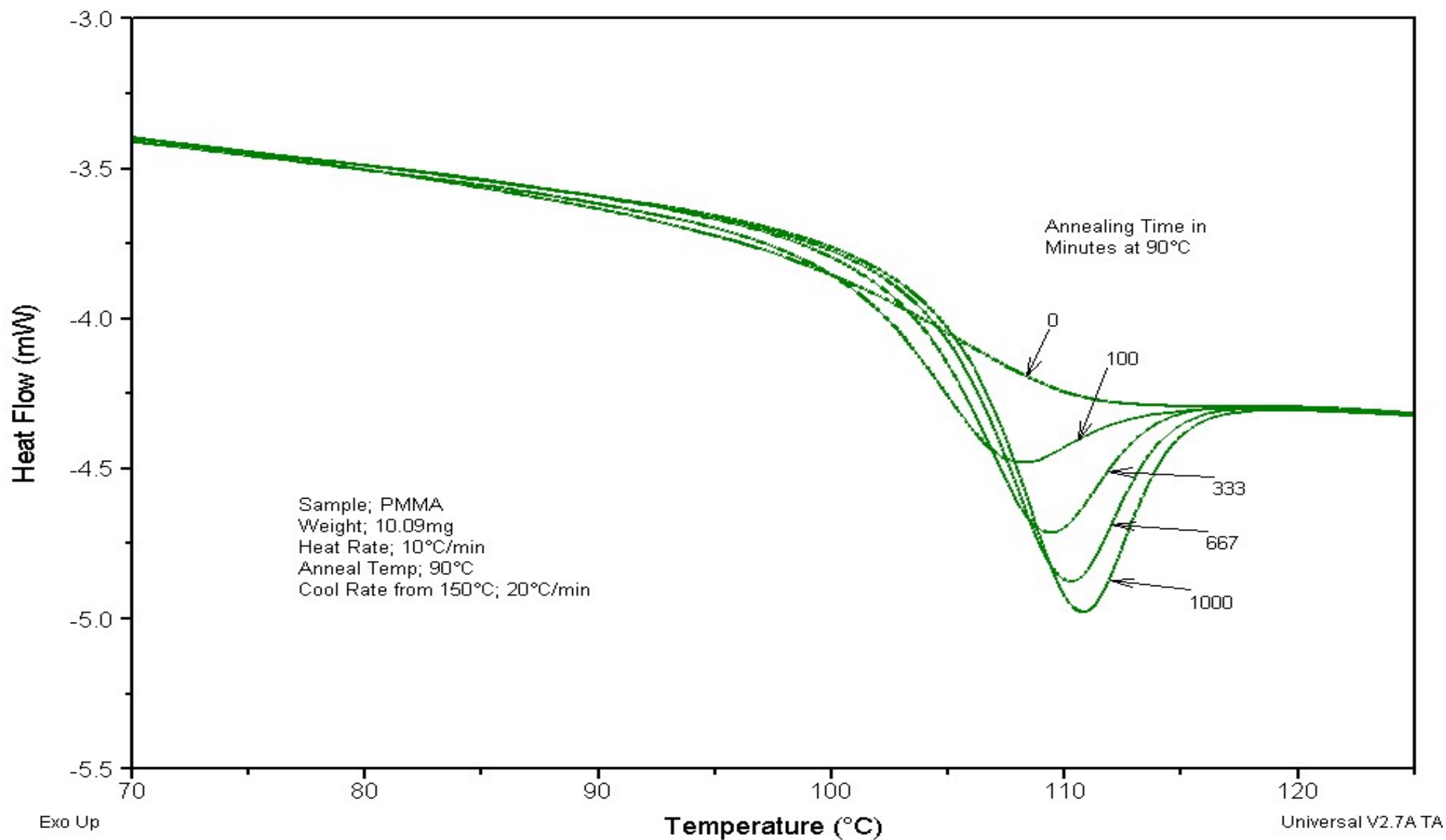
Enthalpic Recovery

- 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 T_g
 - Occurs as the sample is being cooled to temperatures below T_g
 - Occurs as the sample is being stored at temperatures below T_g
- Enthalpic Recovery
 - The recovery of energy (J/g) lost during Enthalpic Relaxation. It (peak in DSC data @ T_g) occurs as the sample is heated to a temperature above T_g

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 C_p

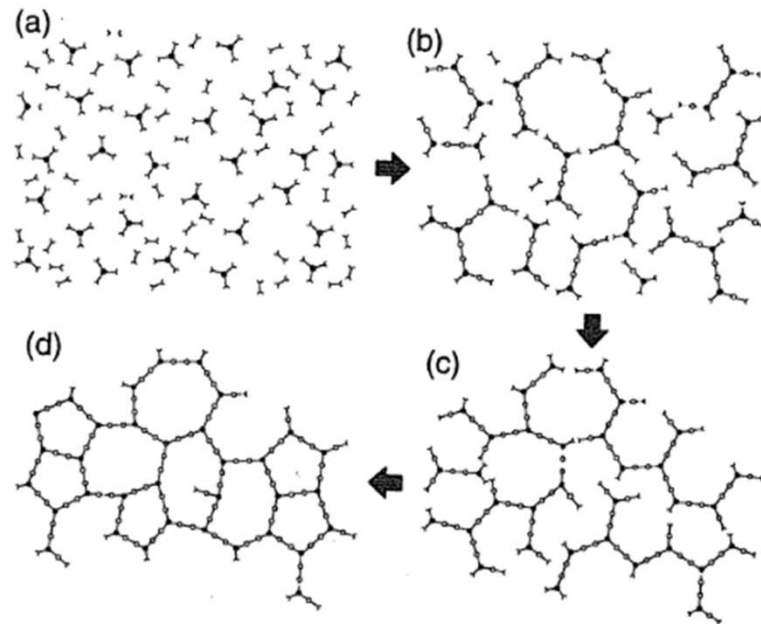
Thermosets



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**).



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 T_g of starting material, heat of reaction and presence of any reactive functional groups.
 - Second Heat is used to measure the T_g of the fully cured sample and any residual cure from the first heat.

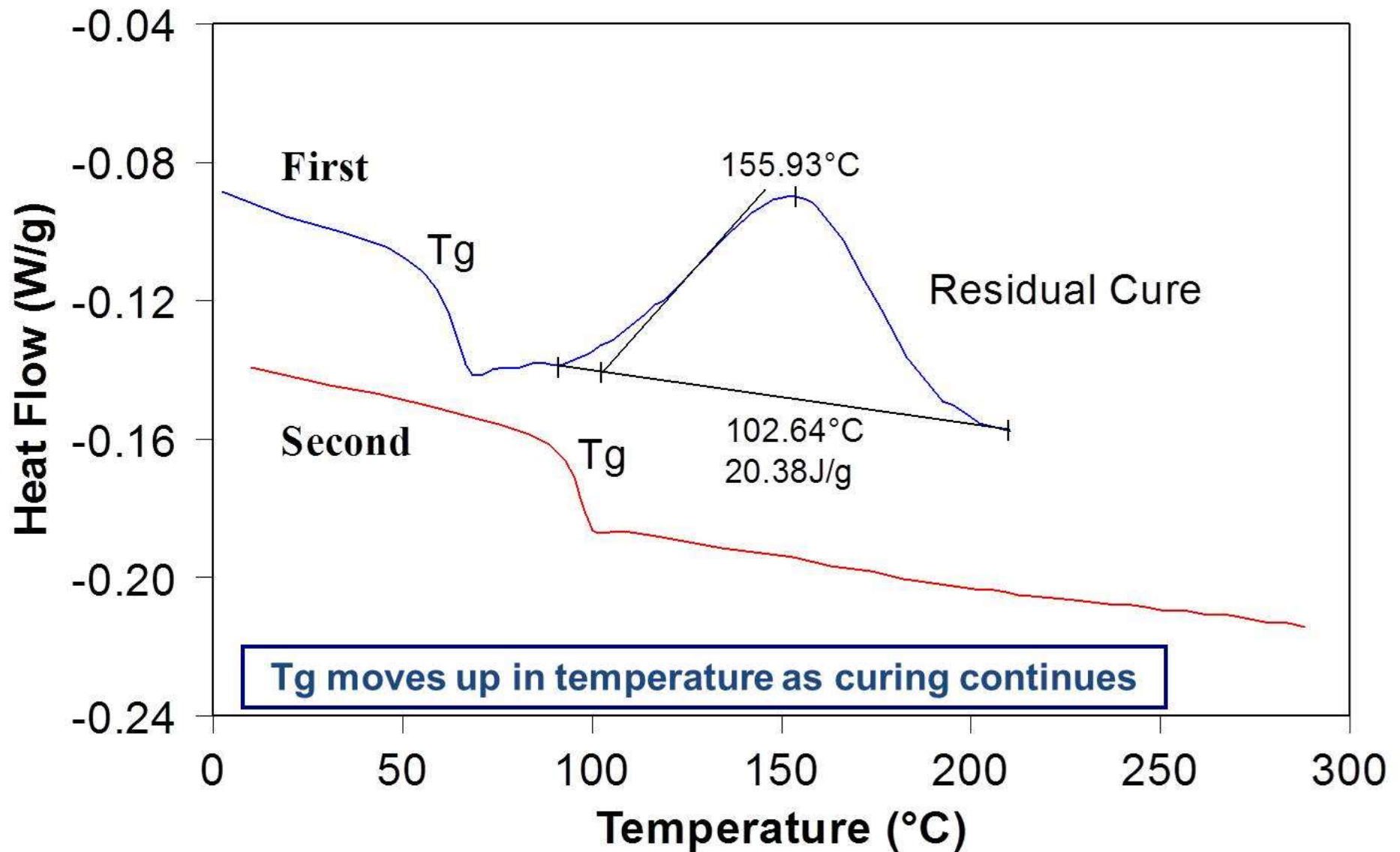
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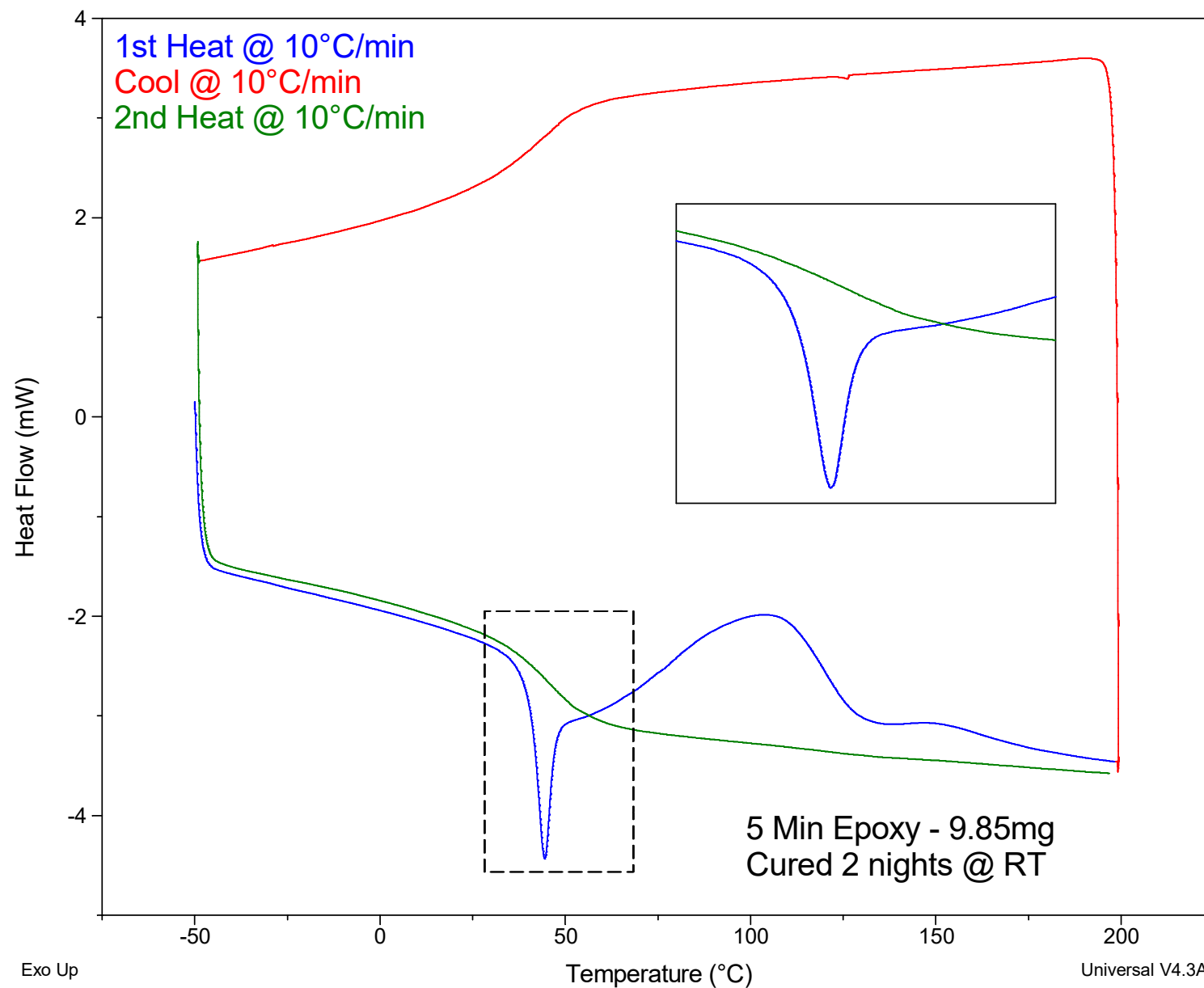
DSC: General considerations for selecting optimum experimental Conditions

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Comparison of First and Second Heats



Epoxy Cured 48 Hours: Heat Cool Heat



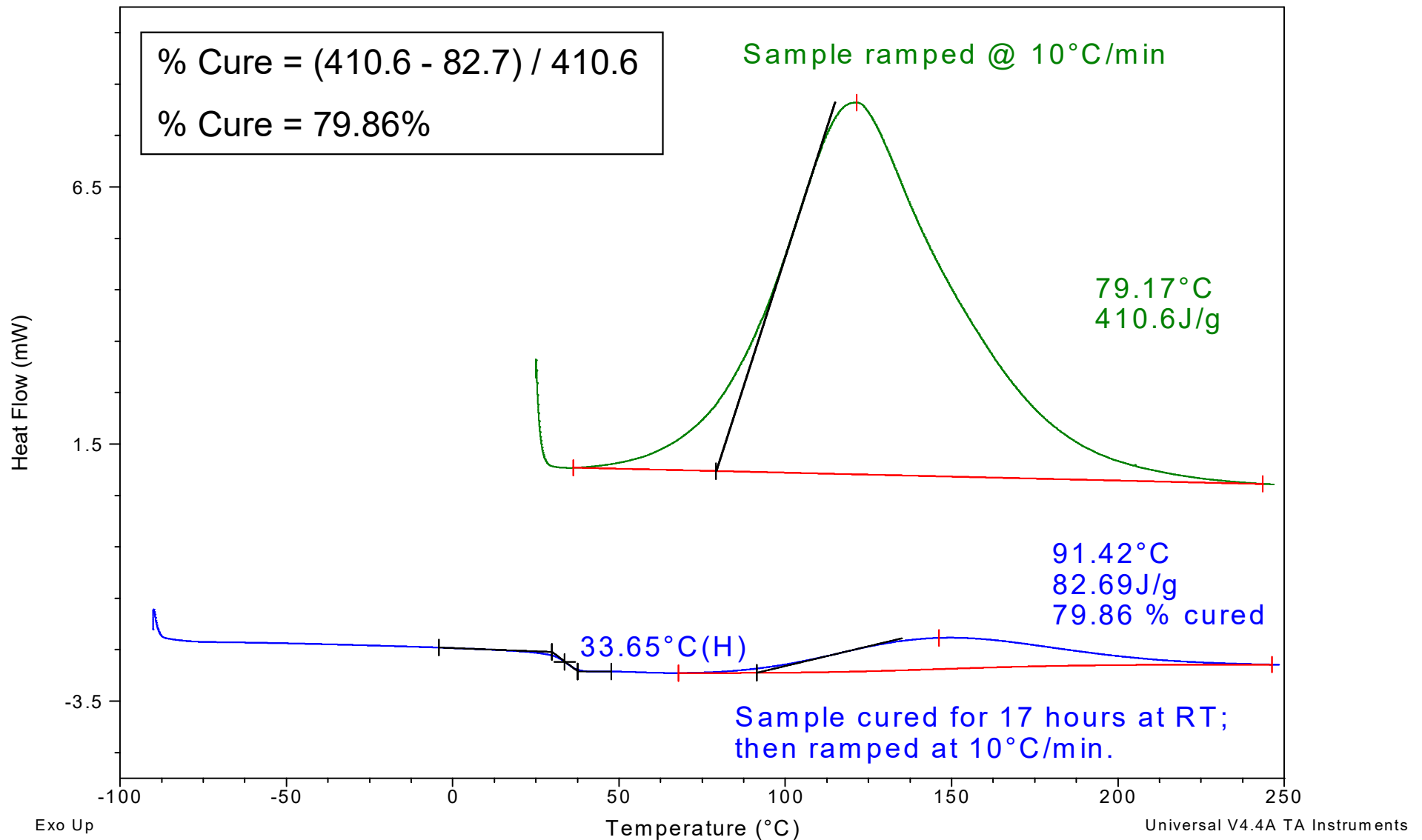
Percent Cure Calculation by DSC

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

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

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

Calculation of % Cure: An Epoxy



Thank You

The World Leader in Thermal Analysis,
Rheology, and Microcalorimetry

