2017 TA儀器 – DSC免費訓練講座

2017年11月7日(二)

集思台大會議中心 米開朗基羅廳

機台的原理與應用

Differential Scanning Calorimetry (DSC)

許炎山

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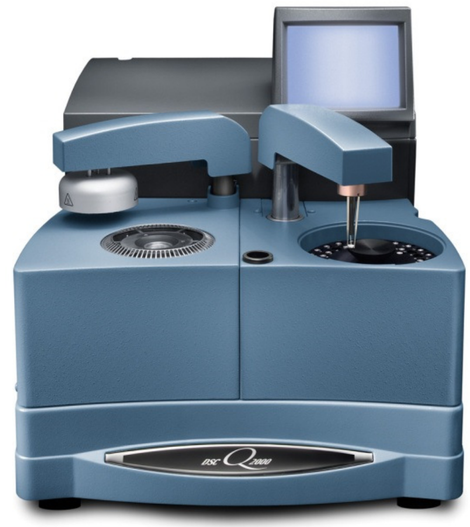
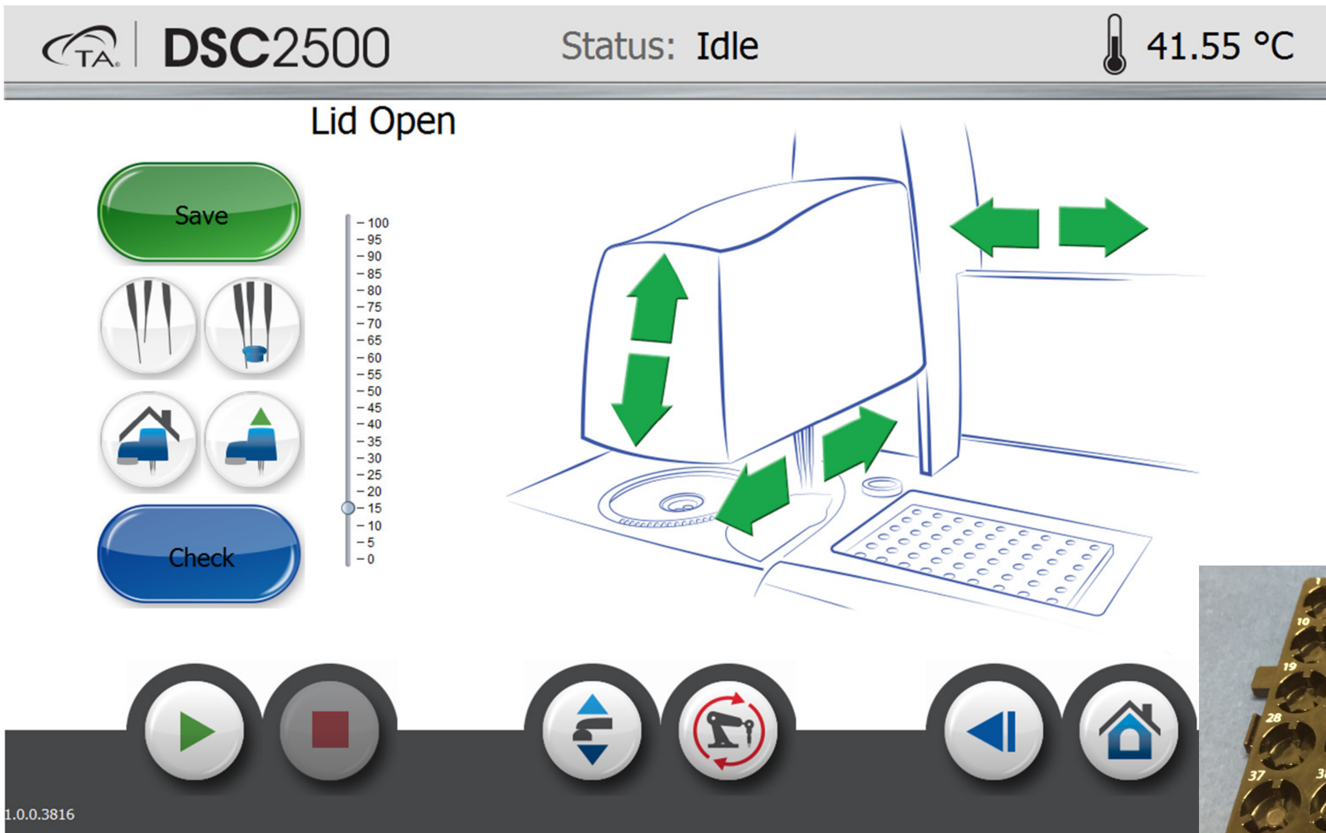
DSC Models

Discovery DSC 2500



AutoQ2000

Discovery DSC Autosampler



Widest Range of Refrigerated Cooling Systems Available

RCS90 (-90℃ to 550℃)
RCS40 (-40℃ to 400℃)

RCS120

- RCS – 1, 2, & ***Now*** 3 stage coolers
- ***NEW*** - RCS120 (-120℃ to 400℃) **ONLY AVAILABLE FOR DSC25, 250, & 2500**
    - 3 stage refrigerated system

Understanding DSC

Understanding DSC - Agenda

- What does a DSC measure?
- How does a DSC make that measurement?
- DSC heat flow models – T1, T4, T4P
- What is Tzero Technology and how does it impact your measurements?

DSC Heat Flow

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

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

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

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

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

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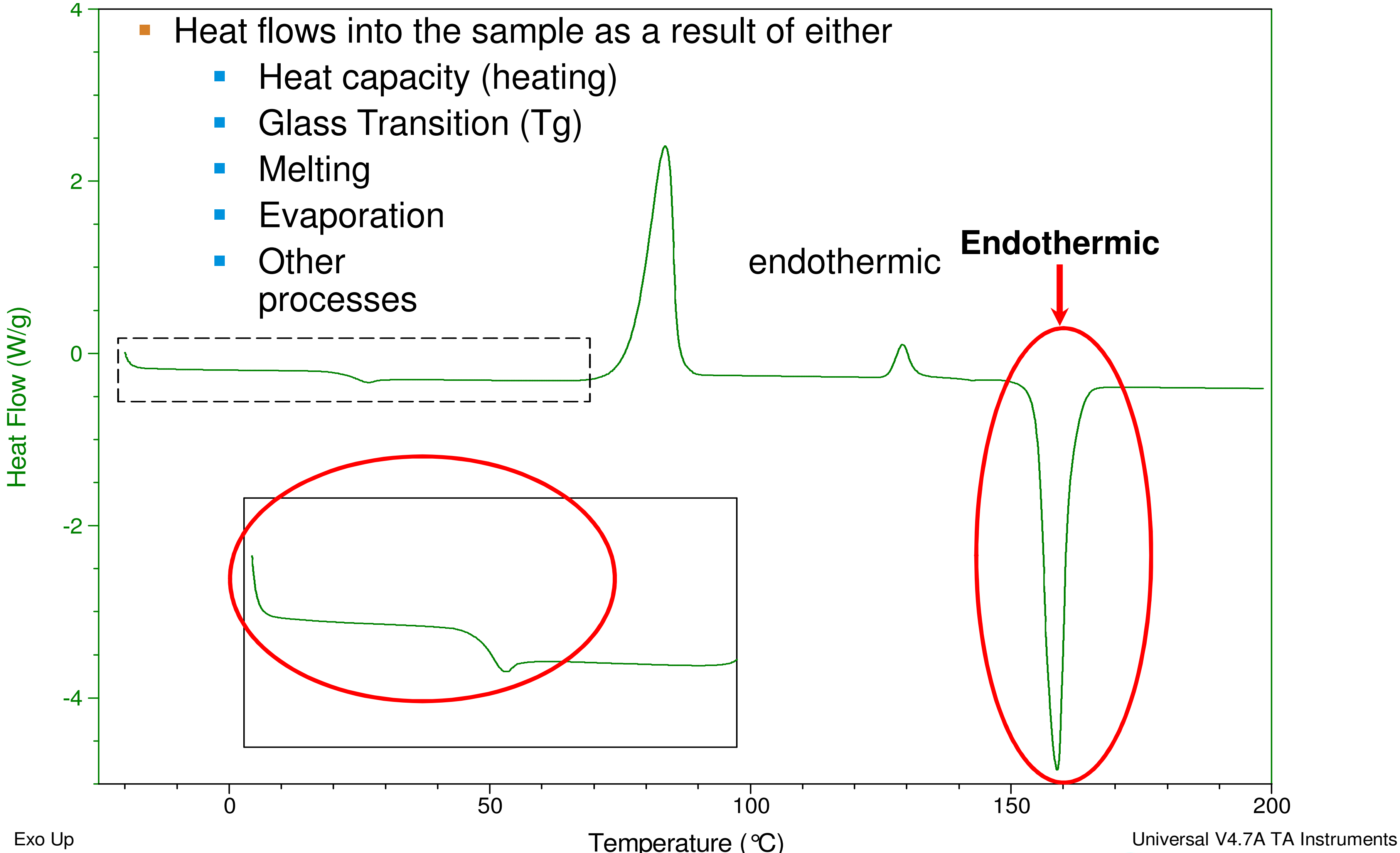
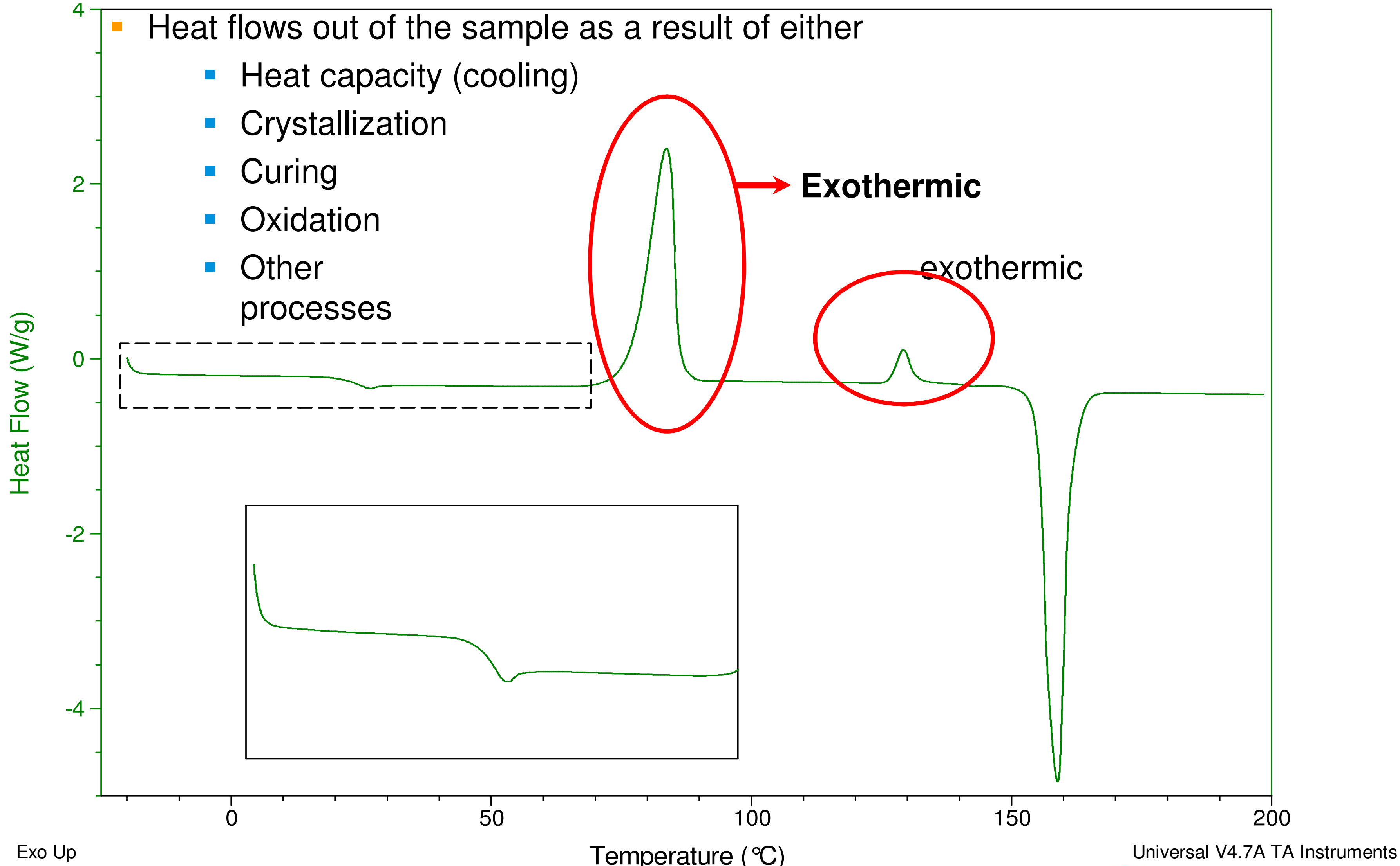
Endothermic Heat Flow

- Heat flows into the sample as a result of either
  - Heat capacity (heating)
  - Glass Transition (Tg)
  - Melting
  - Evaporation
  - Other processes

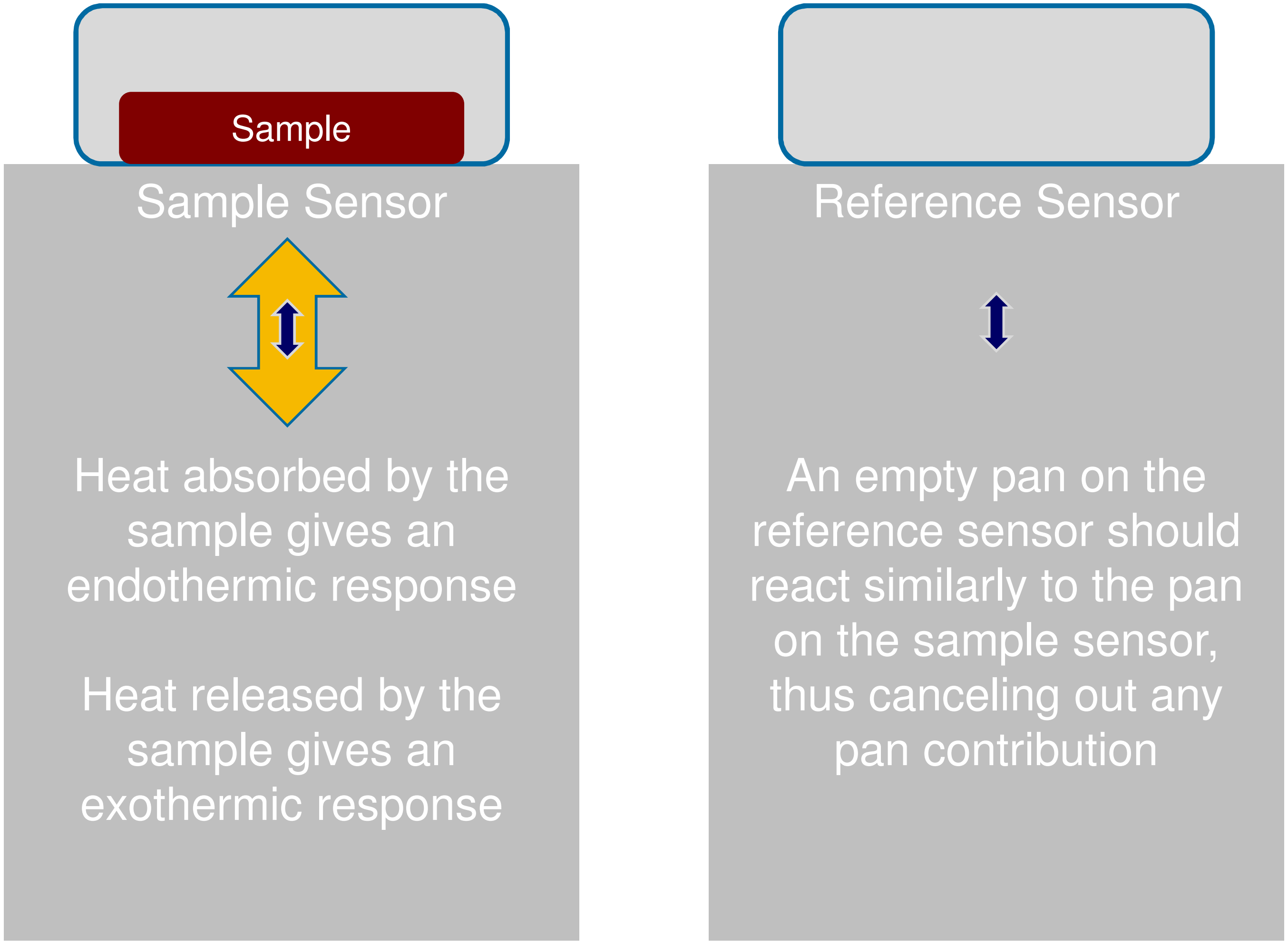


Exothermic Heat Flow

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

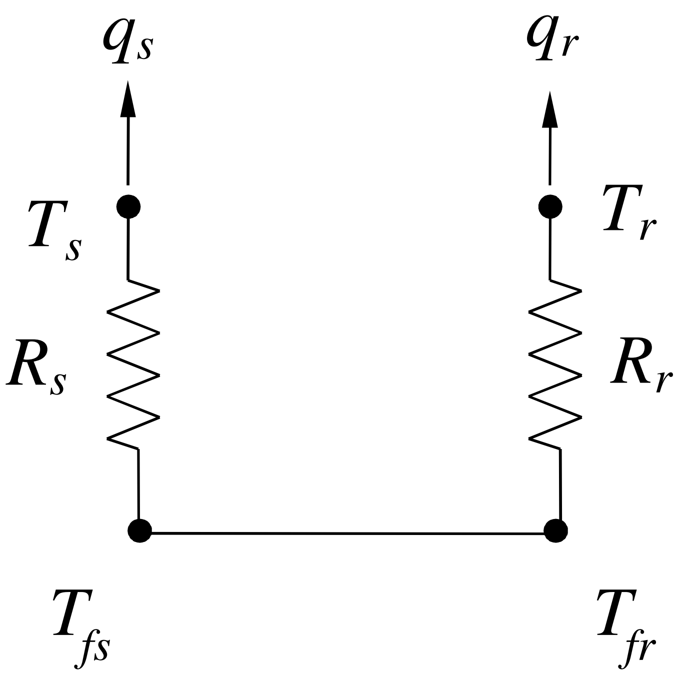


Simple Heat Flux DSC Cell Schematic



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

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Consequences of the Assumptions

- Whenever the heating rate of the sample and reference calorimeters are not identical, the measured heat flow is not the actual sample heat flow rate.
  - This occurs during transitions in standard DSC and always during MDSC
  - MDSC results are strongly period dependent, requiring long periods and slow heating rates.

- The heat flow baseline is usually curved and has large slope and offset. Loss of some resolution and sensitivity may occur as a result of curvature in the baseline.

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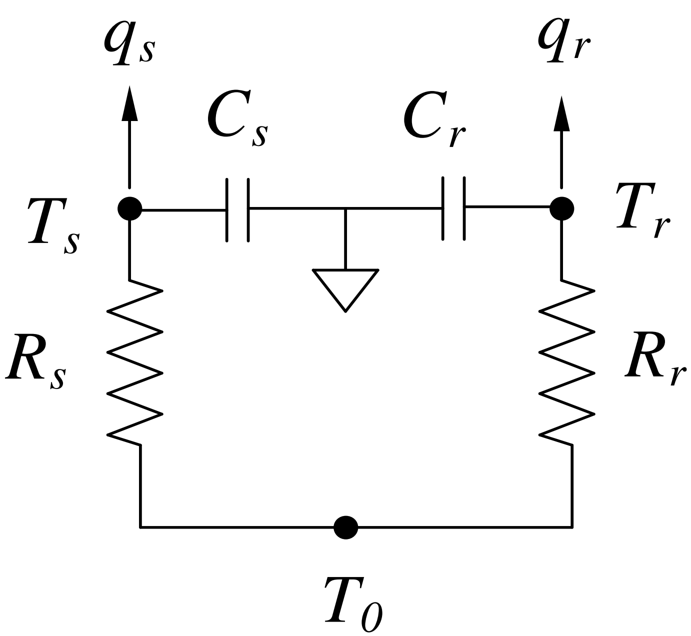
Tzero™ Heat Flow Measurement

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.

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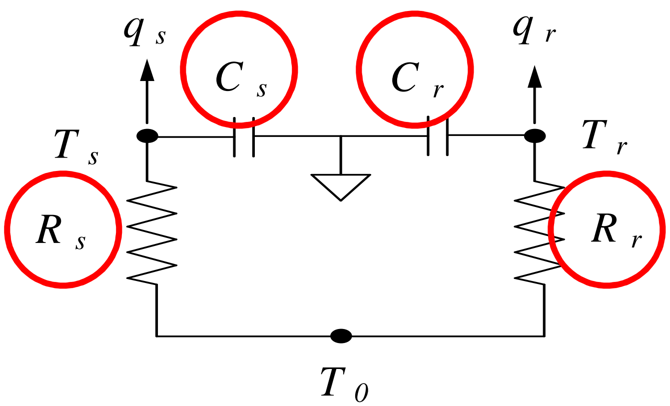
Tzero™ Heat Flow Equation

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

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

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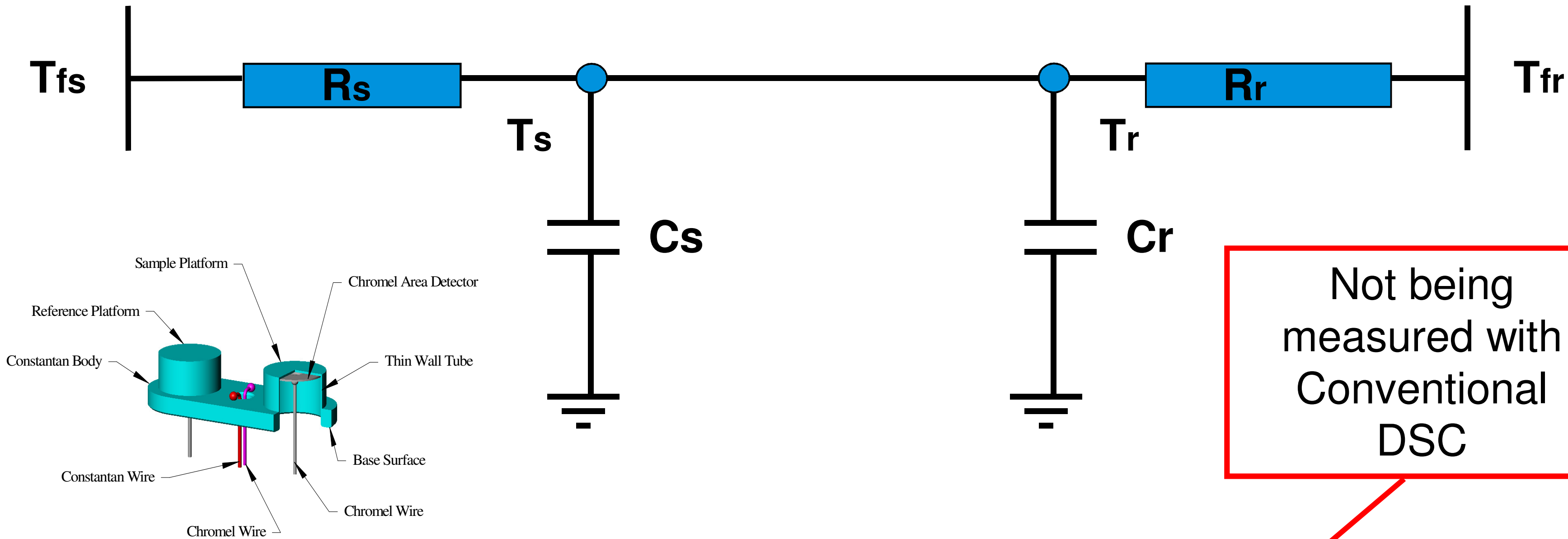
Expanded Principles of DSC Operation Accounting for Imbalances



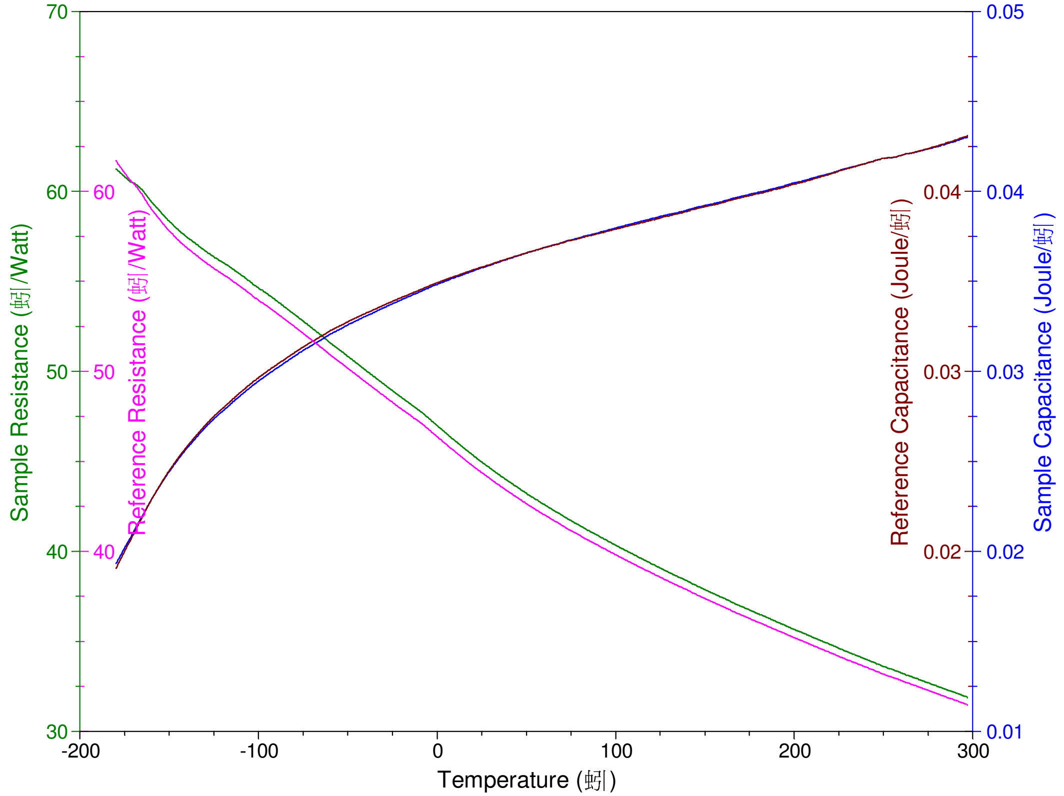
Not being measured with Conventional DSC

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

- A — Thermal Resistance Imbalance
- B — Thermal Capacitance Imbalance
- C — Heating Rate Imbalance

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.

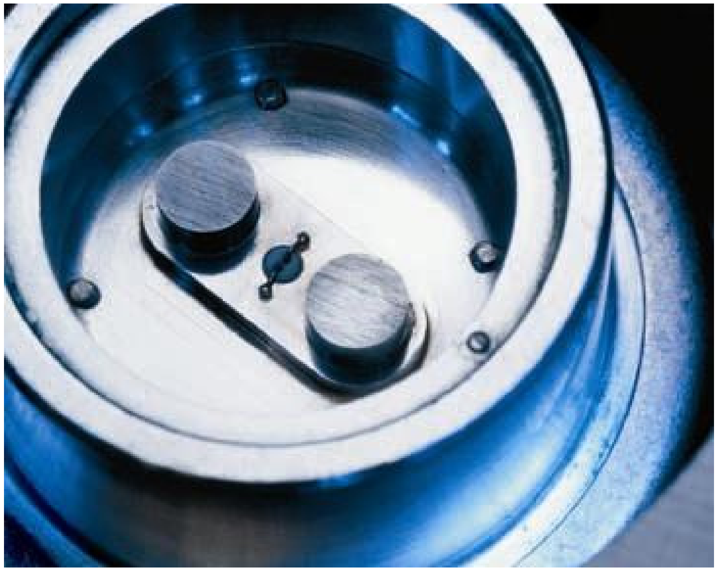


This cell is very well balanced. It is acceptable and usual to have larger differences between sample and reference sensors.

What Does a DSC Measure? Q-Series Cell

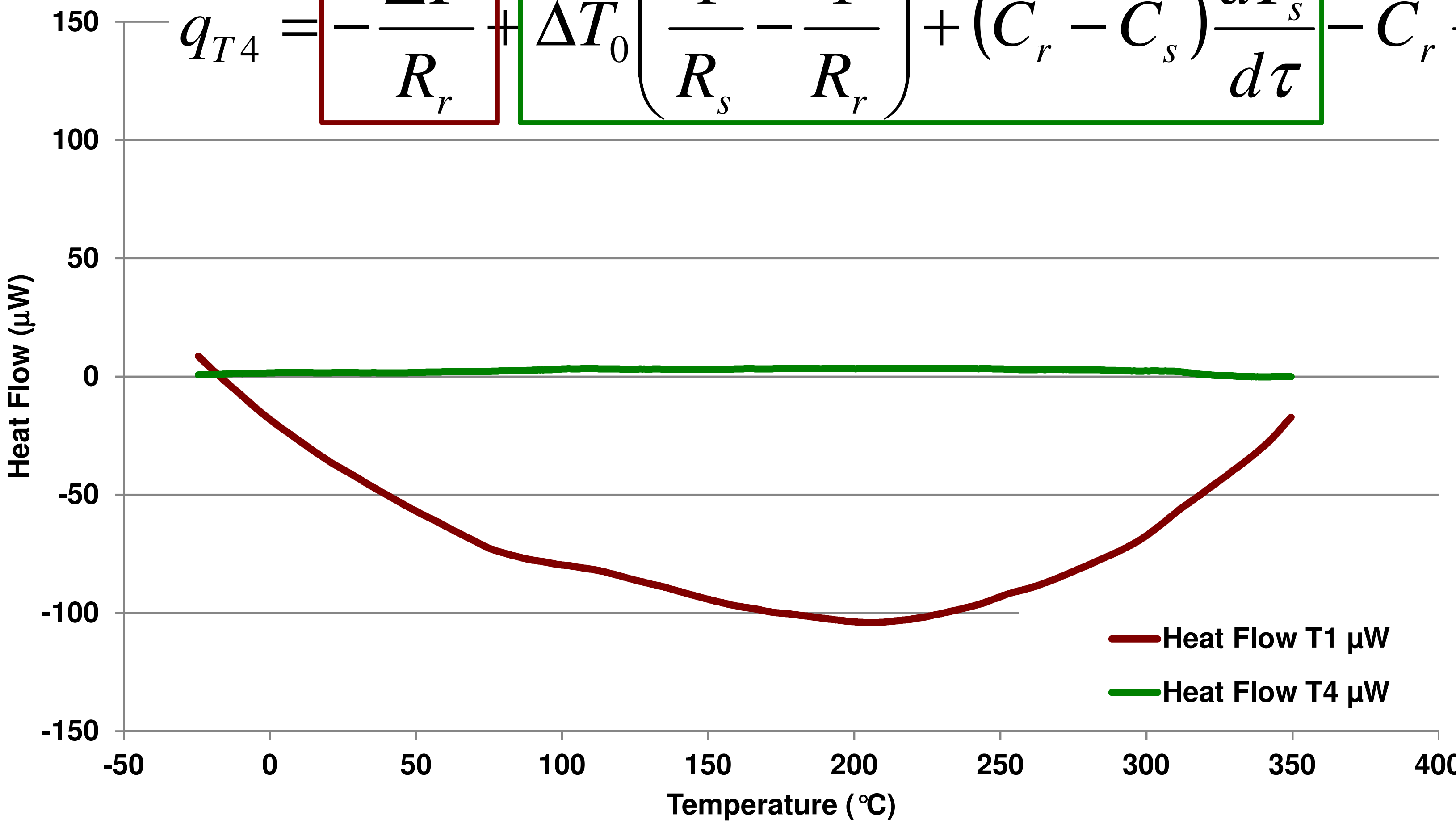
- A DSC measures the difference in Heat Flow Rate between a sample and inert reference as a function of time and temperature

mW = mJ / sec



Tzero Benefit: Improved Baseline Shape

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



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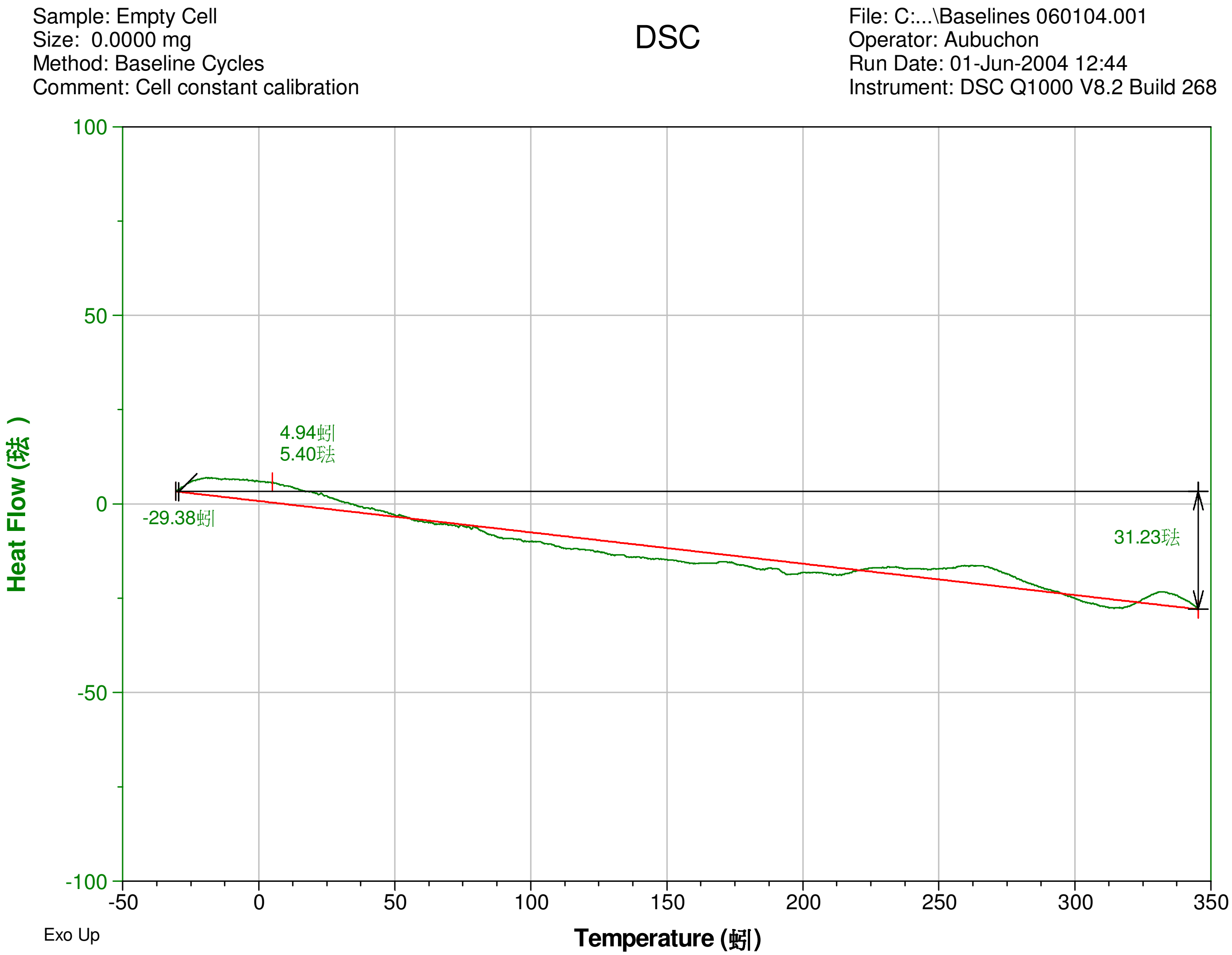
Tzero Baseline Performance



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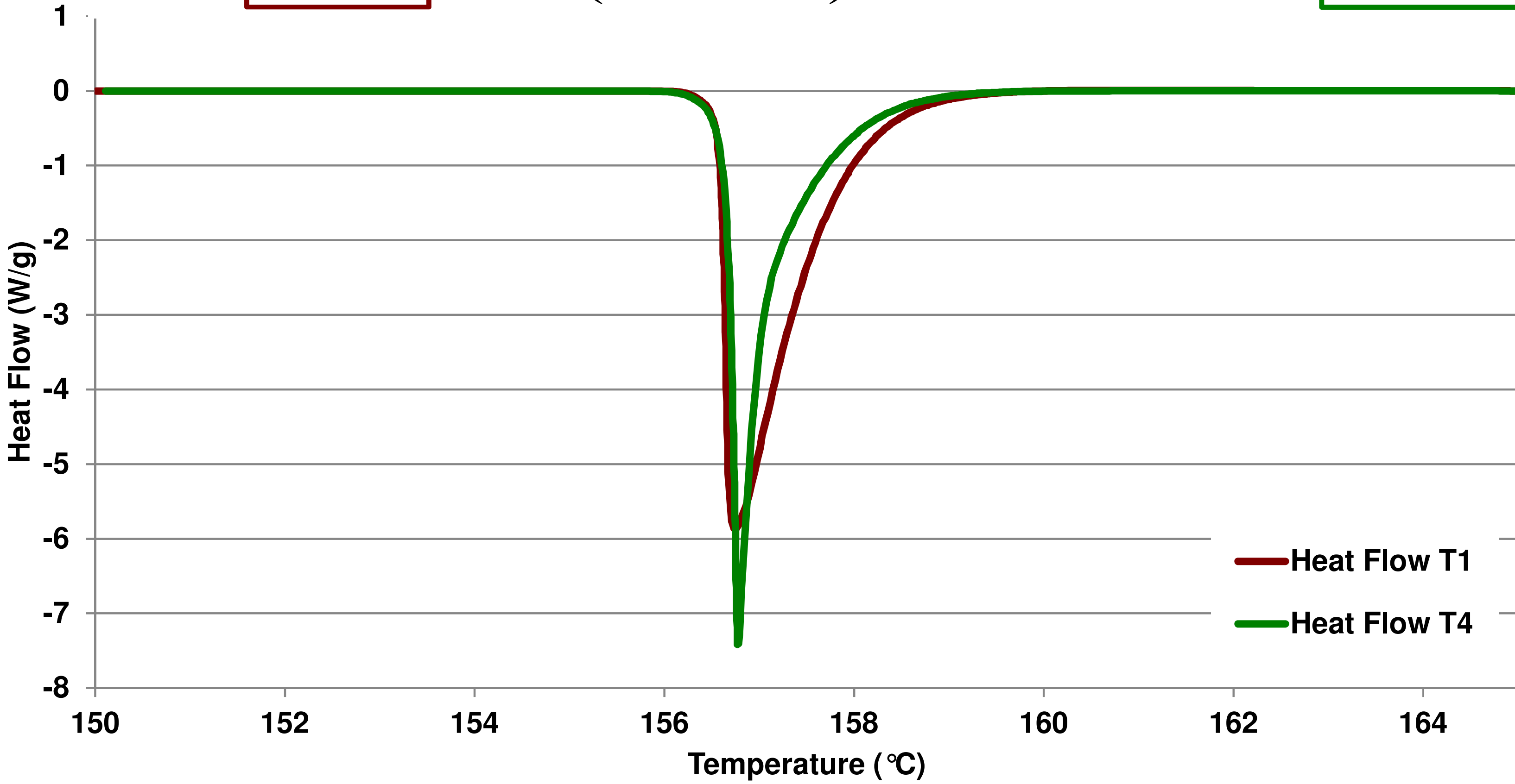
Tzero Benefit: Improved Peak Resolution

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



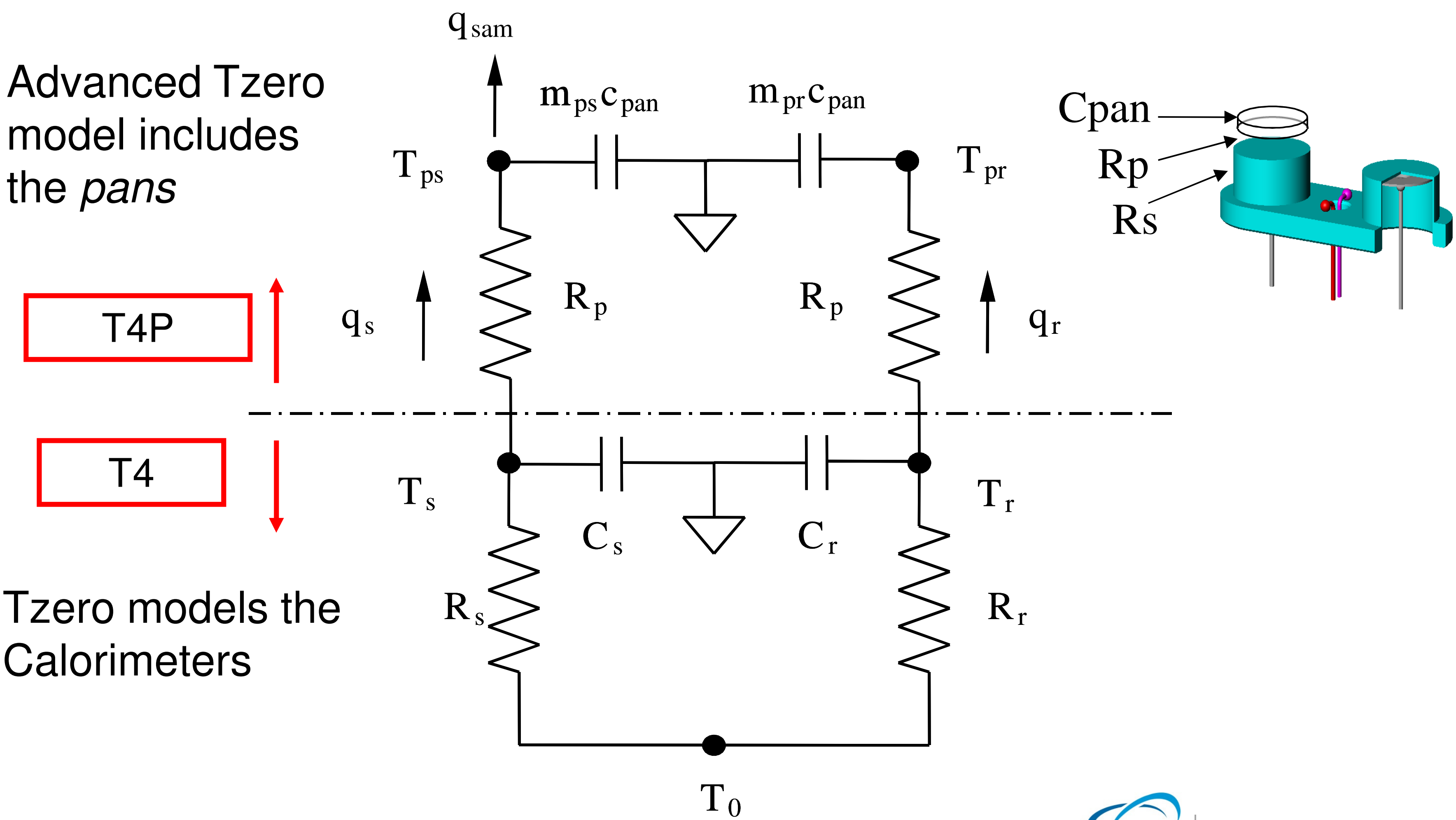
Advanced Tzero Technology (T4P)

- 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***

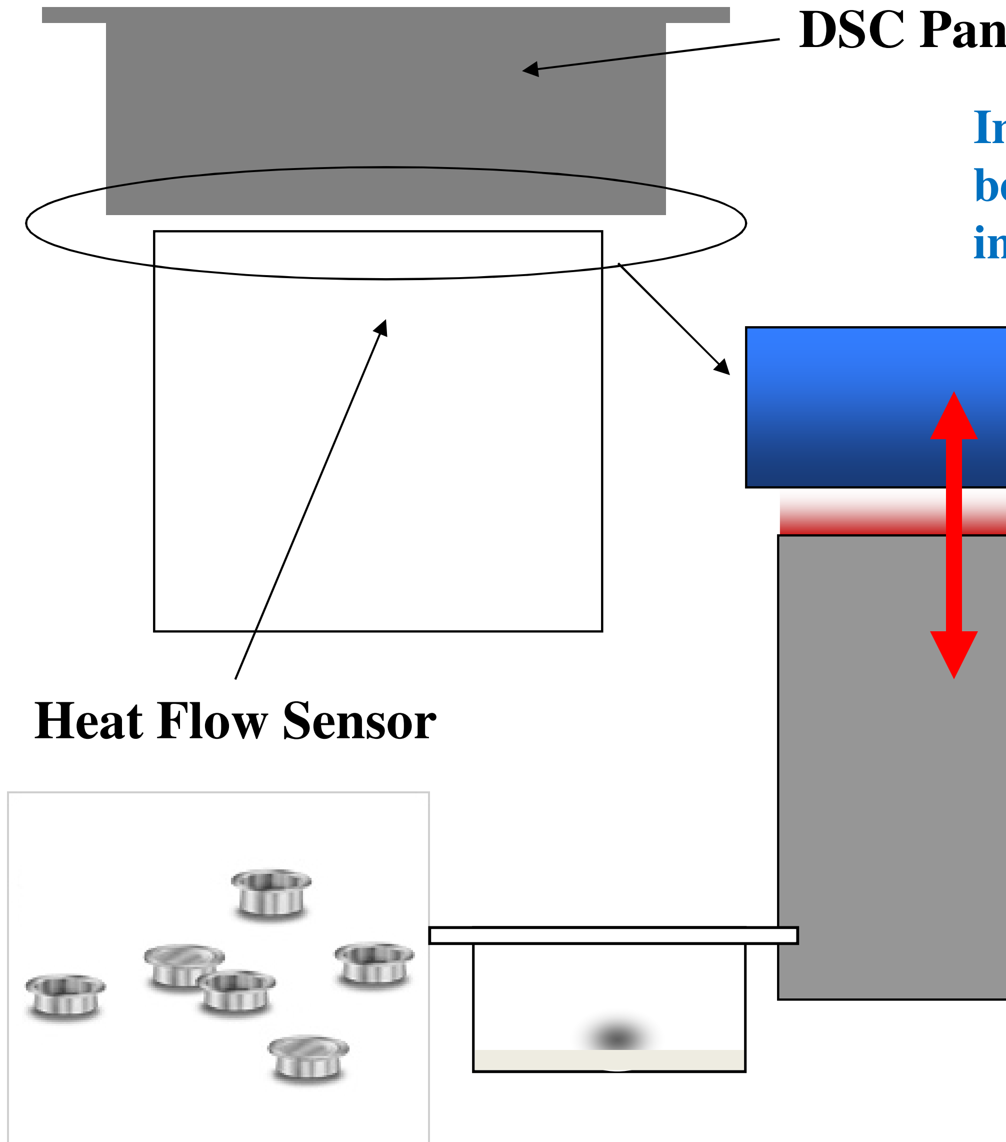
Advanced Tzero model includes the *pans*

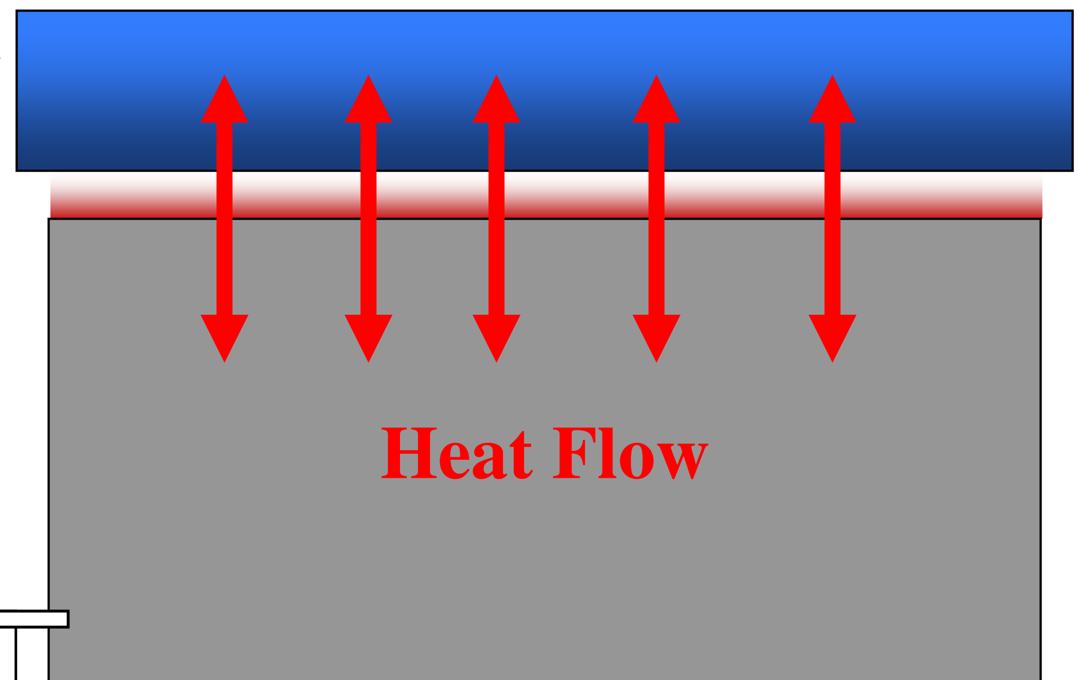


Tzero models the Calorimeters

What is Pan Contact Resistance?

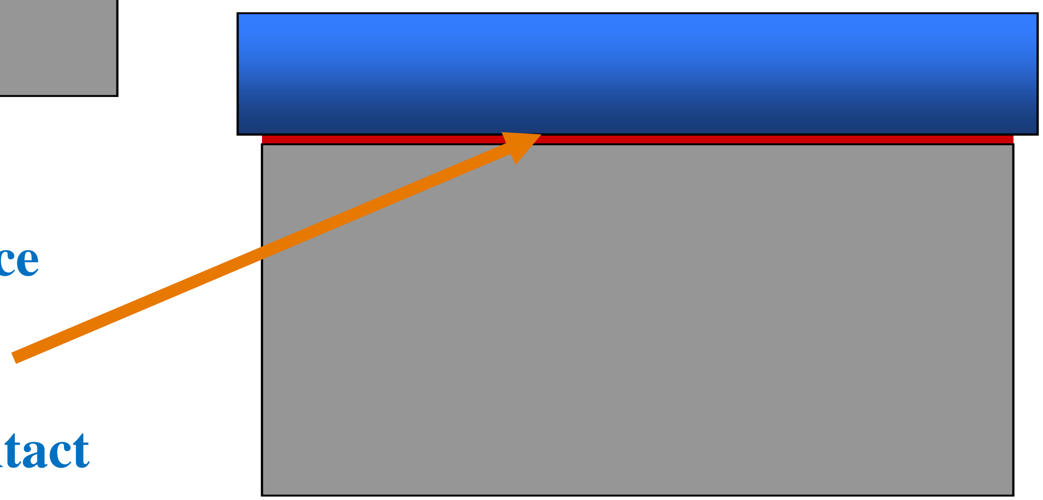
Imperfect (non-intimate) contact between pan and sensor causes lag in heat flow which decreases resolution





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

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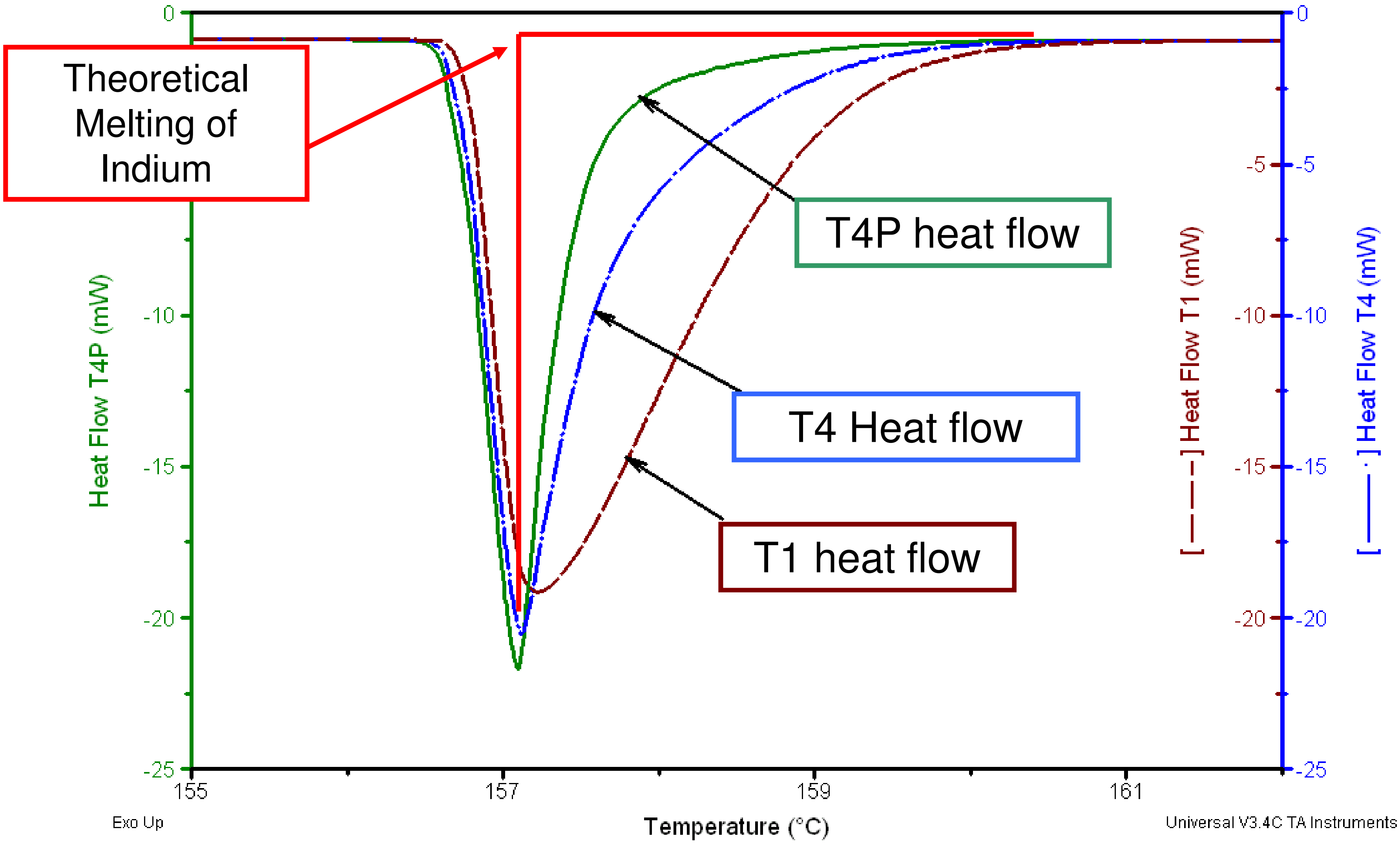
Indium with T1, T4 and T4P Heat Flow Signals Improvements to Sensitivity and Resolution



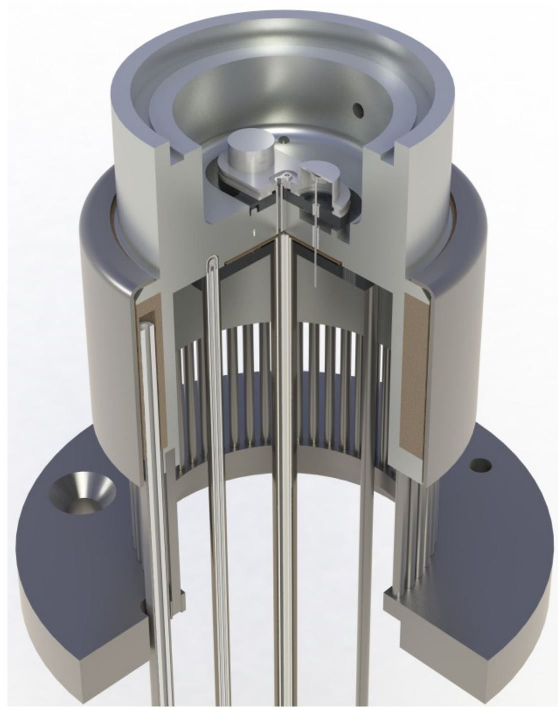
Technology : Fusion Cell™ Discovery-Series Cell

- $\boldsymbol{Fusion\ Cell = Q + Discovery + New\ Manufacturing}$
  - Key features of Q series and the first generation Discovery series, patented Tzero™, and new proprietary manufacturing processes
- **One Cell, One Sensor, - Complete Performance**
  - Unlike competitive designs that require choosing between sensitivity or resolution the Discovery DSC's delivers both in one sensor
- **Purest real-time heat flow possible**
  - Lengthy pre- and post-test manipulations are never needed
    - No baseline subtraction or correction scheme required
    - No de-smearing or deconvolution required

FusionCell™

Patented Tzero ™ Technology: Features and Benefits

- Flattest baselines available of any DSC on the market
  - Purest data without manipulation or subtraction
- Highest resolution and sensitivity,
  - without ever needing lengthy pre- and post-test manipulations as required by competitive designs
- Direct measurement of heat capacity delivering the most uniform and accurate heat flow to and from the sample.
- By improving every aspect of performance, the Discovery DSC delivers data the user can trust, in all applications, all the time.



Competitive Measurement | Thermal Resistance Imbalance | Thermal Capacitance Imbalance | Heating Rate Imbalance

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

Heat Flow | Principal Heat Flow

TA Measurement

Understanding Modulated DSC (MDSC)

Understanding Modulated DSC (MDSC) - Agenda

- What does a MDSC measure?
- When & Why to Run MDSC?

What Does MDSC Measure?

- MDSC separates the Total heat flow of DSC into two parts based on the heat flow that does and does not respond to a changing heating rate
- MDSC applies a changing heating rate on top of a linear heating rate in order measure the heat flow that responds to the changing heating rate
- In general, only heat capacity and melting respond to the changing heating rate
- The Reversing and Nonreversing signals of MDSC should never be interpreted as the measurement of reversible and nonreversible properties

MDSC Heat Flow Signals

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

Total Heat Flow	Reversing Heat Flow	Non-Reversing Heat Flow
•All Transitions	•Heat Capacity •Glass Transition •Most Melting	•Enthalpy Recovery •Evaporation •Crystallization •Thermoset Cure •Denaturation •Decomposition •Some Melting

MDSC – Instantaneous Heating Rate

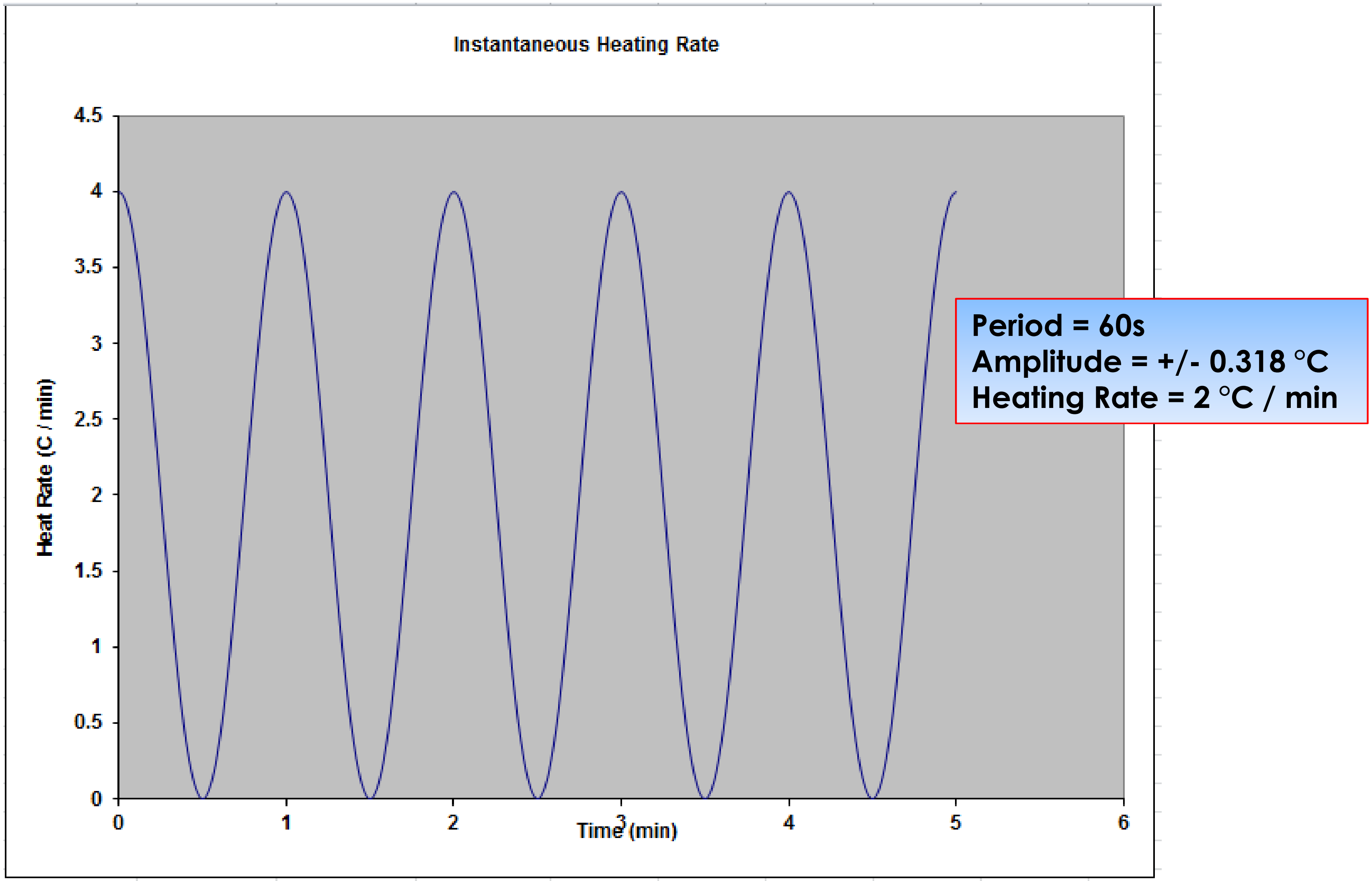
- The instantaneous heat flow is given by the equation:

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

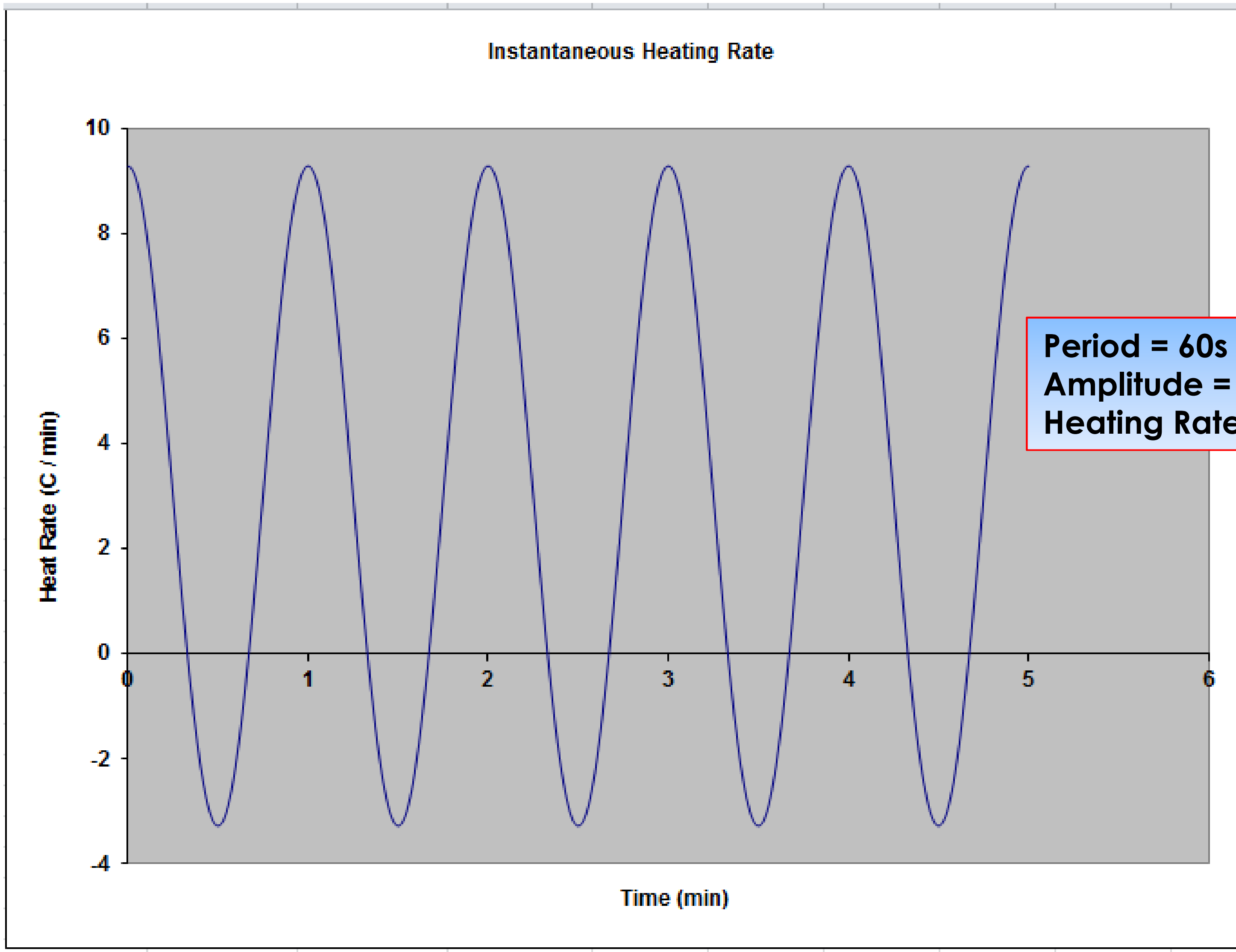
- where
  - dT/dt = instantaneous heating rate (°C / min)
  - β* = underlying heating rate (°C / min)
  - A_T* = modulation amplitude (°C)
  - ω* = angular frequency = 2π / Mod period (min^{-1})
  - t = experiment time (min)

* User Parameters

MDSC – Instantaneous Heating Rate (Heat Only)



MDSC – Instantaneous Heating Rate (Conventional MDSC)



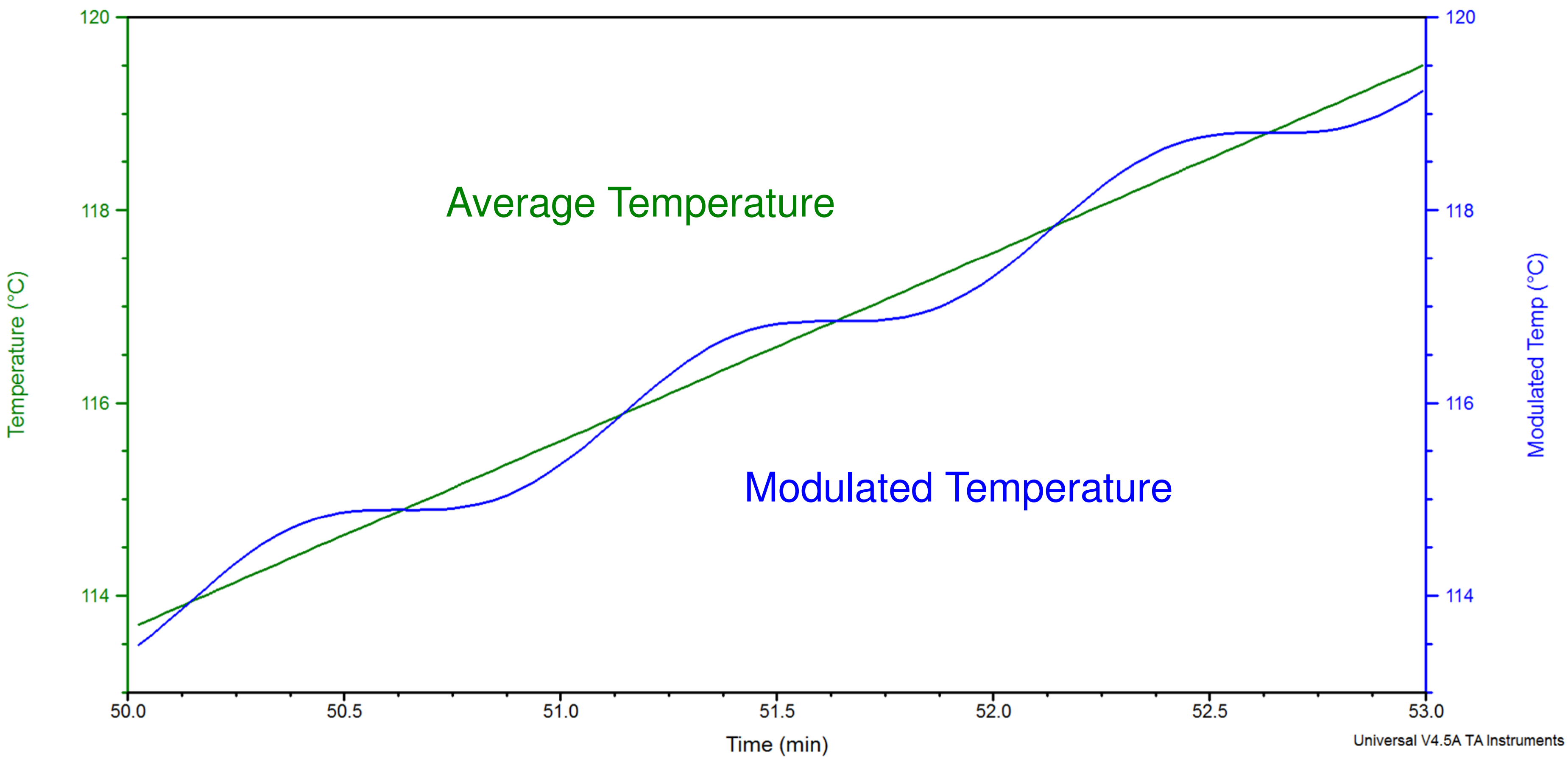
Period = 60s
Amplitude = +/- 1 °C
Heating Rate = 3 °C / min

Calculation of MDSC Signals

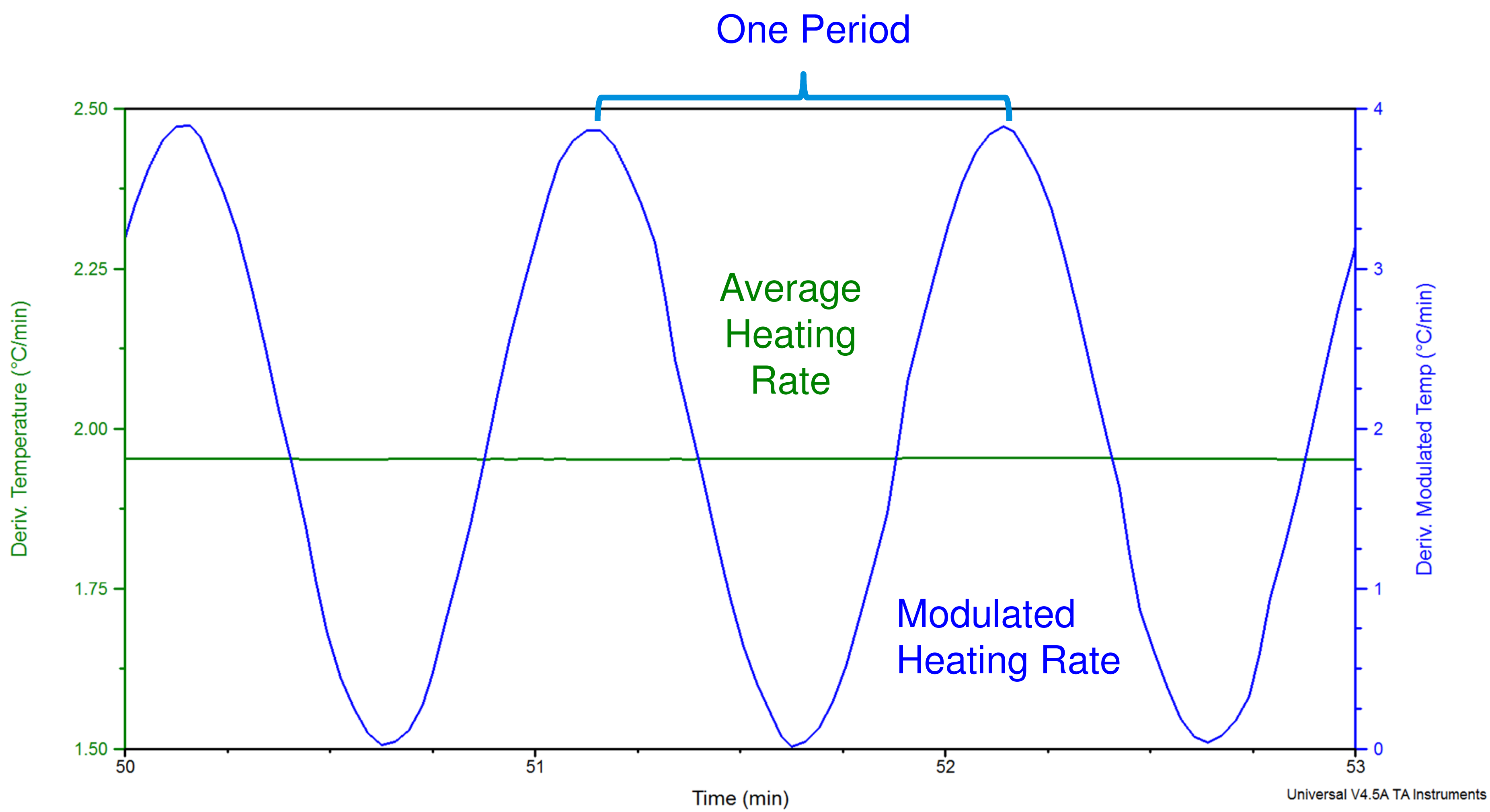
- All MDSC signals are calculated from three measured signals.
  - Time
  - Modulated Temperature (Heating Rate)
  - Modulated Heat Flow

Average & Modulated Temperature

MDSC, 2℃/min, ±0.32/60 s

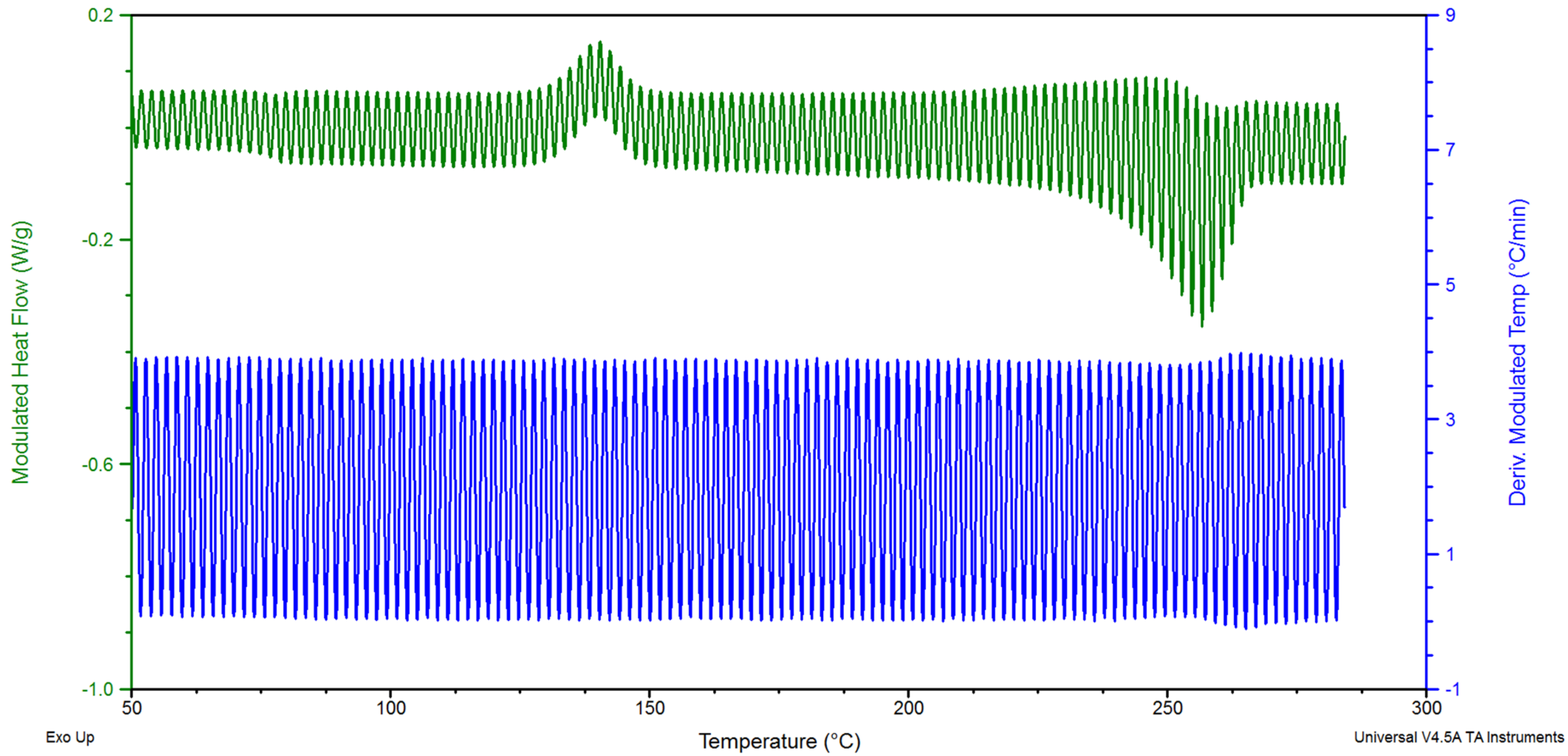


Average & Modulated Heating Rate



MDSC Raw Data Signals: Modulated Heat Flow and Modulated Temperature (Heating Rate)

Signals have an Average and an Amplitude

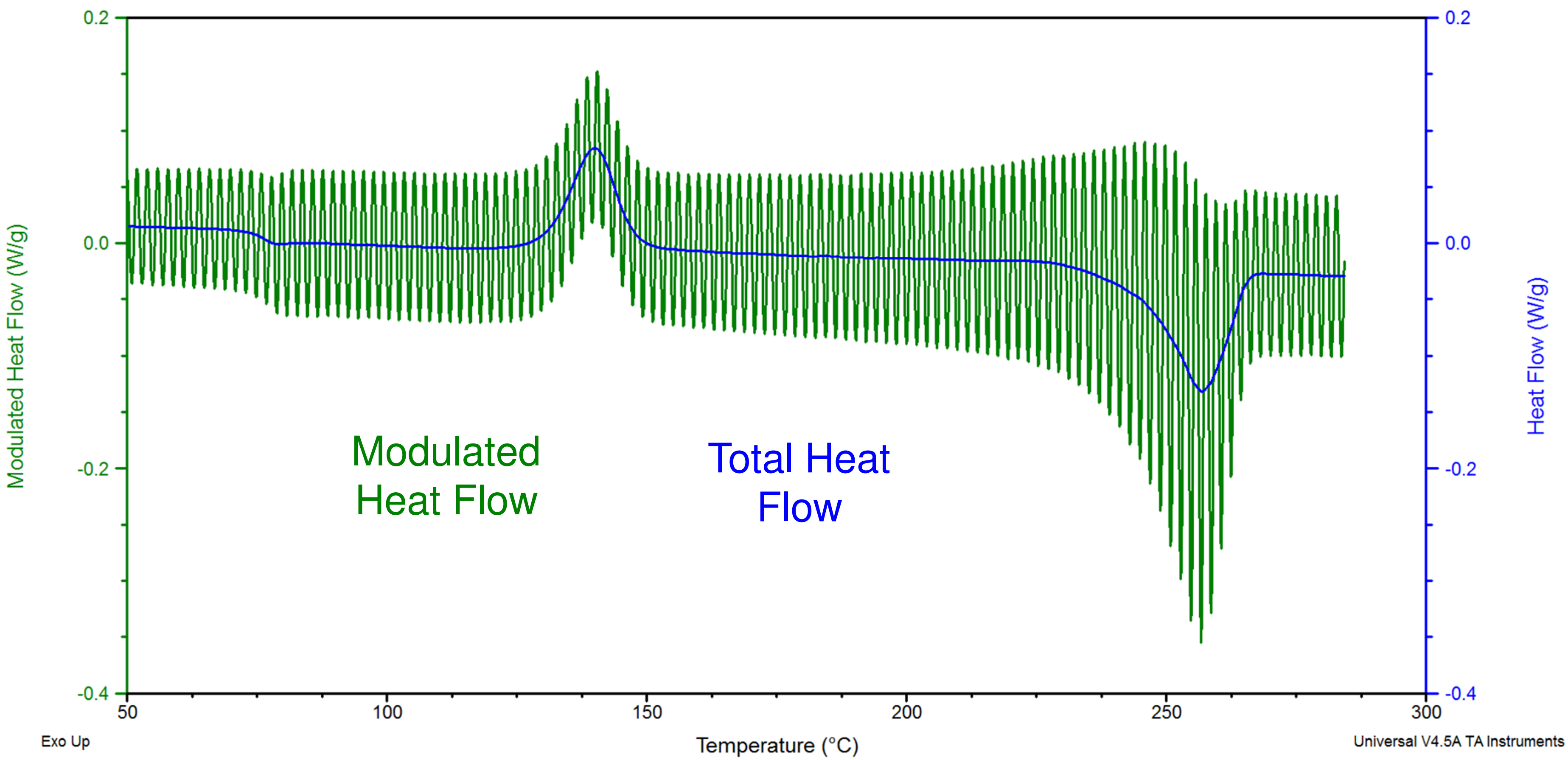


Signal Calculations

Total Heat Flow

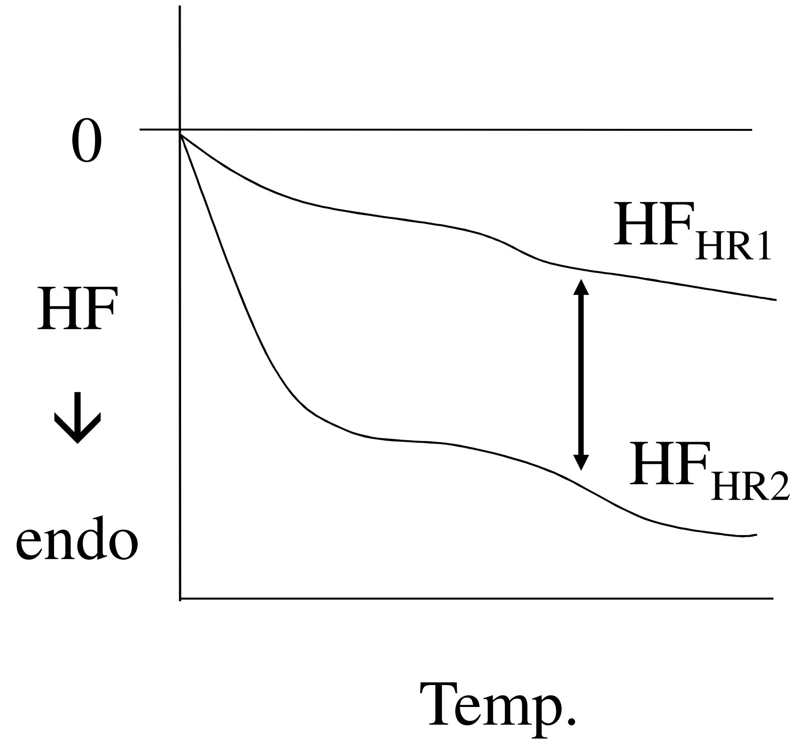
- Equivalent to standard DSC at the same average heating rate
- Calculated from the average value of the Modulated Heat Flow
- The average and amplitude values of the Modulated Heat Flow are calculated continuously (every 0.1 seconds) using Fourier Transform analysis. This provides much better resolution than would be obtained from using the actual average and amplitude values that occur only twice over each modulation cycle. The recommended data storage rate is 2 sec/pt. for MDSC.

Calculation of MDSC Total Heat Flow



ASTM E1269: Heat Capacity Measurement

$$Cp = K \ x \ \frac{HF_{HR2} \ ? \ HF_{HR1}}{(HR_2 \ ? \ HR_1) \ wt}$$



Where:

K = Calibration constant

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

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

HR_2 = Heating rate 2

HR_1 = Heating rate 1

wt = weight of sample

MDSC Signal Calculations

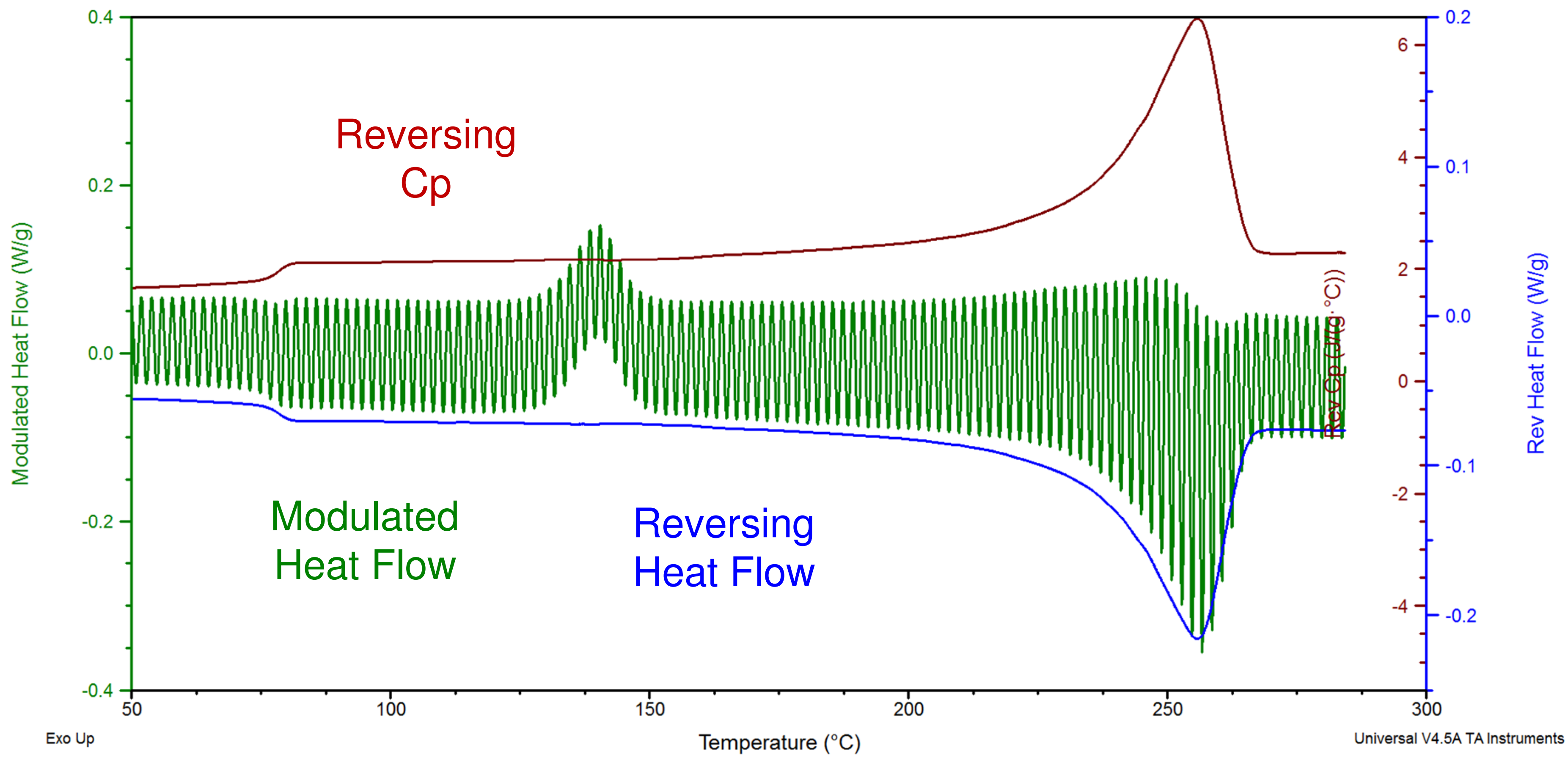
Reversing Heat Flow

- Calculated from Reversing Heat Capacity signal

$$\text{Rev Cp} = \frac{\text{Heat Flow Amp}}{\text{Heating Rate Amp}} \text{ x KCp Rev}$$

$$\text{Rev Heat Flow} = \text{Rev Cp x Avg Heat Rate}$$

Calculation of MDSC Reversing Heat Flow and Reversing Cp



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Signal Calculations (cont.)

Nonreversing Heat Flow

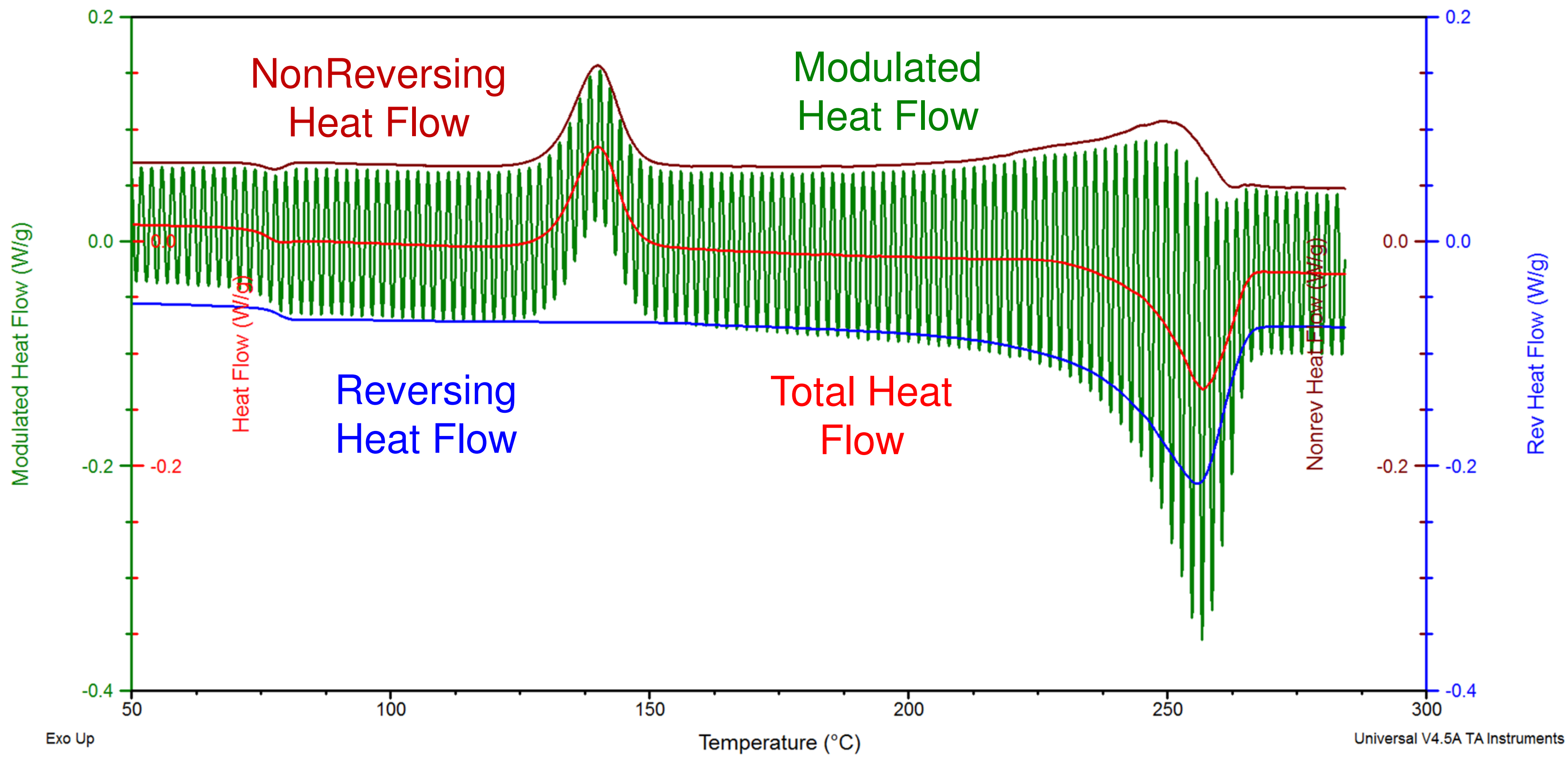
- Calculated by subtracting the Reversing Heat Flow signal from the Total Heat Flow signal

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

Total = Reversing + Nonreversing

Nonreversing = Total – Reversing

Calculated MDSC Heat Flow Signals



Comparison of DSC and MDSC Signals

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

DSC	**MDSC**	**COMMENTS**
Total Heat Flow	Modulated Heat Flow	Signals contain all thermal events occurring in the sample
	Total Heat Flow	Quantitatively the same in both techniques **at the same average heating rate**
	Reversing Heat Flow	Heat capacity component of total heat flow
	Nonreversing Heat Flow	Kinetic component of total heat flow
	Heat Capacity	All calculated heat flow signals are also available in heat capacity units

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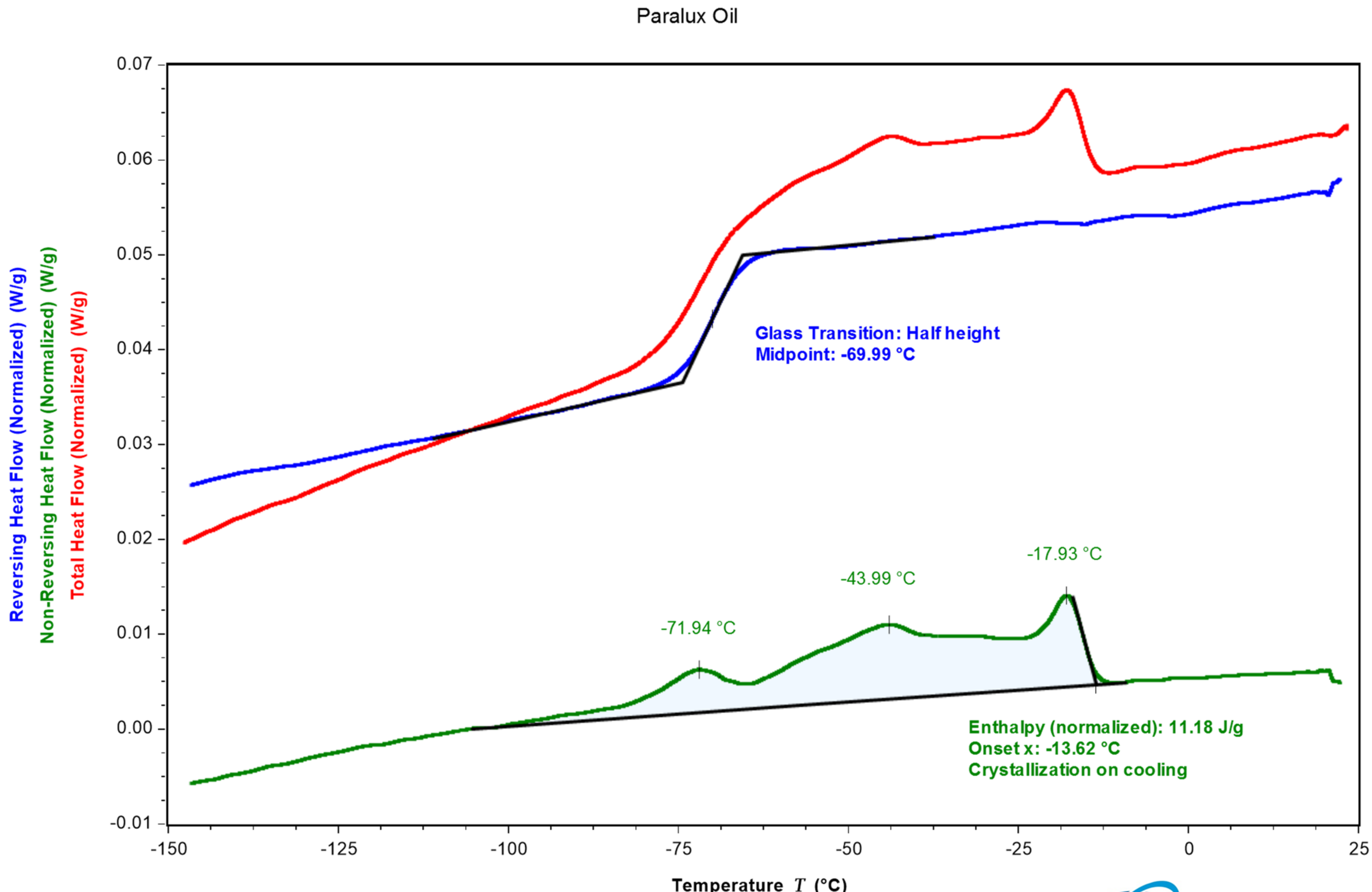
When & Why to Run MDSC: Hard to detect Tg

- Run a standard DSC at conditions you typically use.
  - Decide what you still need to learn
  - Can MDSC help you?

- **If you're trying to measure a Tg**
  - If the Tg is detectable and can be routinely analyzed, then you may not need to use MDSC
  - However, if the Tg is hard to detect, or has overlapping events, then run MDSC

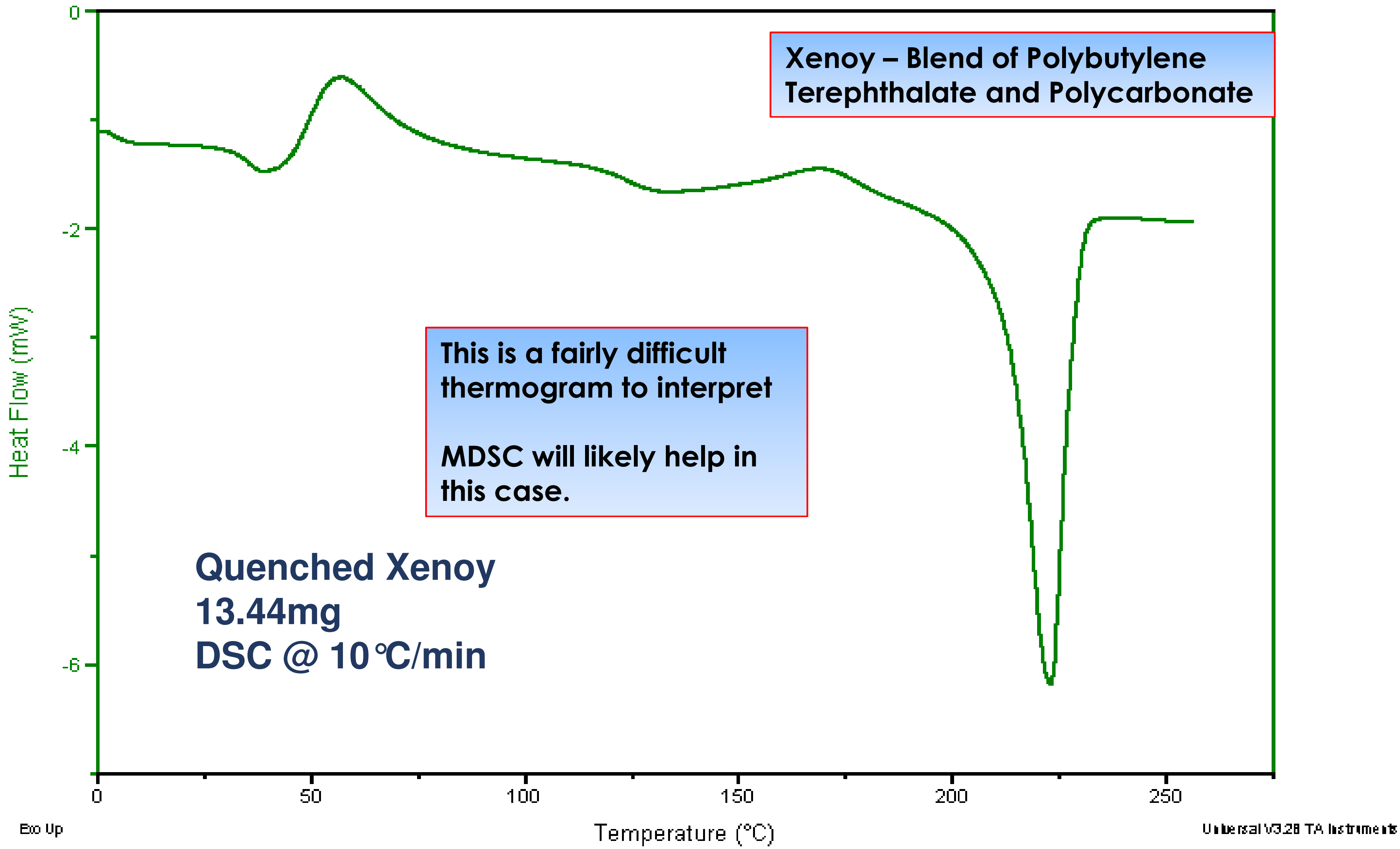
MDSC of a Process Oil



When & Why to Run MDSC: Crystallinity

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

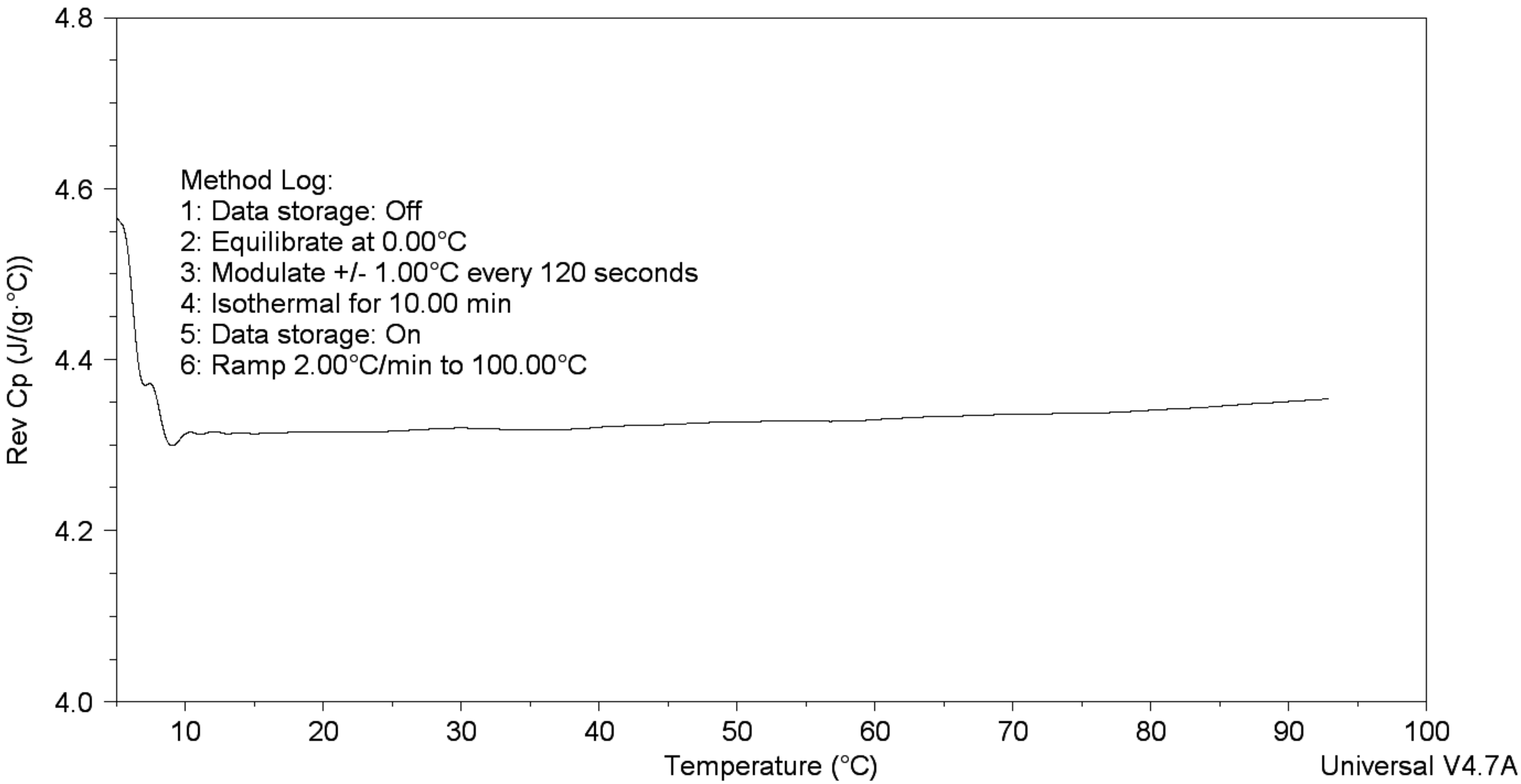
DSC of Complex Polymer Blend



When & Why to Run MDSC: Heat Capacity Determination

- If you want to measure accurate heat capacity (Cp), or the change in Cp as a function of time at an isothermal temperature – run MDSC
- Modulated DSC offers two methods for obtaining heat capacity
  - Dynamic Ramp – Use the ‘Reversing Heat Capacity’ signal, after obtaining a KCp value.
  - Quasi Isothermal - Very simple and accurate means for measuring specific heat capacity. No calibration is needed, KCp is determined at each temperature so accuracy is excellent.

MDSC Scan of Water in an Alodined Hermetic Pan



Tabulated Results of Water

	A	B	C	D
1	Temperature	Experimental Rev Cp	Lit. Cp	% error
2	°C	J/(g·°C)	J/(g·°C)	
3	20	4.315	4.1819	3.18
4	25	4.316	4.1796	3.26
5	30	4.32	4.1785	3.39
6	35	4.317	4.1782	3.32
7	40	4.32	4.1786	3.38
8	45	4.323	4.1795	3.43
9	50	4.327	4.1807	3.50
10	55	4.328	4.1824	3.48
11	60	4.329	4.1844	3.46
12	65	4.333	4.1868	3.49
13	70	4.336	4.1896	3.49
14	75	4.337	4.1928	3.44
15	80	4.34	4.1964	3.42
16	85	4.345	4.2005	3.44
17	90	4.35	4.2051	3.45
18	95	NA	4.2103	NA
19	100	NA	4.216	NA
20				
21				
22		Heat Capacity of Water		

Experimental data vs. literature Values for the Cp of water.

Over the temperature range, the %error is less than 3.5%.

Experimental Design:
Sample Preparation and Considerations

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℃/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

TGA: The Technique

- 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.

Mechanisms of Weight Change in TGA

- Weight Loss:
  - **Decomposition: The breaking apart of chemical bonds.**
  - **Evaporation: The loss of volatiles with elevated temperature.**
  - Reduction: Interaction of sample to a reducing atmosphere (hydrogen, ammonia, etc).
  - Desorption.
- Weight Gain:
  - Oxidation: Interaction of the sample with an oxidizing atmosphere.
  - Absorption.

All of these are kinetic processes (i.e. there is a rate at which they occur).

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Typical TGA Methods

- **Ramp (heating) experiment (Thermal Stability)**
  Ramp 20°C/min. to 1000°C

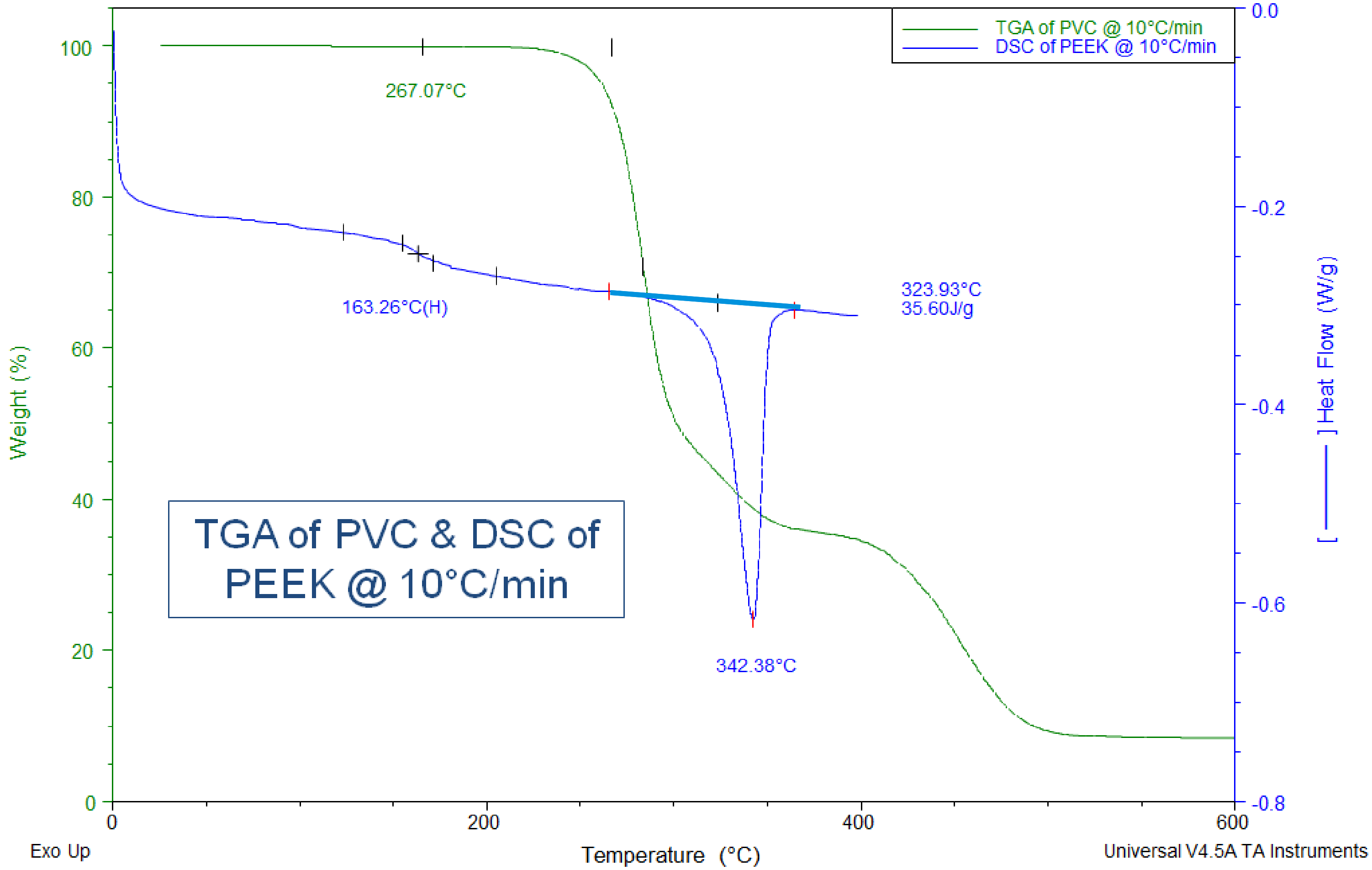
- Ramp (heating) and Isothermal Hold (Out-gassing)
  Ramp 20°C/min. to 100°C
  Isothermal 100 min

- Ramp and switch gas (carbon black and filler content)
  Ramp 20°C/min. to 650°C (in an inert atmosphere)
  Select gas: 2 (switch to air or oxygen, a reactive atmosphere)
  Ramp 20°C/min. to 1000°C

- All of the above methods can be used for selecting the optimum experimental conditions for your DSC, though the ramp method is most commonly used.

TGA vs DSC : Unknown Sample should be Dangerous for DSC Cell if Decomposition Occur!

The graph illustrates the fact that some polymers can decompose before others start to melt.



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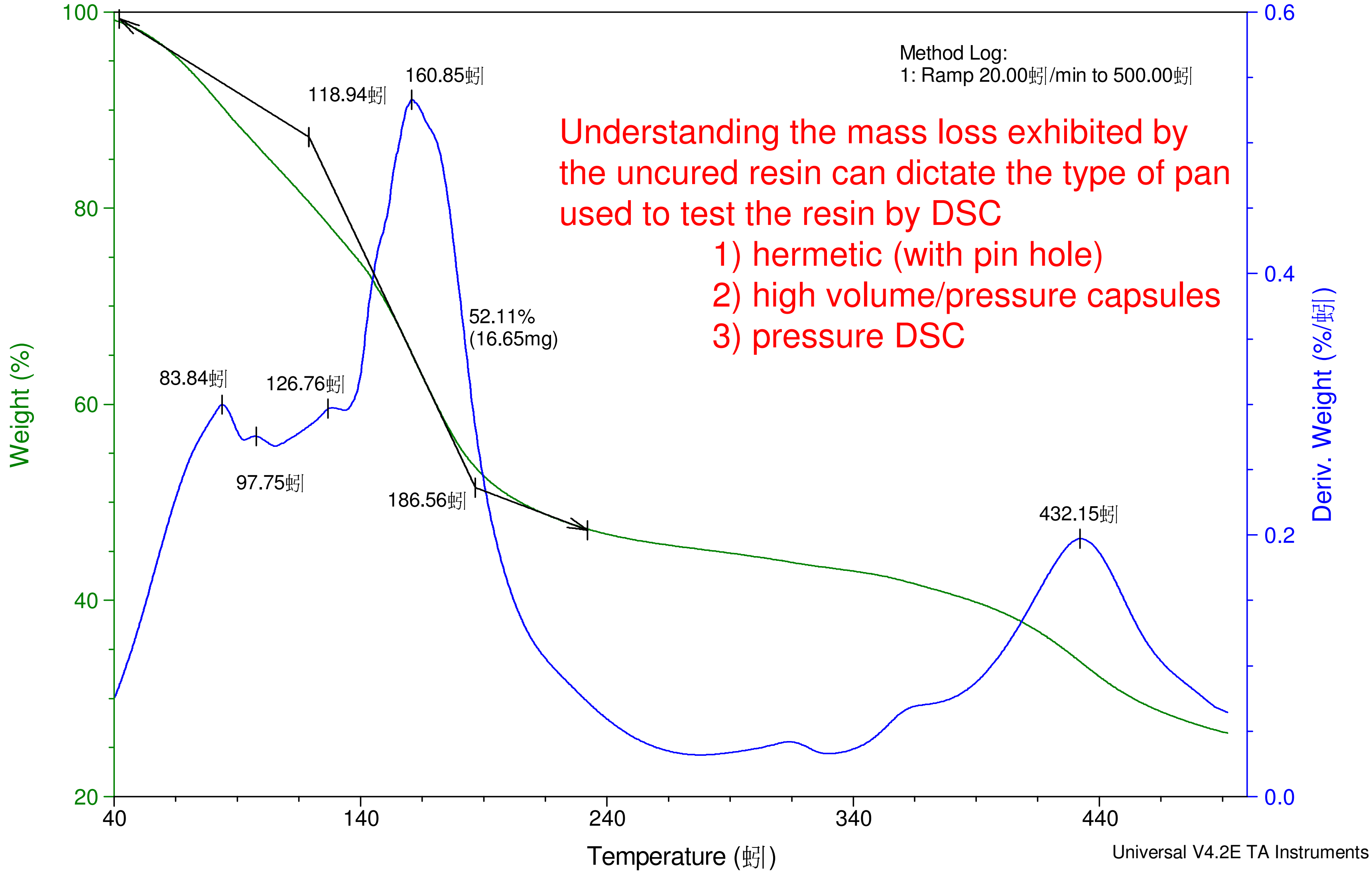
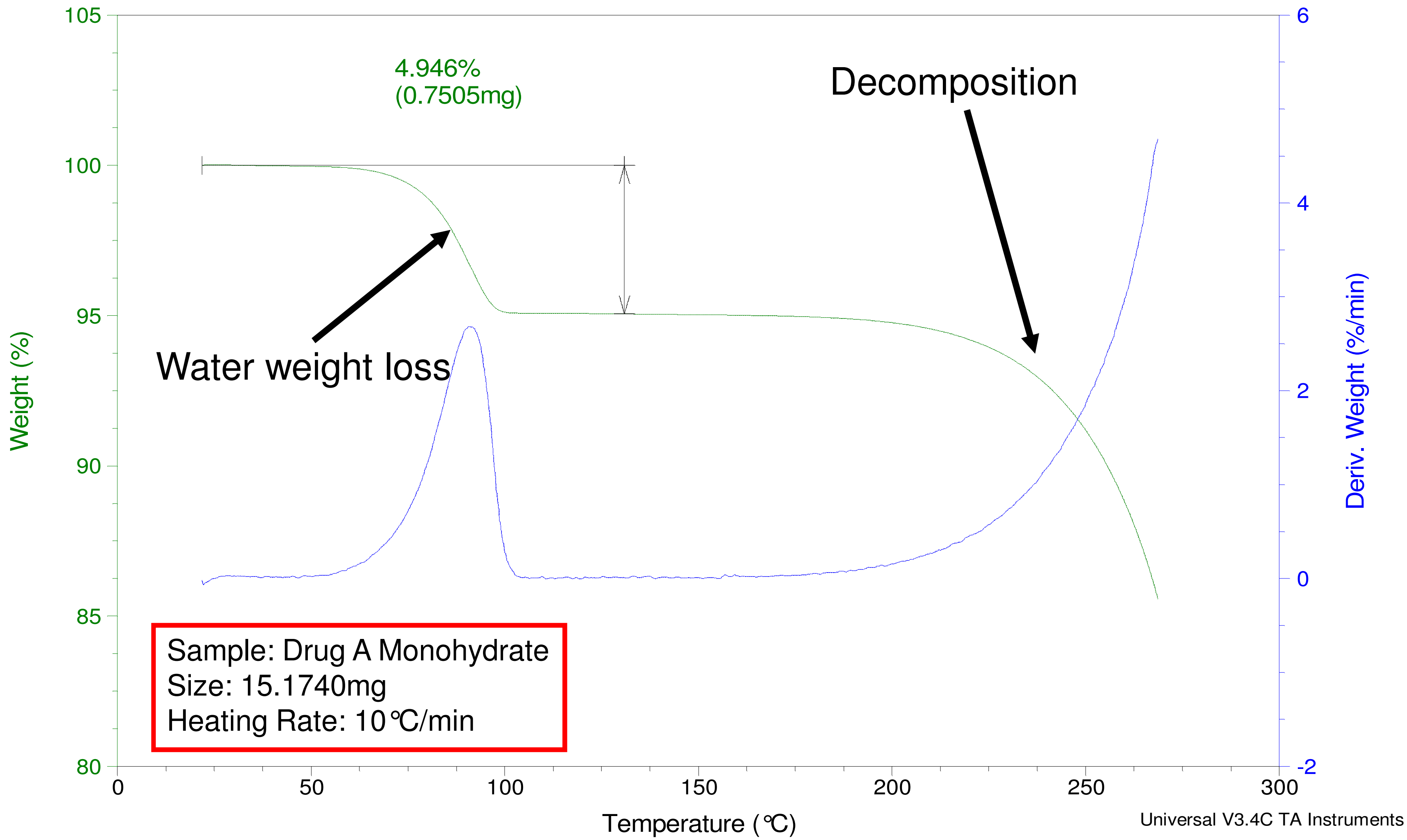
Typical TGA data: Decomposition of an uncured resin



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

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

Tzero Press (P/N 901600.901)

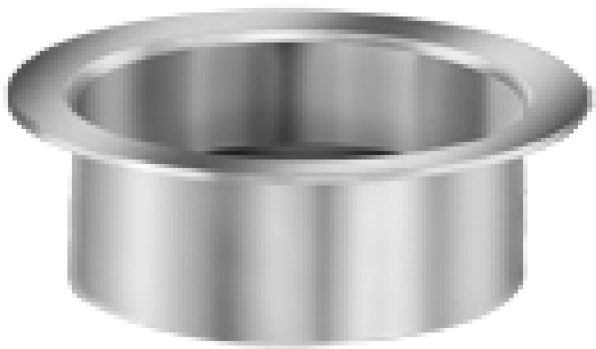
Tzero Press kit includes die sets for:

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 Pan

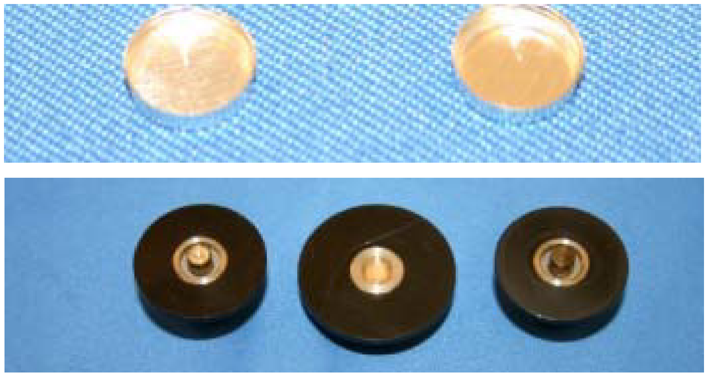


Tzero Low-Mass Pan

- 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.

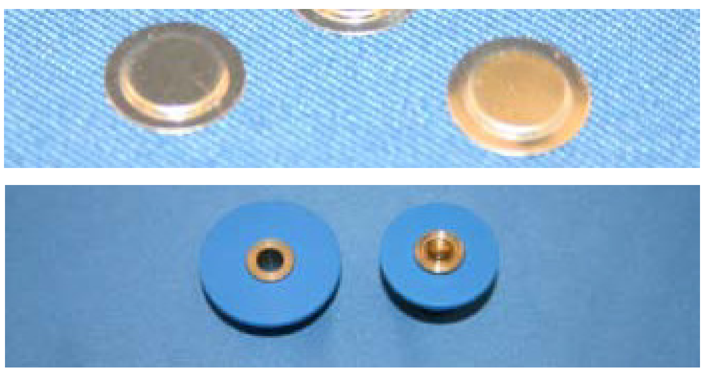
TA Instruments Tzero Pans

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.

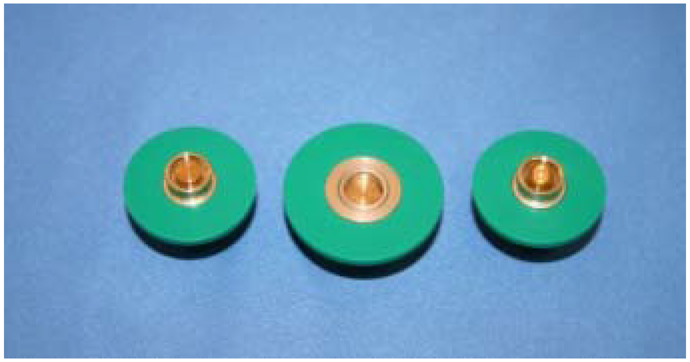
Tzero Hermetic Lid



- 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℃ maximum
  - Gold (p/n 900866.901 pan, p/n 900868.901 lid):up to 725℃
  - Graphite (p/n 900874.901 pan, p/n 900873.901 lid): up to 725℃ (in N2)

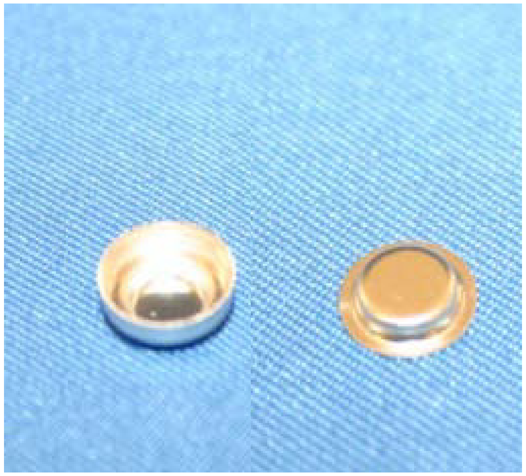
- Standard Pans without lids
  - Platinum (p/n 900578.901): up to 725℃
  - Copper (p/n 900867.901) : up to 725℃ (in N2)

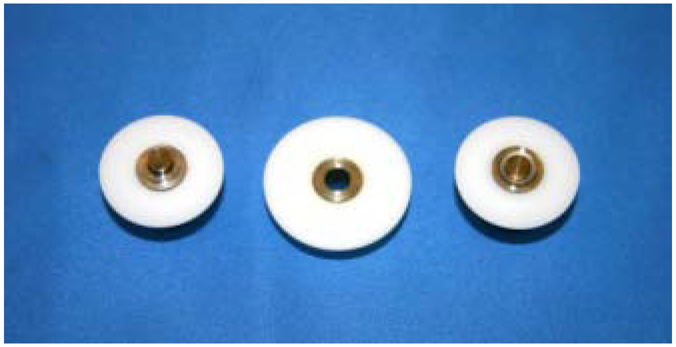
Sample Shape

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

Standard Series Hermetic Pans (Sealed)

- Part numbers for the pans and lid
  - 900793.901 Aluminum Sample Pans, Hermetic (pkg. of 200)
  - 900794.901 Aluminum Lids, Hermetic (pkg. of 200)
  - 900860.901 Hermetic Lids with Pinhole (pkg. of 50)
- Pan & Lid weigh ~55mg, bottom of pan is not as flat as standard pans
- Used for liquid samples and samples with volatiles
- Always use lid (same exceptions as before)
- After sealing pans, the lid should form a dome



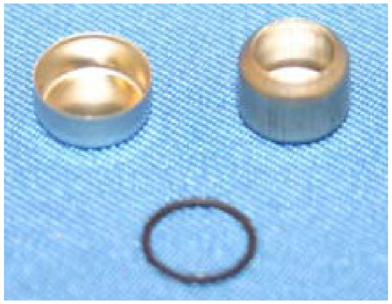


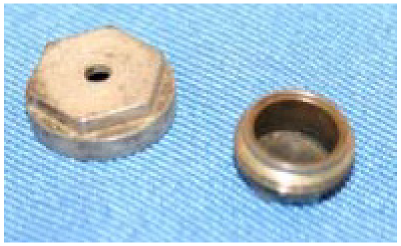
Hermetic Pans (Sealed)

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

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

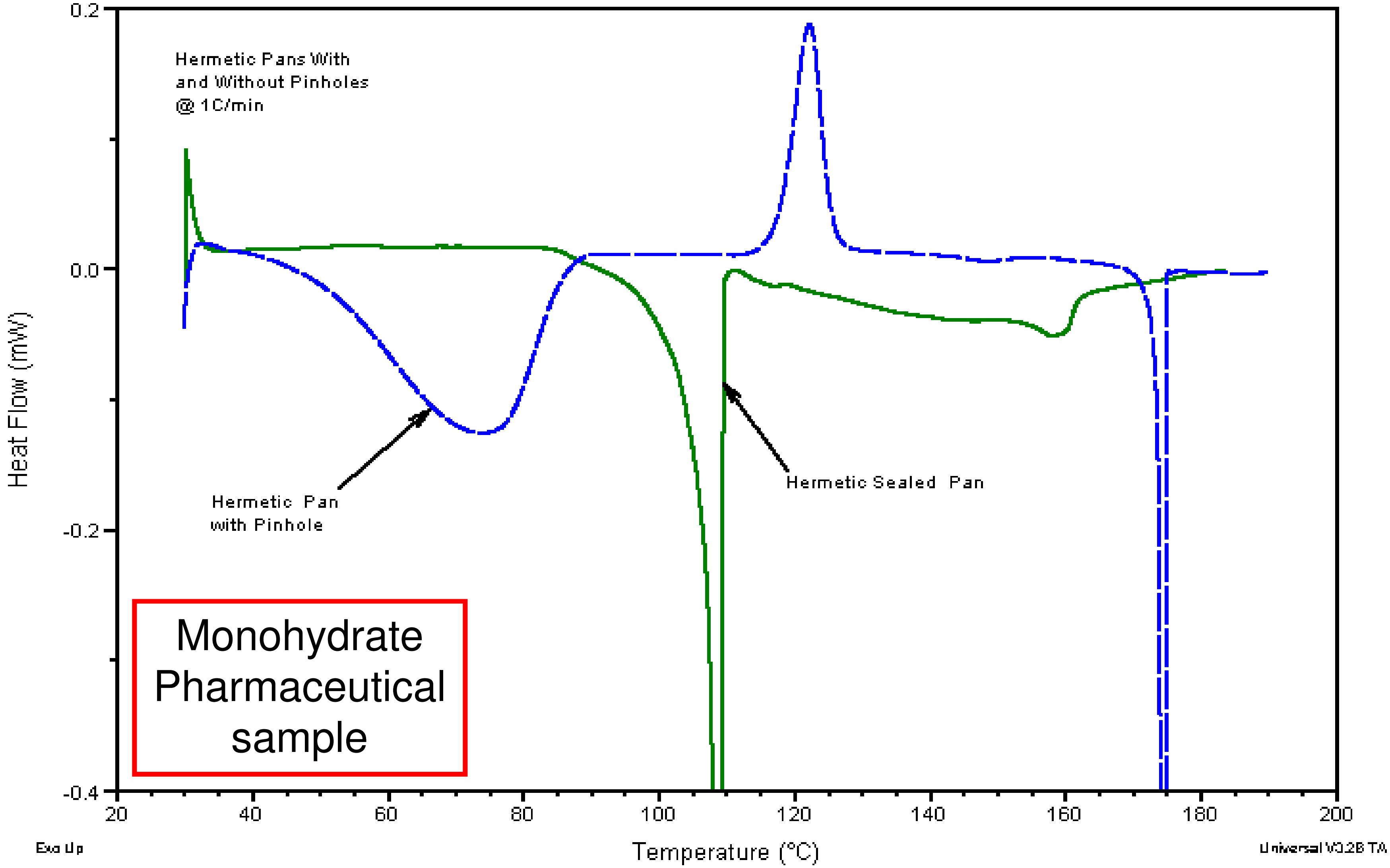
  - High Pressure: 35µL; <300°C; 1450 psig
  - P/N 900808.901





Note: 3 atm is approximately 44 psig

It Can Matter What Pan You Use



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

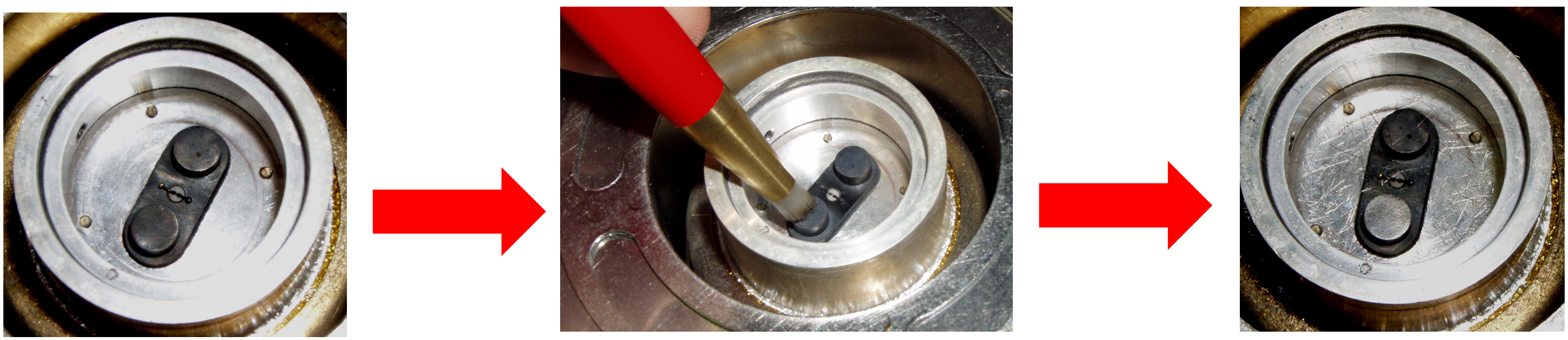
- One of the first steps to ensuring good data is to keep the DSC cell clean

- 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 – include link to tech tip video

- Use solvent – slightly damp swab with an appropriate solvent
  - Heat cell to 200℃ 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℃/min to appropriate temp (max of 550℃ on Q series, max. 400℃ 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:

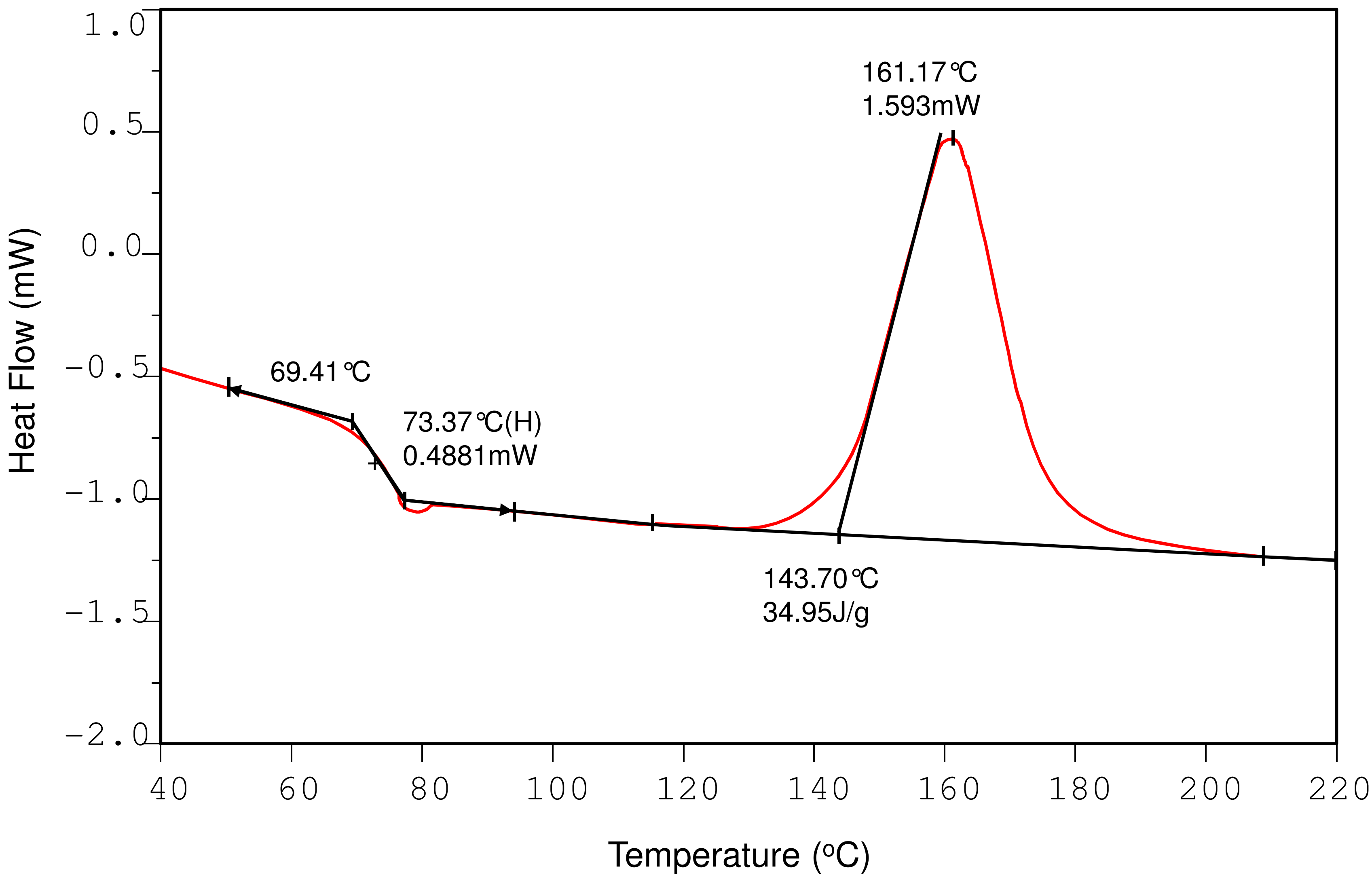
https://www.youtube.com/watch?v=cclJXrbUICA

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

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

Heat Flow Change During a Transition



Method Development

Method Design: DSC Segment List

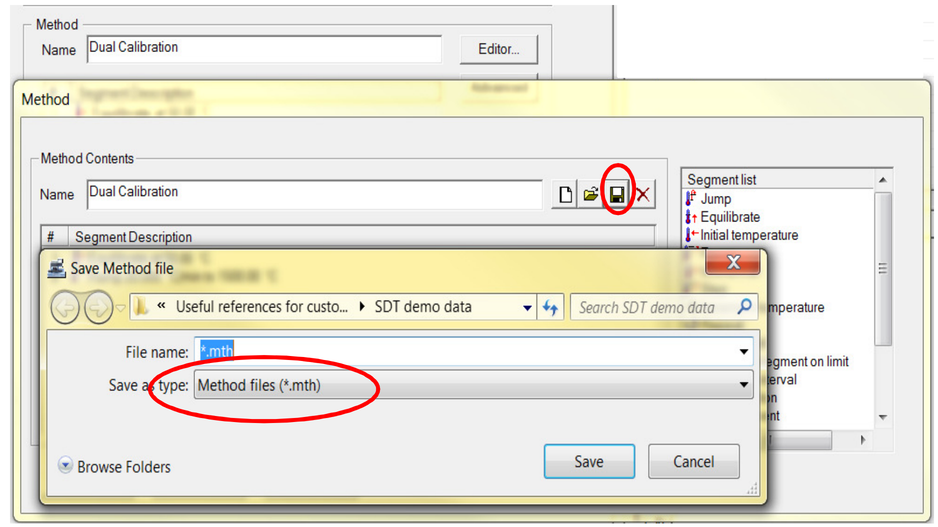
Segment list

- Jump
- Equilibrate
- Initial temperature
- Ramp
- Isothermal
- Step
- Increment temperature
- Repeat
- Repeat until
- Abort next segment on limit
- Sampling interval

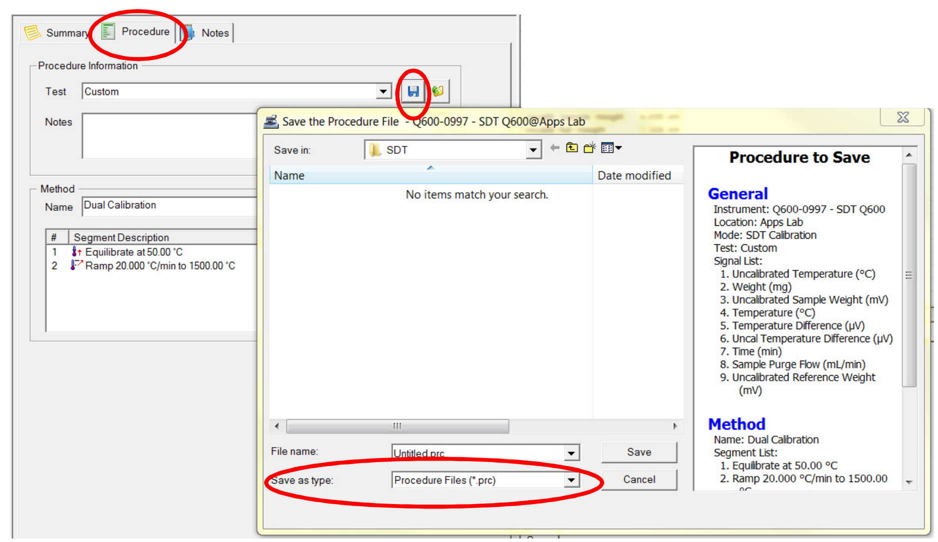
- External event
- Data storage
- Air Cool
- Mark end of cycle
- Heater PID
- Zero heat flow
- Fill Cooler
- Modulate temperature
- Gas selection
- Flow Rate
- Shutter

Method Design:
Methods (*.mth) vs. Procedures (*.prc)

- The logic of the instrument control software is based upon the concepts of methods and procedures.
  - METHODS are the actual steps that the DSC executes during a run.
    - The software provides custom templates built around types of experiments.



  - PROCEDURES include, along with the method, all other options that the user sets in creating a run.
    - For example, the data sampling interval, method end conditions, etc.

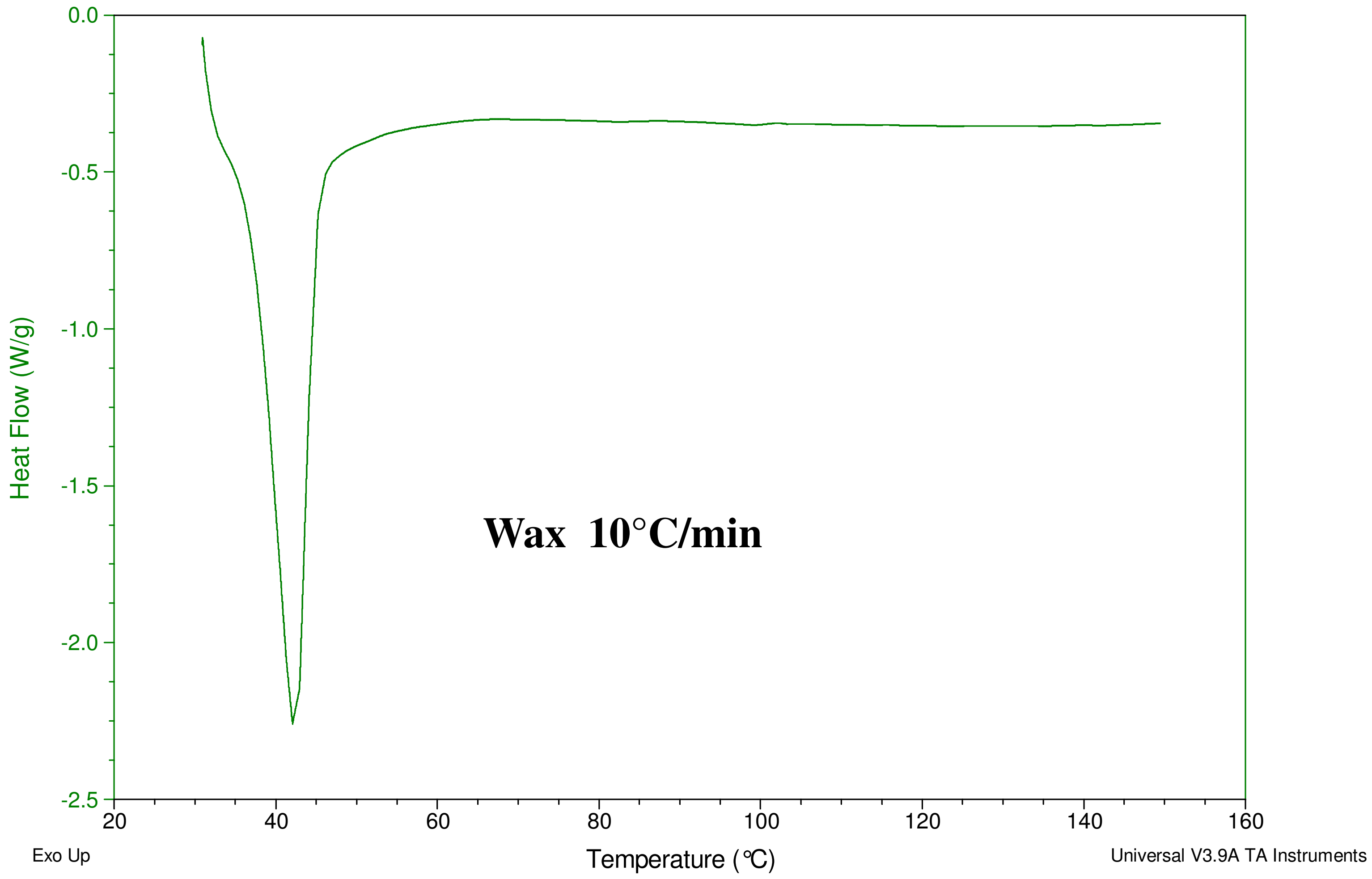


- Both methods and procedures can be saved and loaded for use at any time

Method Design Rules

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

Why have 2 min of baseline?



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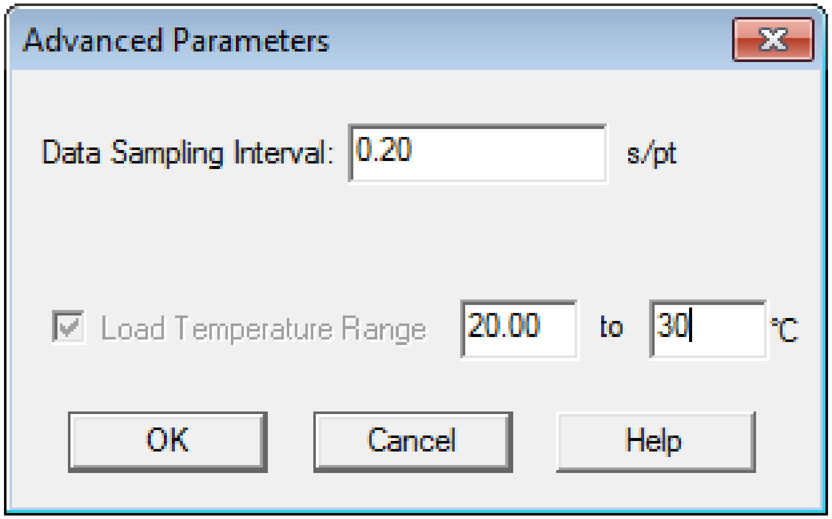
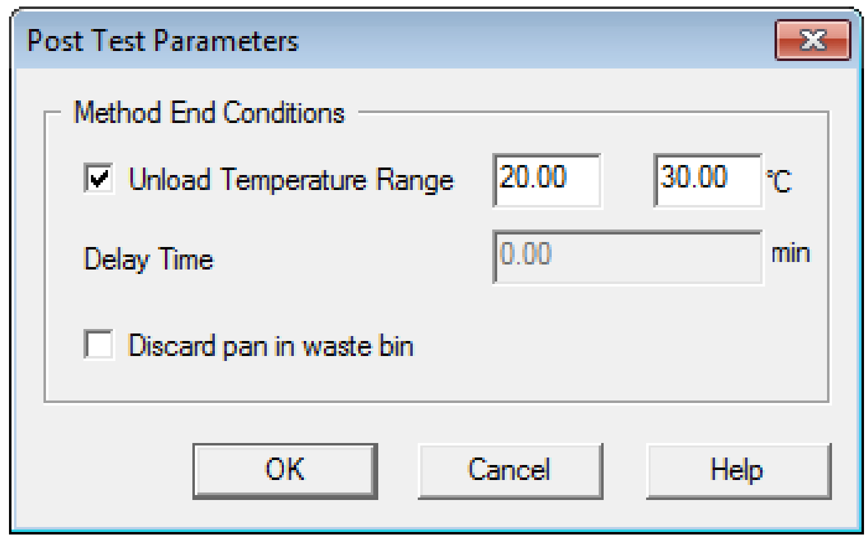
Advanced and Post Test Conditions





DSC General Method Recommendations

- Run a Heat-Cool-Heat @ 10-20 ℃/min
- Use specific segments as needed, i.e. gas switch, abort, etc.
- Modify heating rate based on what you're looking for

Heating/Cooling Methods

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

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

Don't decompose samples in DSC Cell

Heat-Cool-Reheat (HCH) Method

- Typical Heat-Cool-Heat Method

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

Don't decompose samples in DSC Cell

Oxidative Stability (OIT) Method

- OIT Method
  1) Equilibrate at 60°C
  2) Isothermal for 5.00 min.
  3) Ramp 20°C/min. to 200°C
  4) Isothermal for 5.00 min.
  5) Select gas: 2 → O_2
  6) Abort next seg. if W/g > 1.0
  7) Isothermal for 200.00 min.

Don't decompose samples in DSC Cell

Modulated® DSC Method

- Typical MDSC Methods

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

Don't decompose samples in DSC Cell

Modulated® Quasi Isothermal MDSC Method

Procedure

Mode: Modulated

Test: MDSC Quasi-Isothermal

Name: MDSC Quasi-Isothermal

Template | Segments

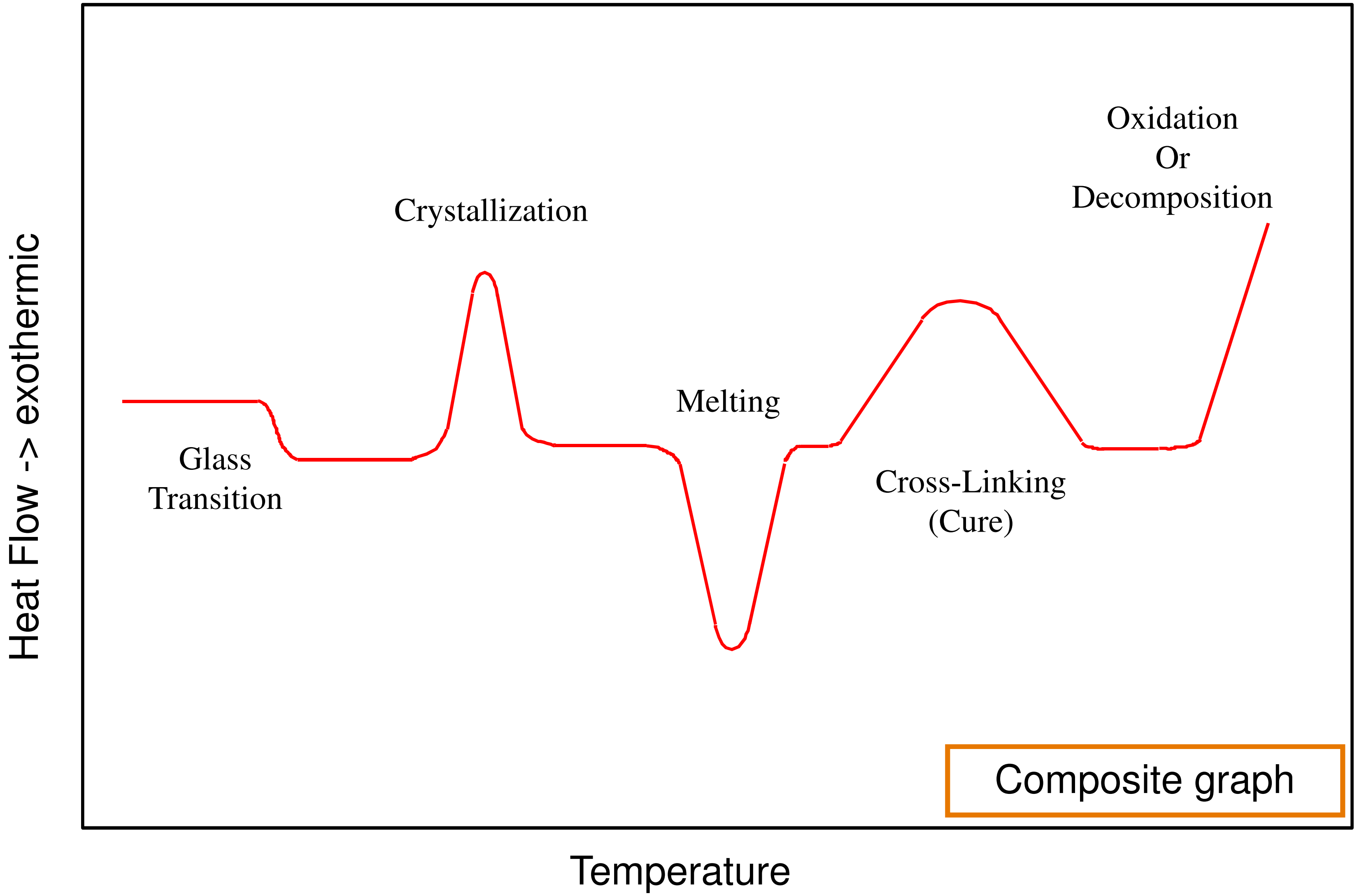
No.	Description
1	Data Off
2	Equilibrate 10.00 °C
3	Modulate Temperature Amplitude 1.0000 °C , Period 120.0 s
4	Isothermal 5.0 min
5	Data On
6	Isothermal 10.0 min
7	Data Off
8	Increment Temperature 5.00 °C
9	Repeat Segment 4 for 7 times

Applications

Applications Agenda

- The Glass Transition Temperature (Tg)
- Thermosets: Curing and Crosslinking
- Thermoplastics
- Pharmaceuticals
- Melting and Crystallization Analysis
- Heat Capacity

Typical DSC Transitions



The Glass Transition Temperature (Tg)

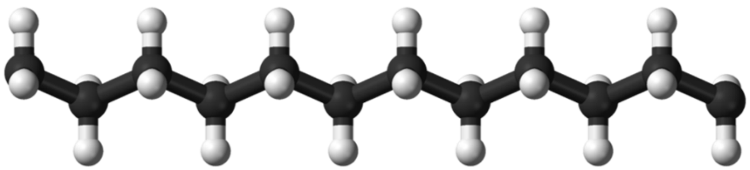
The Glass Transition (Tg)

- "The glass transition is associated with the onset of long-range cooperative segmental mobility in the amorphous phase, in either an amorphous or semi-crystalline polymer."
- Any factor that affects segmental mobility will affect T_g, including…
  - the nature of the *moving segment*,
  - chain stiffness or steric hindrance
  - the free volume available for segmental motion

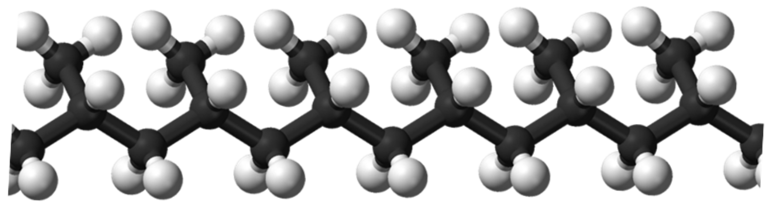
Turi, Edith, A, Thermal Characterization of Polymeric Materials, Second Edition, Volume I., Academic Press, Brooklyn, New York, P. 508.

Chemical Composition of Polymers

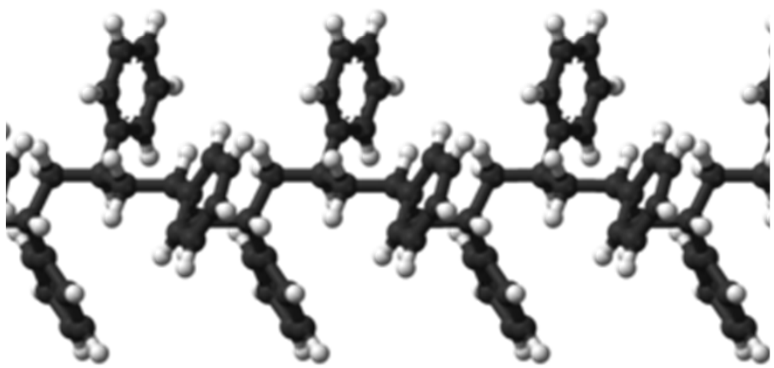
- Polymers are long chains of repeating units (monomers)
- The chemical composition determines mechanical properties, and the temperature where transitions occur



Polyethylene T_g = -128° C



Polypropylene T_g = -20° C



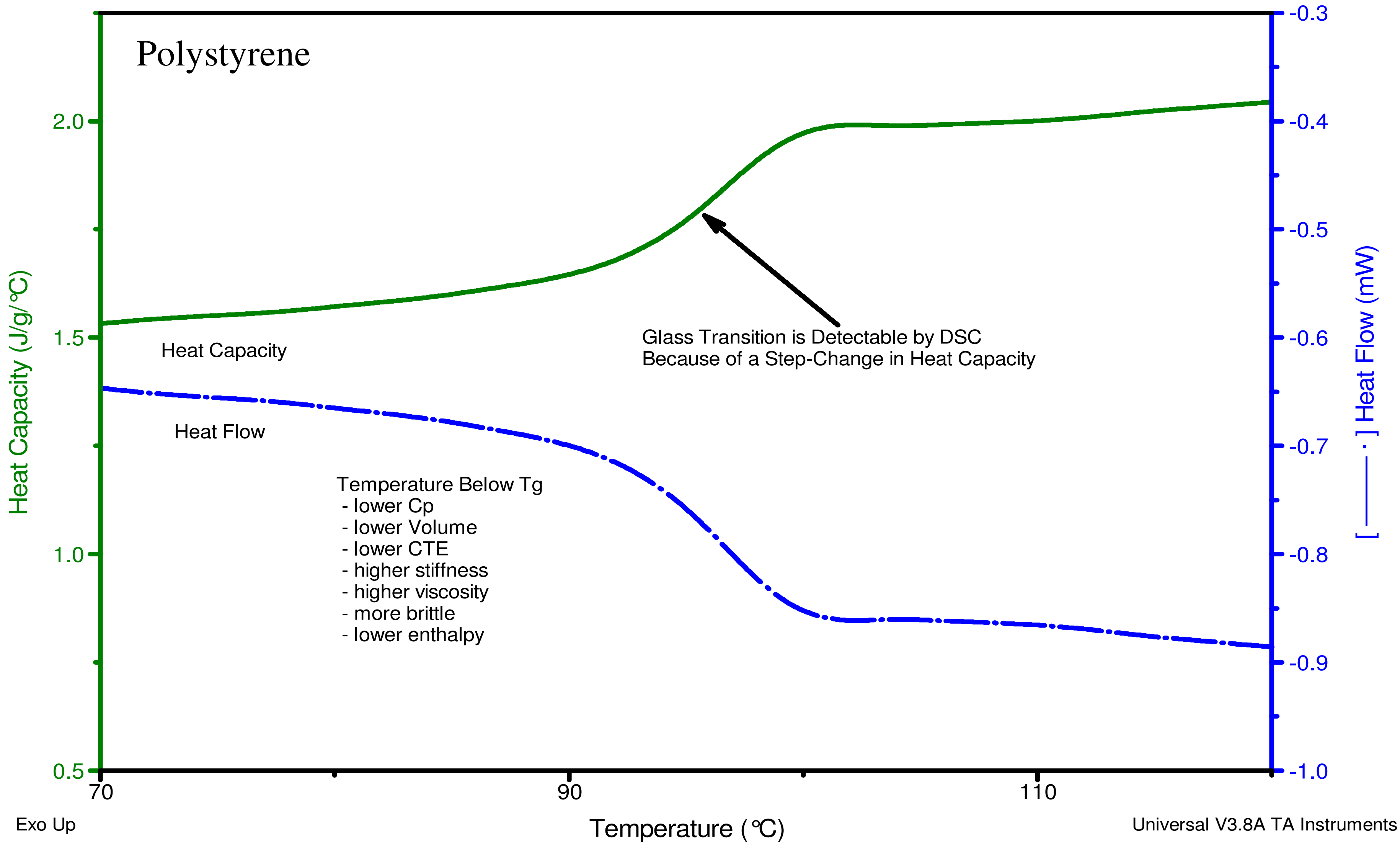
Polystyrene T_g = 100 ° C

"Introduction to Polymer Viscoelasticity," 2nd Edition. Aklonis, John J; MacKnight, William J. Wiley-Interscience

Glass Transitions

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

Heat Flow & Heat Capacity at the Tg



Shifts in the Baseline Due to Tg

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

Measuring/Reporting Glass Transitions

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

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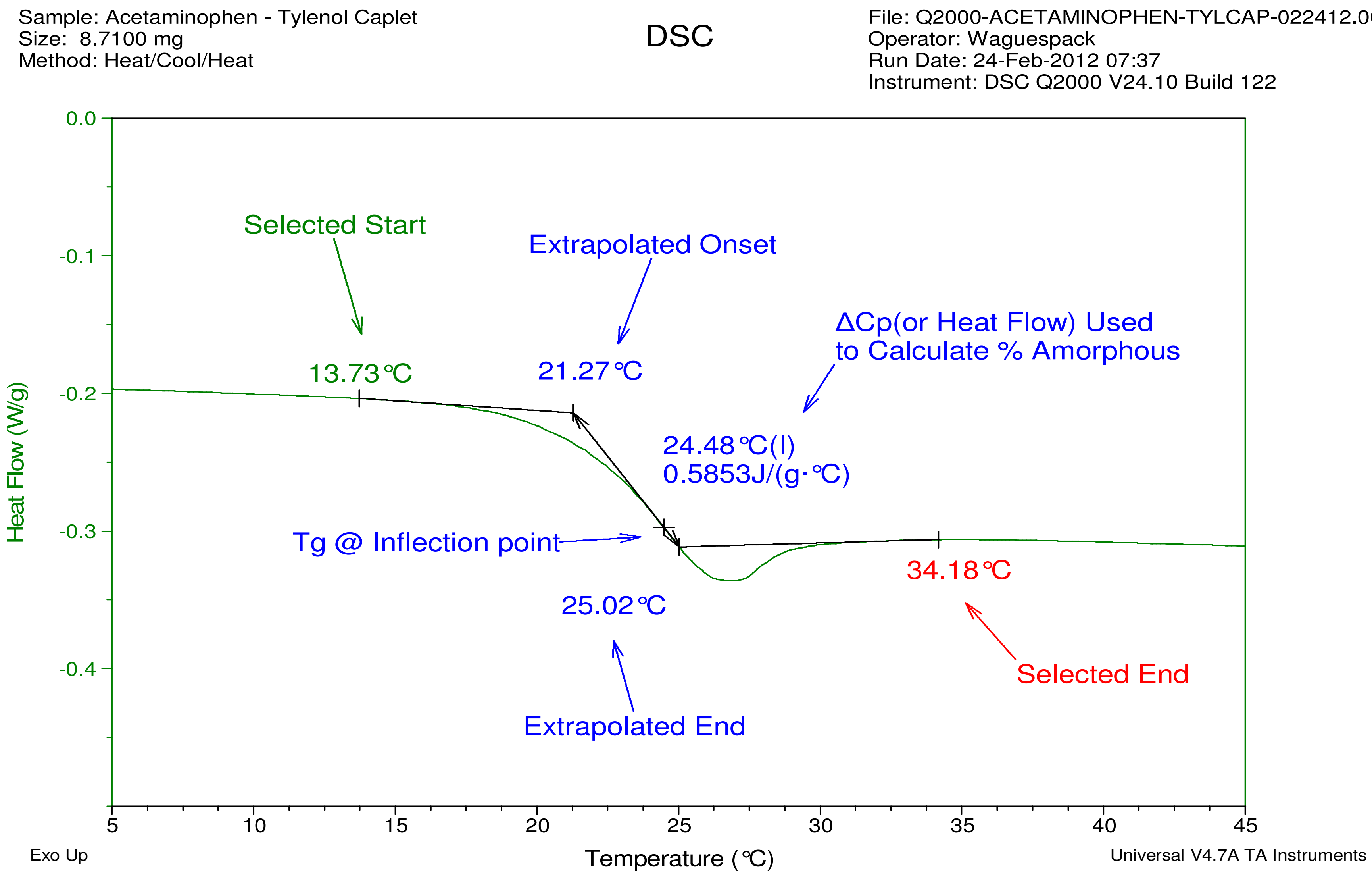
DSC Tg Analysis – Inflection



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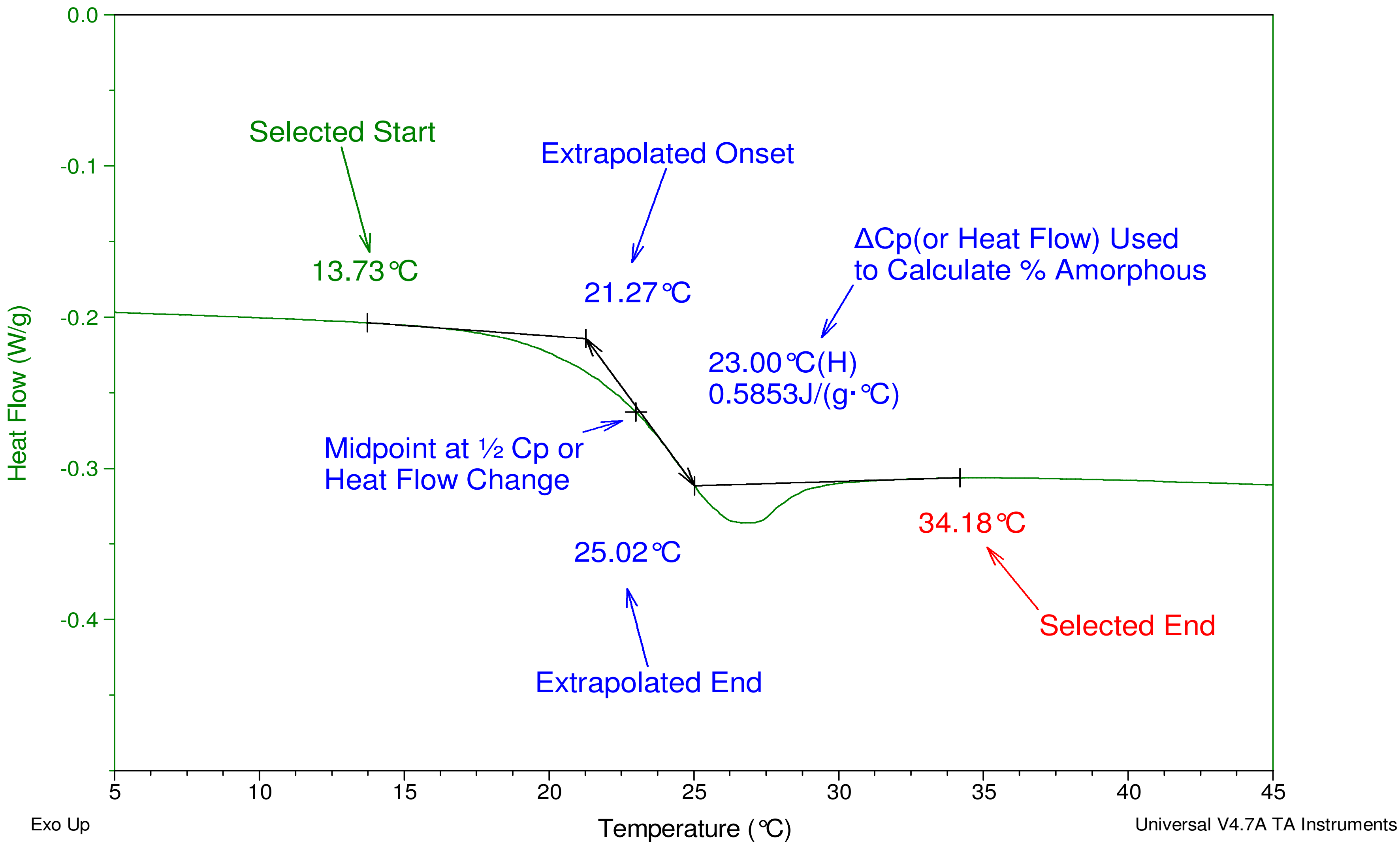
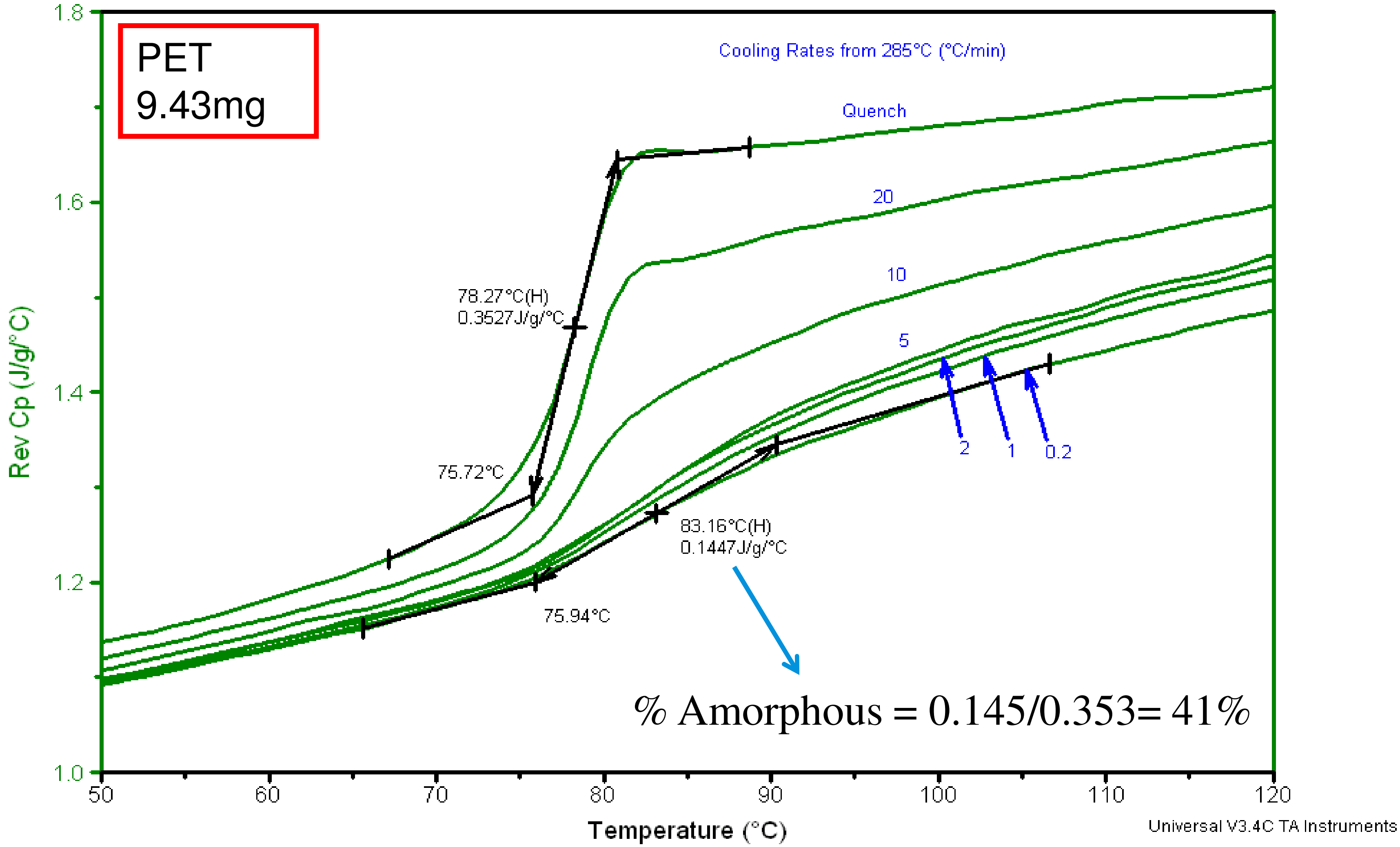
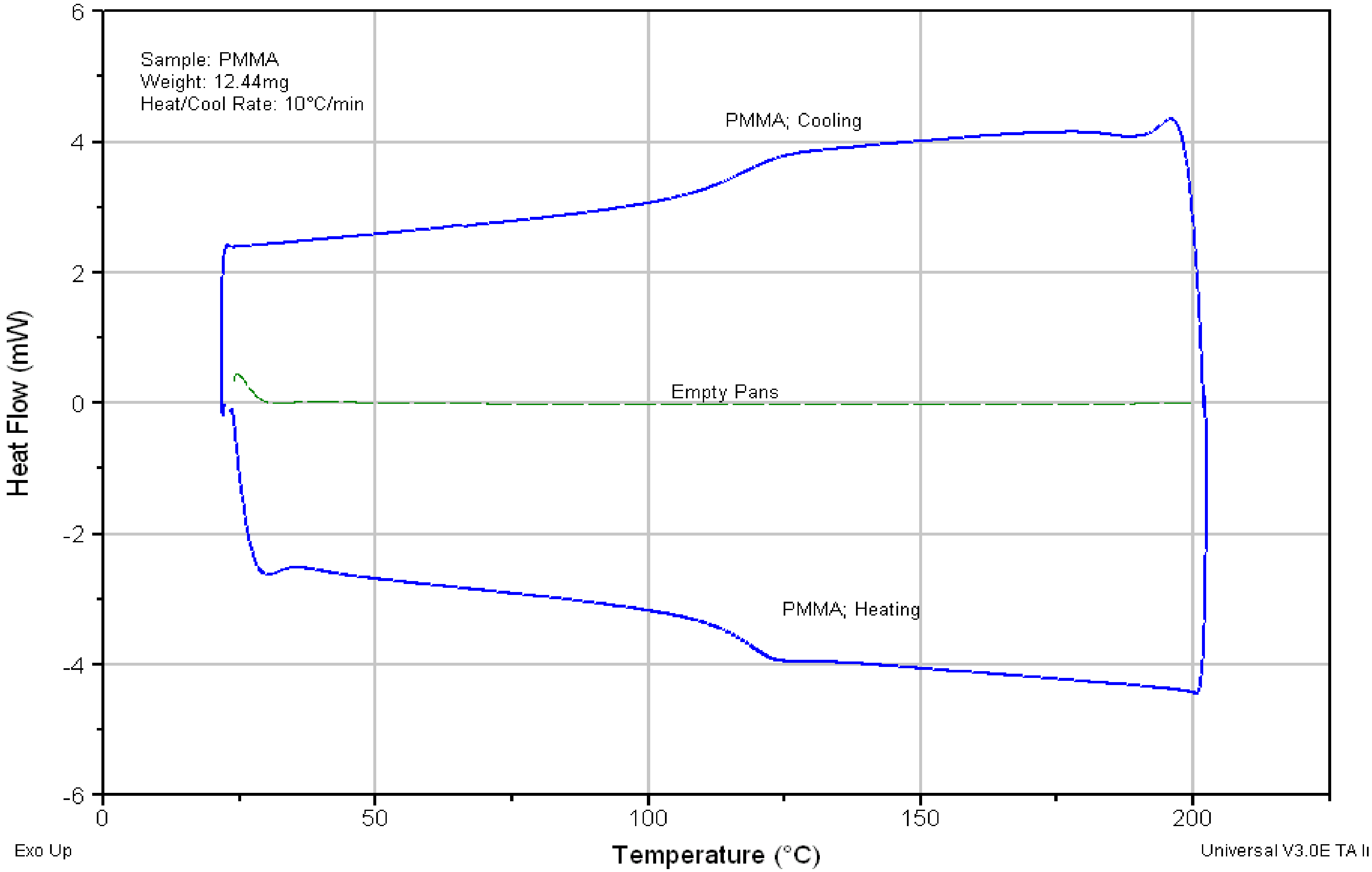
DSC Tg Analysis – Half-Height



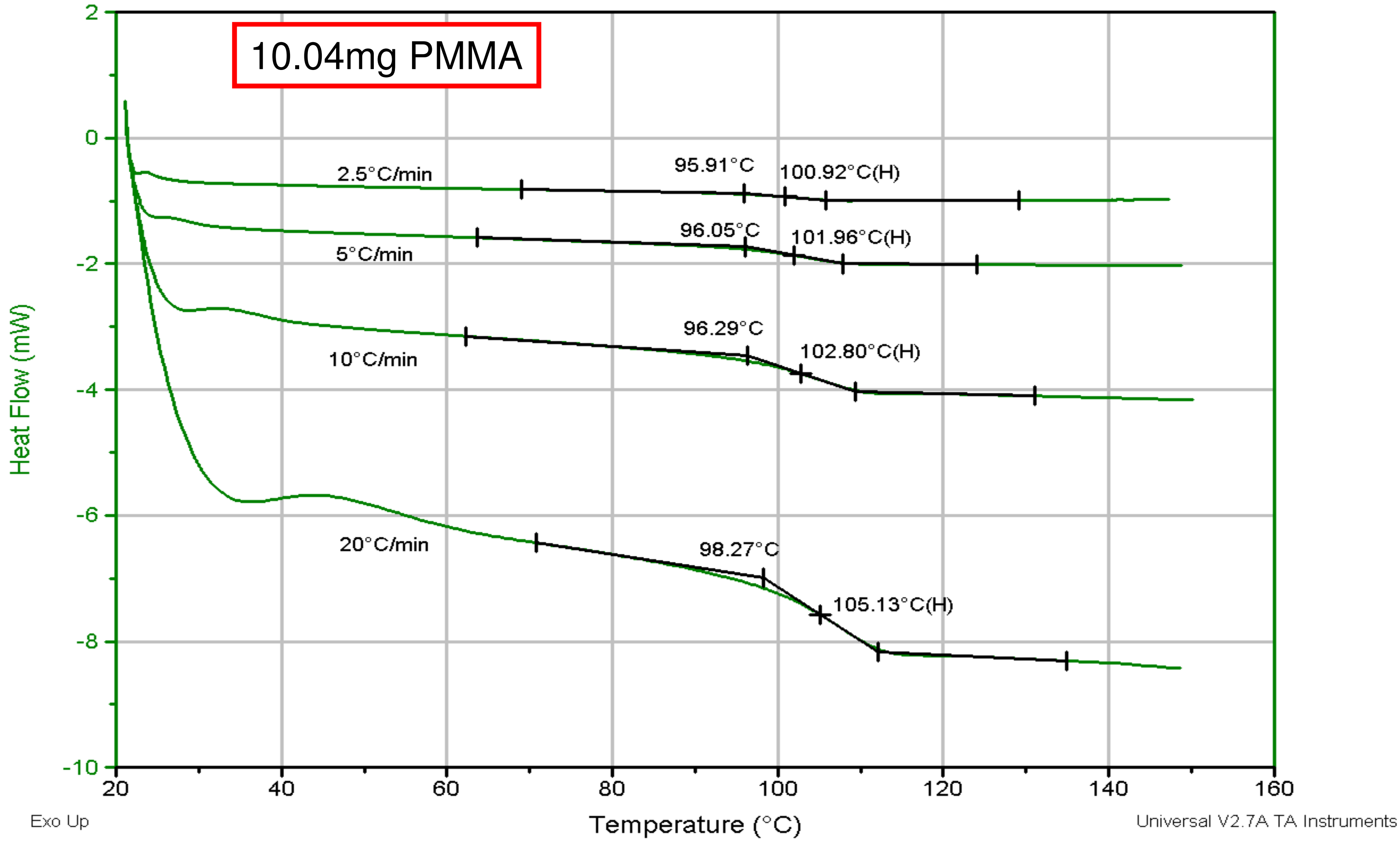
Step Change in Cp at the Glass Transition



A Glass Transition is Reversible



Effect of Heating Rate on the Tg



Effect of Heating Rate on the Tg

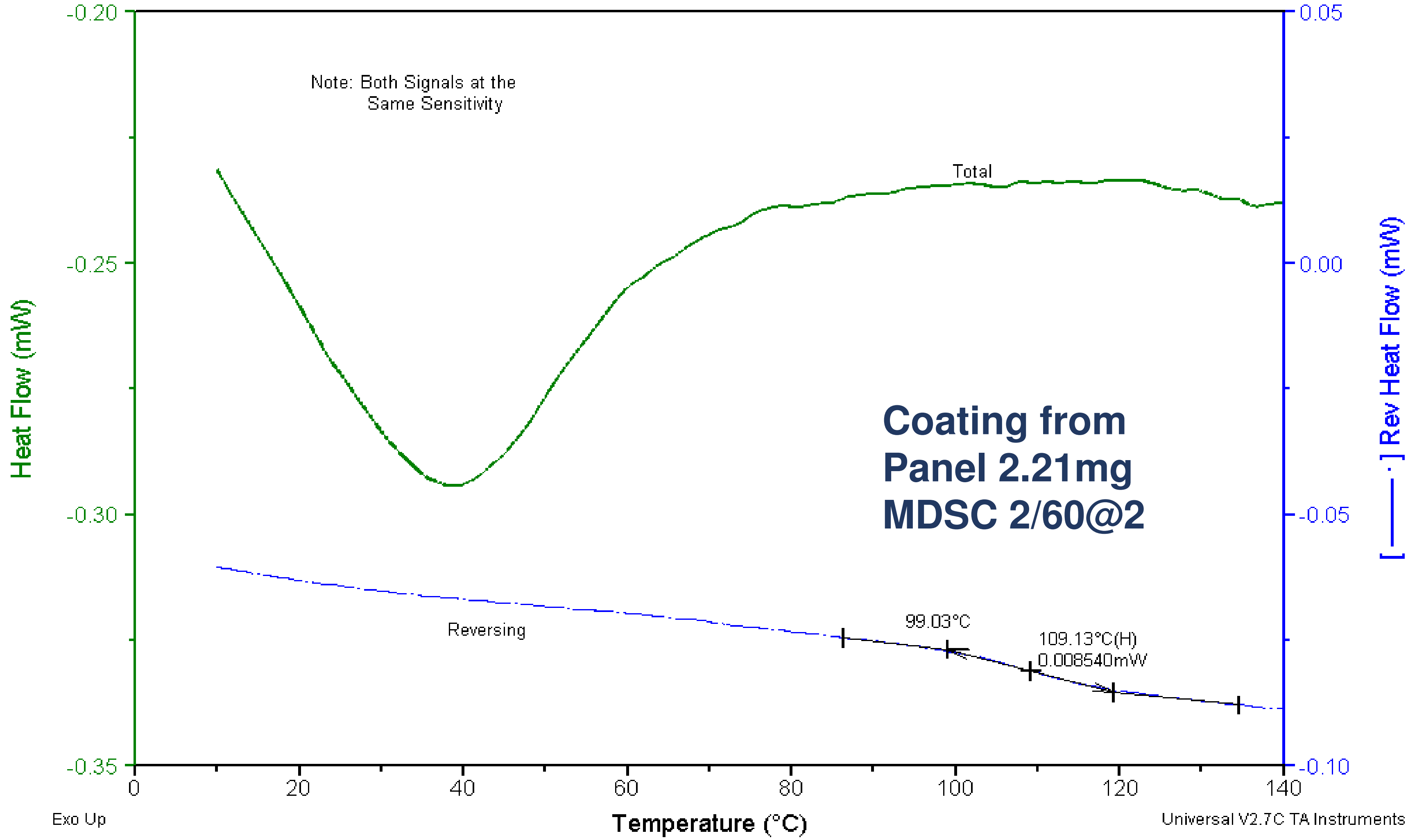
Heating Rate (°C/min)	Heat Flow @ 80°C	Tg Onset (°C)	Tg Midpoint (°C)	½ Width of Tg (°C)
2.5	-0.84	95.9	100.9	5.0
5.0	-1.66	96.0	102.0	6.0
10.0	-3.31	96.3	102.8	6.5
20.0	-6.62	98.3	105.1	6.8

Glass transition 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

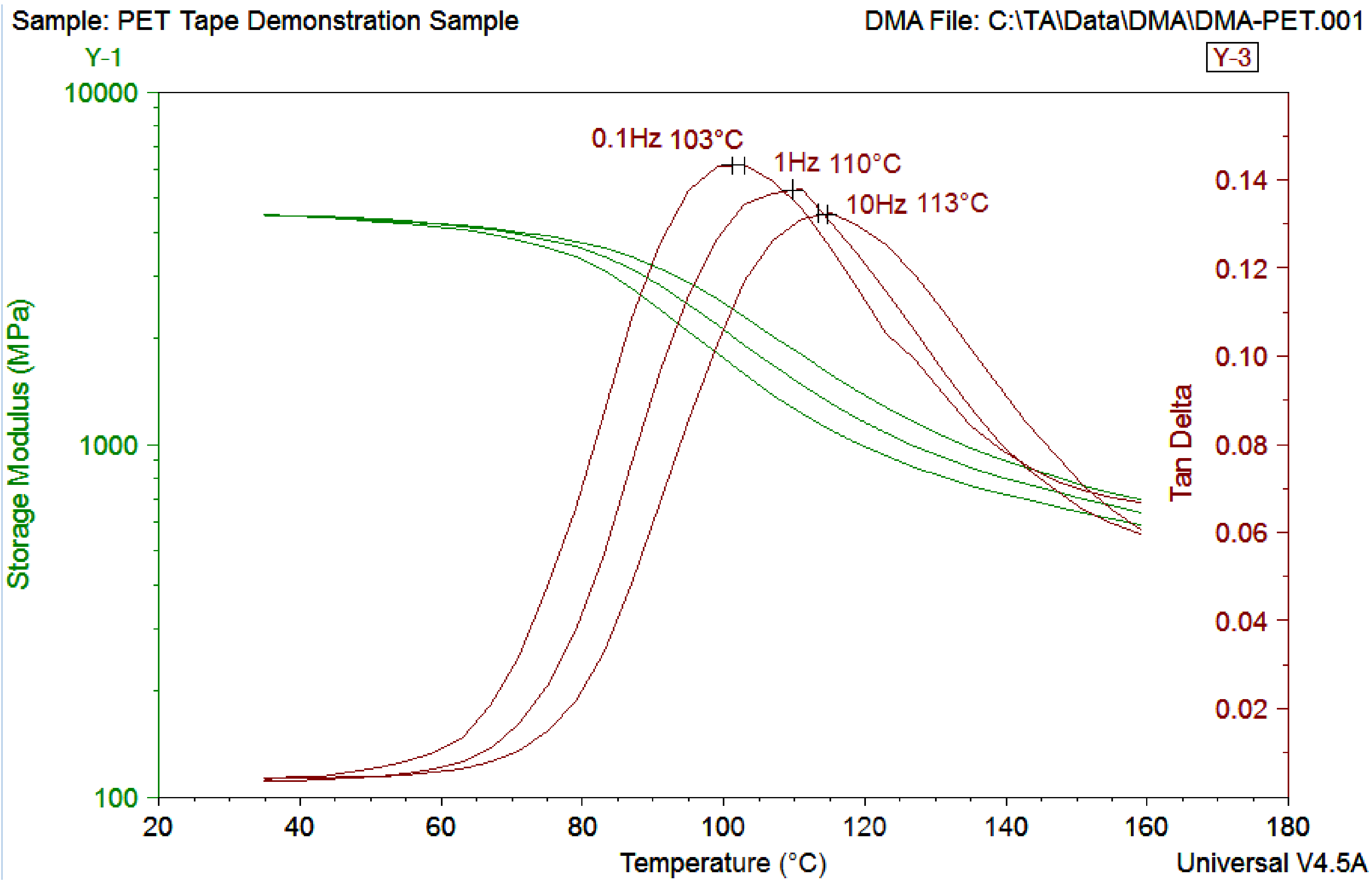
MDSC® of Weak Tg



How does modulated DSC work?

- MDSC applies a changing heating rate on top of a linear heating rate in order measure the heat flow that responds to the changing heating rate
- In MDSC, the heat flow is still given by the equation: $\frac{dH}{dt} = Cp\frac{dT}{dt} + f(T, t)$
- But: $$\frac{dT}{dt} = \beta + A_T\omega\cos(\omega t)$$
    - dT/dt = instantaneous heating rate (°C / min)
    - β* = underlying heating rate (°C / min)
    - A_T* = modulation amplitude (°C)
    - ω* = **angular frequency** = 2π / Mod period (min^{-1})
    - t = experiment time (min)

DMA: Effect of Frequency on Tg



The Effect of Test Frequency on Tg

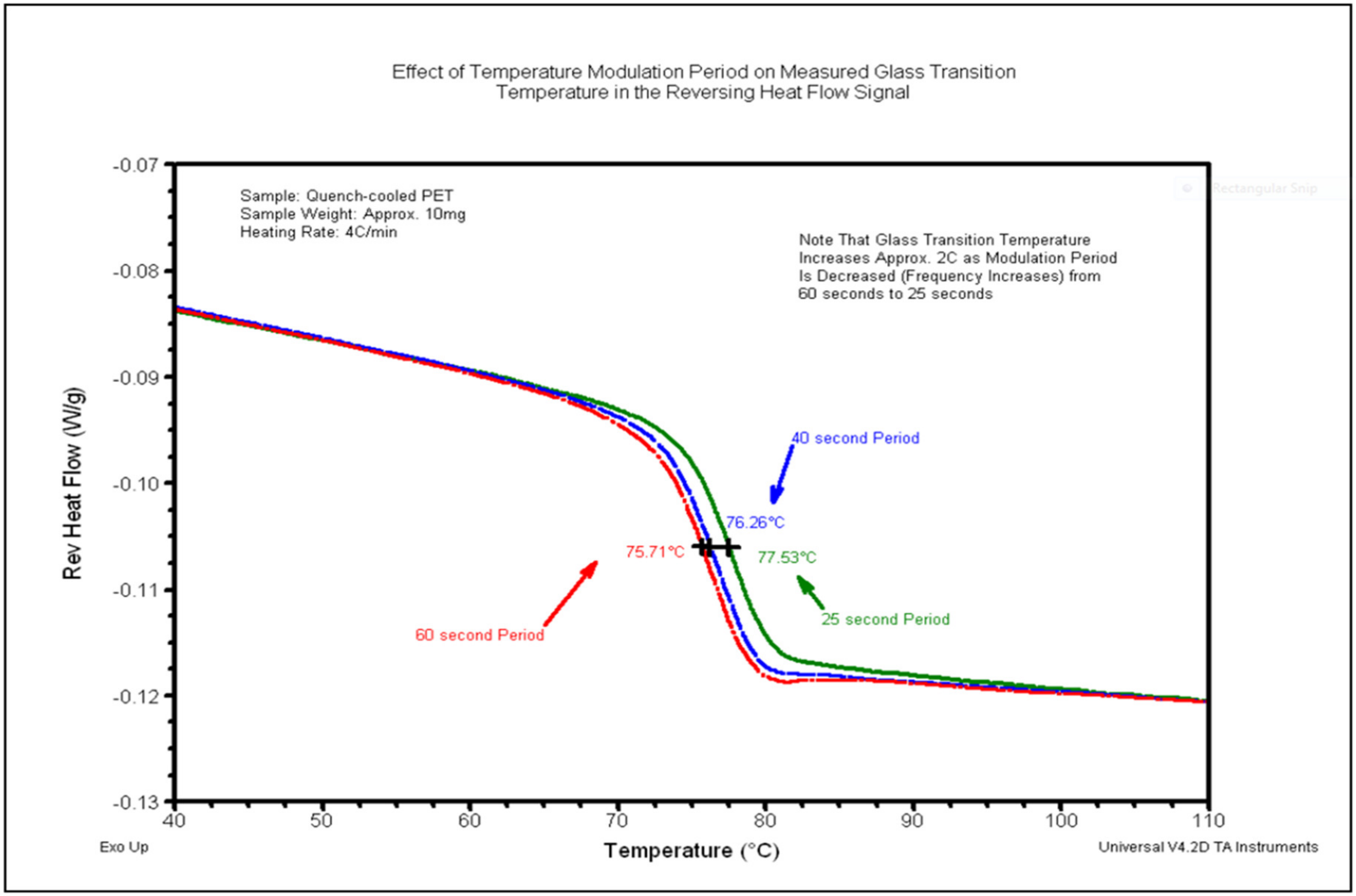
- The glass transition is a kinetic transition. It is therefore influenced strongly by the frequency of the test. The T_g is a molecular relaxation that involves cooperative segmental motion.

- Because the *RATE* of segmental motion depends on temperature, as the frequency increases, the relaxations associated with the T_g can only happen at higher temperatures.

- In general, increasing the frequency will
  - Increase the Tg
  - Decrease the intensity of tan δ or loss modulus
  - Broaden the peak
  - Decrease the slope of the storage modulus curve in the region of the transition.

Turi, Edith, A, Thermal Characterization of Polymeric Materials, Second Edition, Volume I., Academic Press, Brooklyn, New York, P. 529.

MDSC: Effect of Frequency on Tg

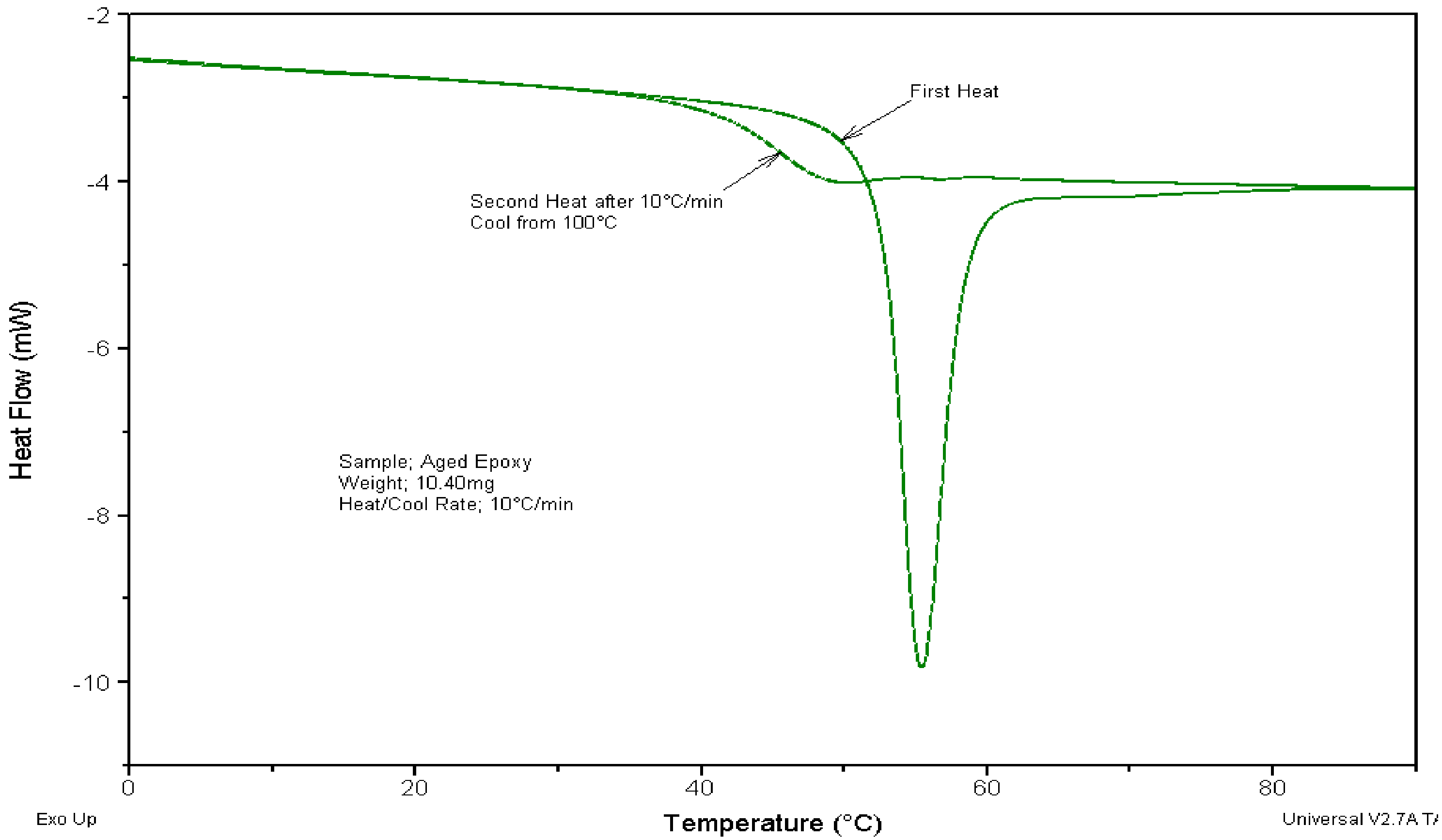


What Affects the Glass Transition?

- 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

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.

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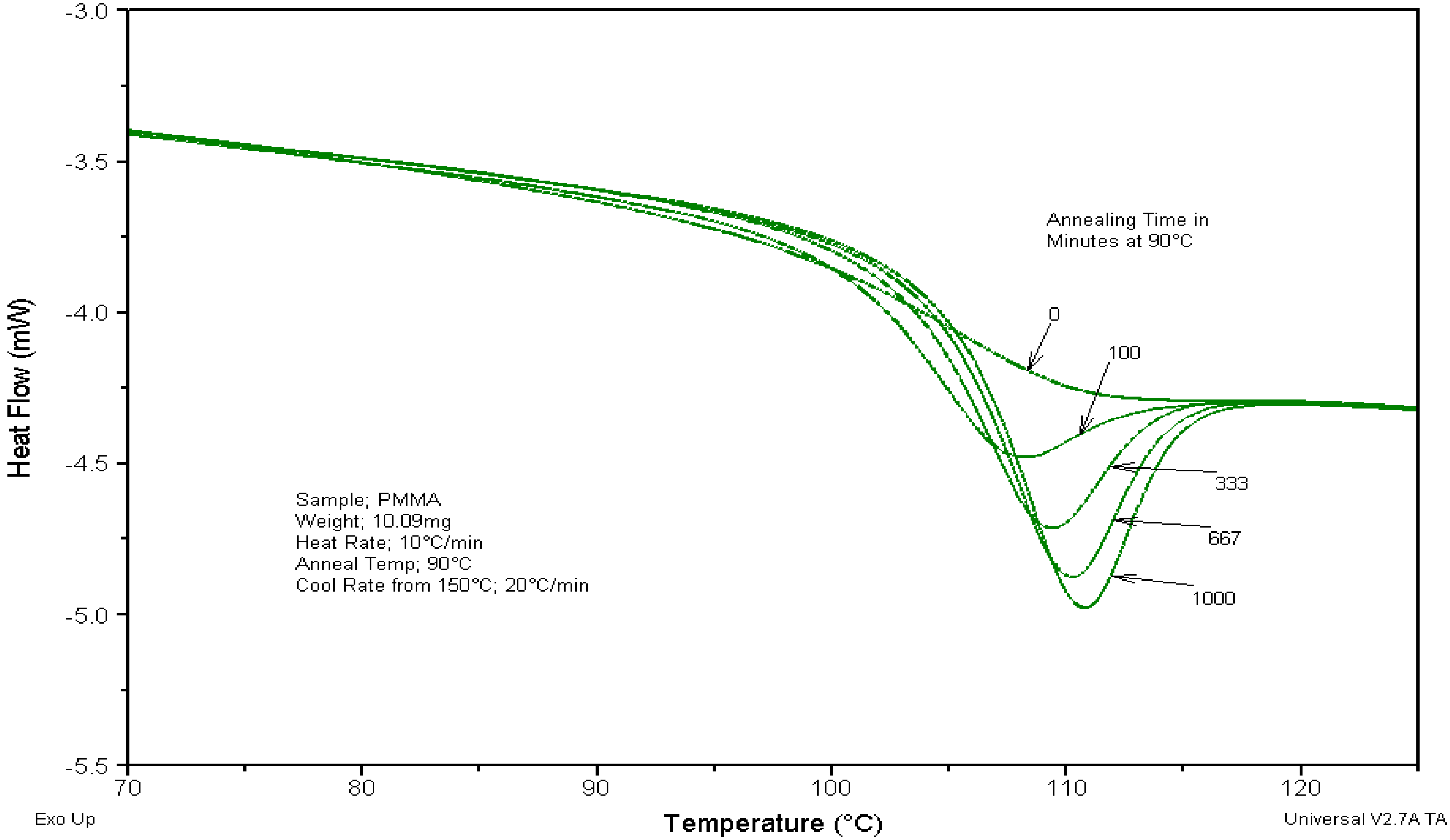
Enthalpic Relaxation and Recovery

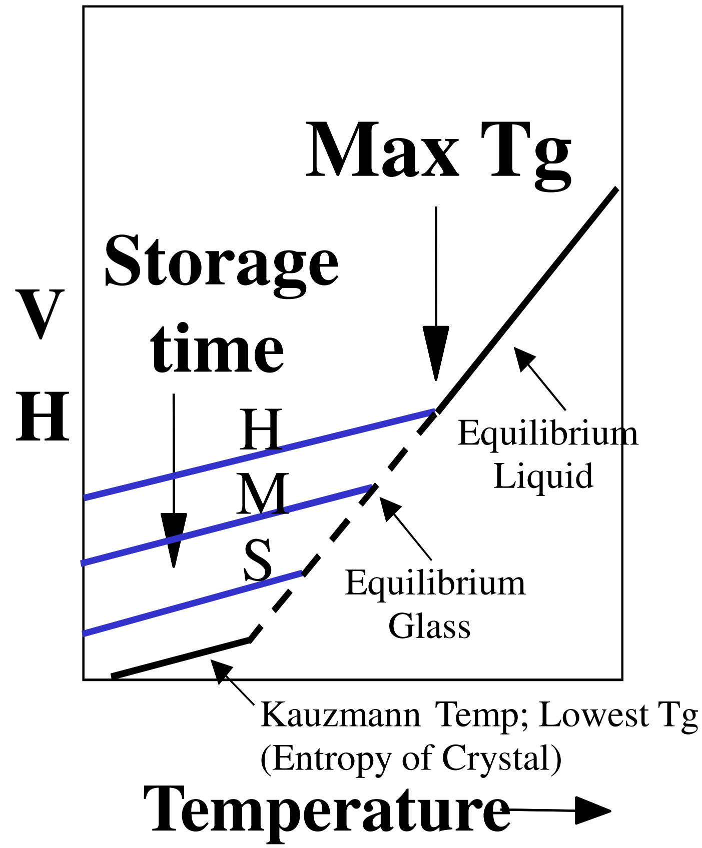
- Enthalpic Relaxation
  - The process of a meta-stable glass relaxing towards equilibrium at a temperature below Tg
  - Occurs as the sample is being cooled to temperatures below Tg
  - Occurs as the sample is being stored at temperatures below Tg
- Enthalpic Recovery
  - The recovery of energy (J/g) 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



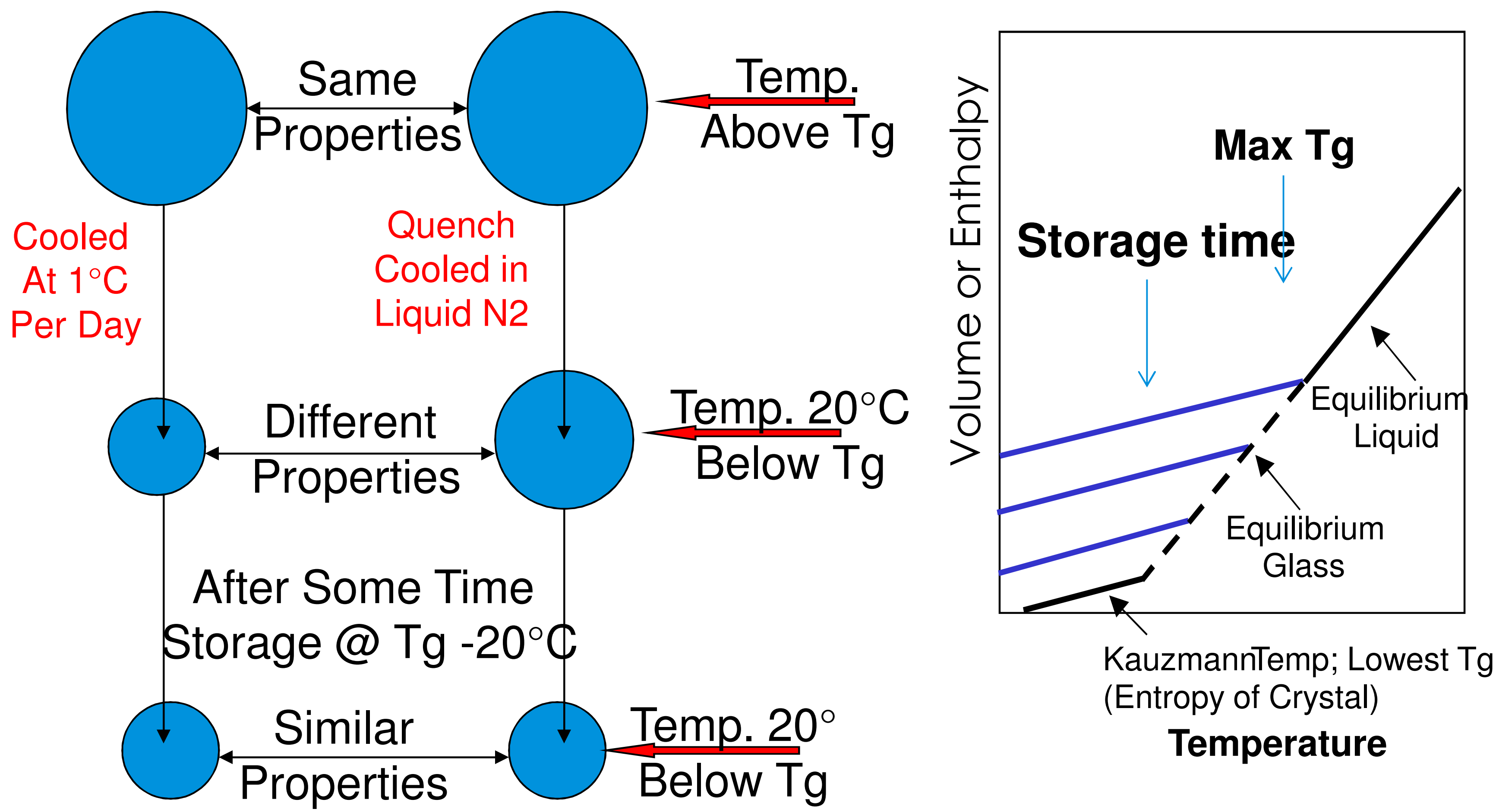
Effect of Aging on Amorphous Materials

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

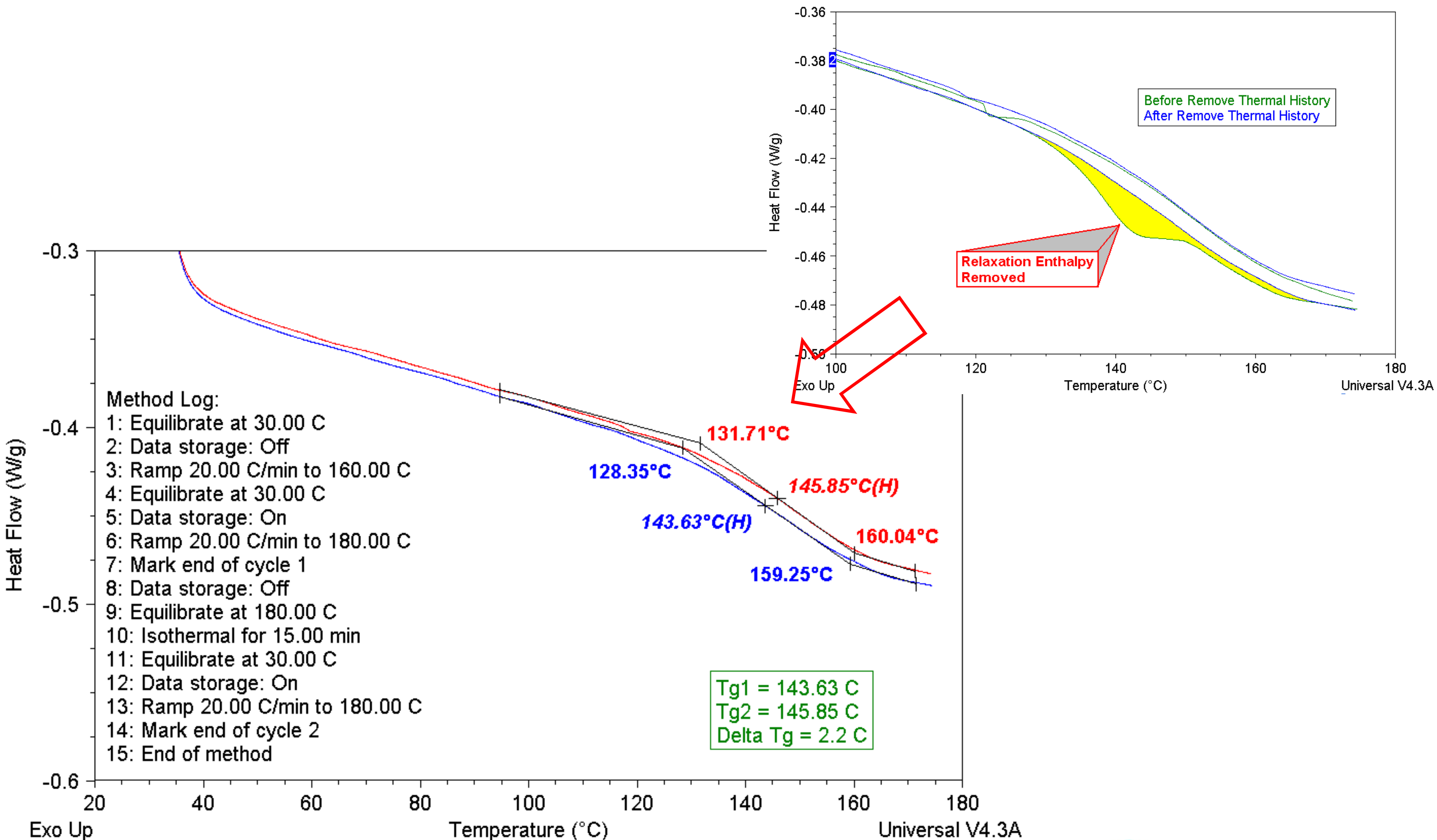


Where H = High relative cooling rate
M = Medium relative cooling rate
S = Slow relative cooling rate

Effect of Aging on Amorphous Structure



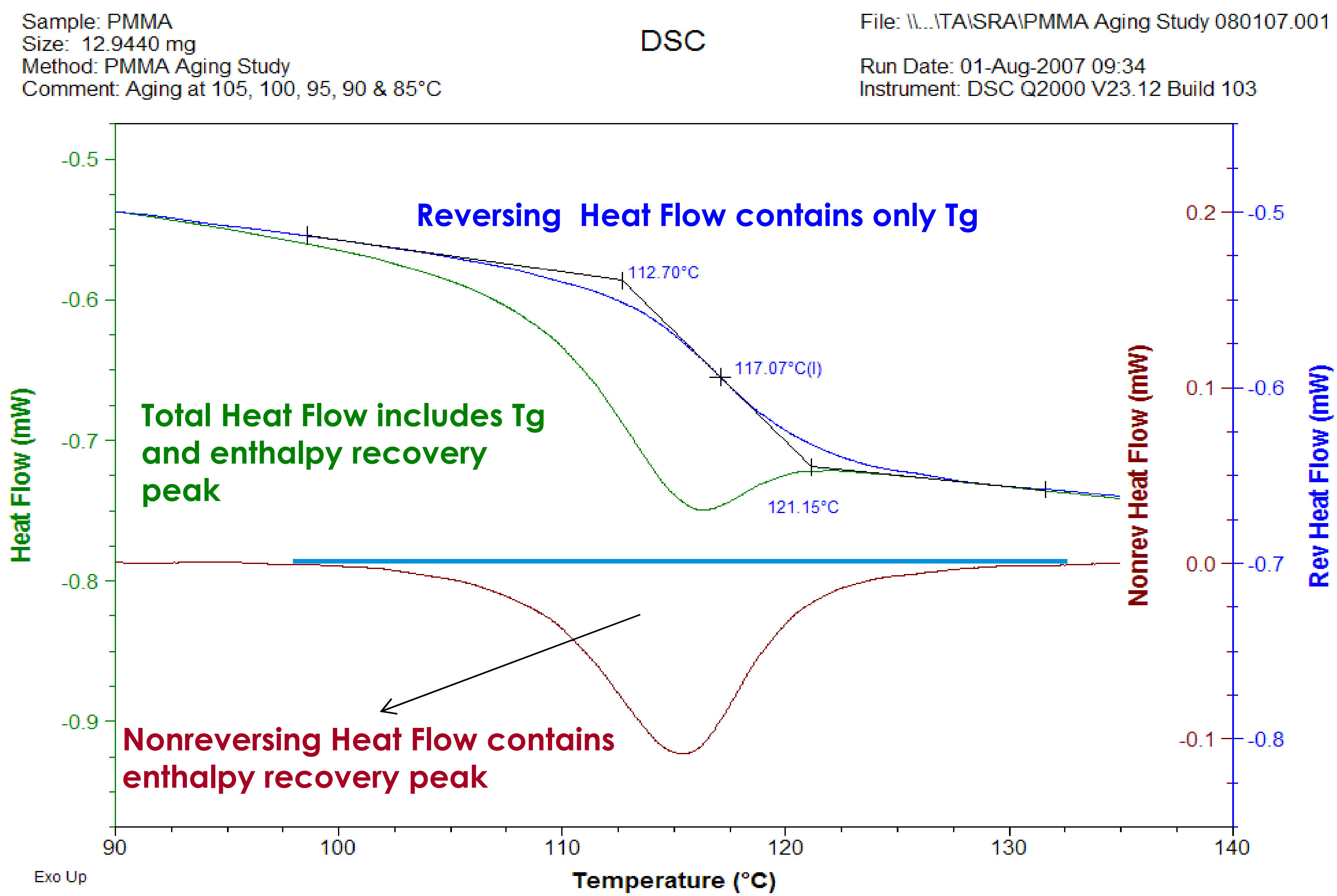
剖析 ΔTg 的爭議 - 革新DSC實驗手法的結果



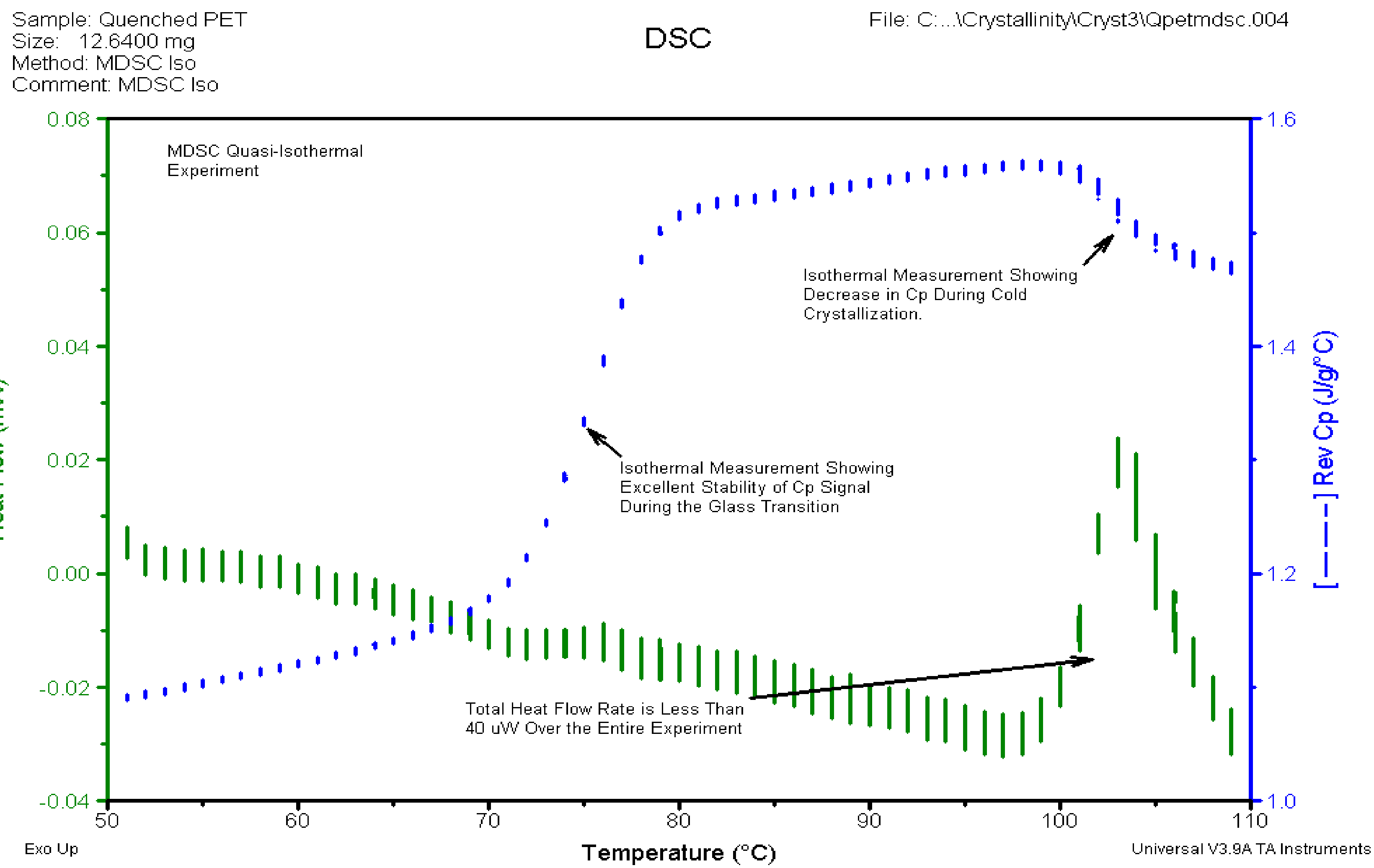
Importance of Enthalpic Relaxation

- 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.

MDSC Separation of Enthalpy Recovery Peak



Quasi-Isothermal MDSC : Cp Change



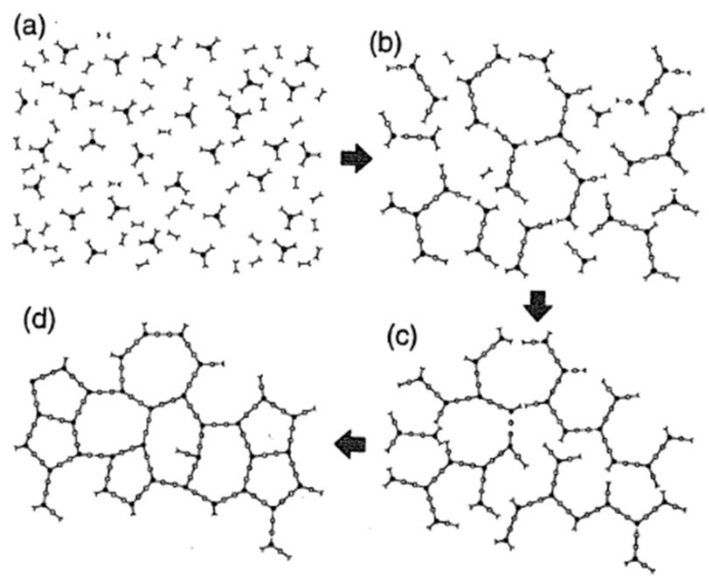
Thermosets

Thermosetting Polymers

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

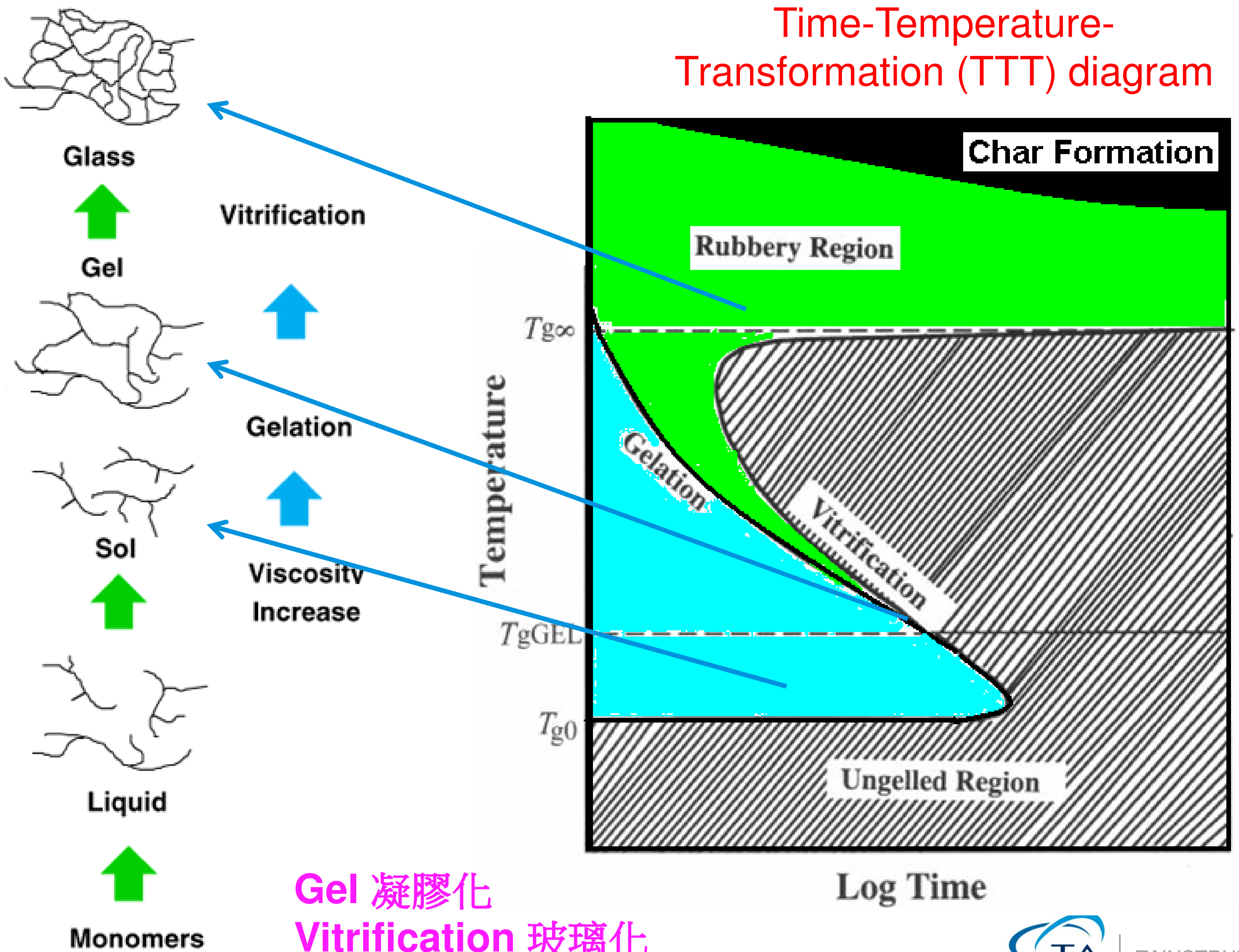
Thermosetting polymers react (cross-link) irreversibly. A+B will give out heat (exothermic) when they cross-link (cure).

A + B → C



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

Tg Increasing with Conversion Growth, TTT Plot



Gel 凝膠化
Vitrification 玻璃化

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.

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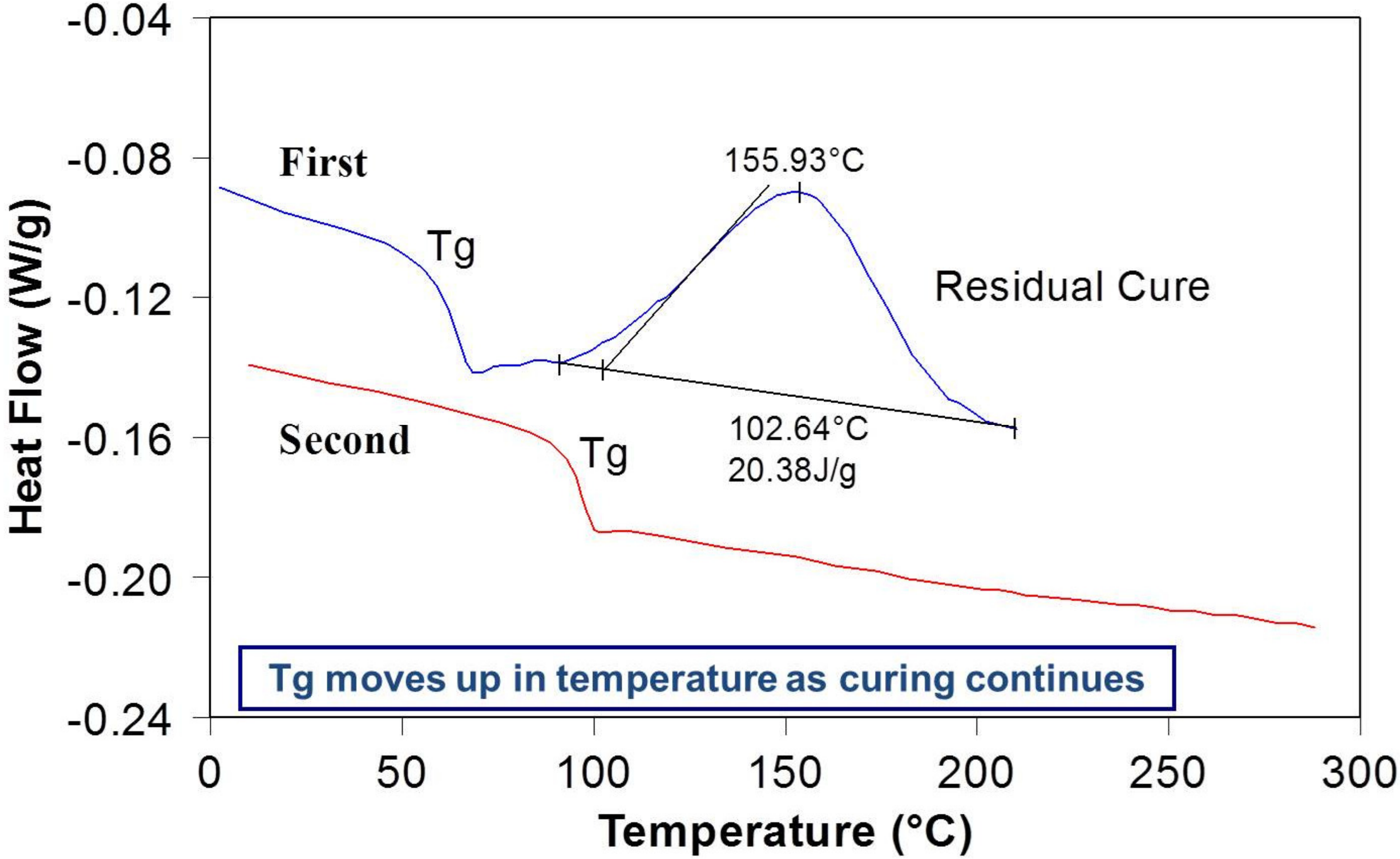
Comparison of First and Second Heats



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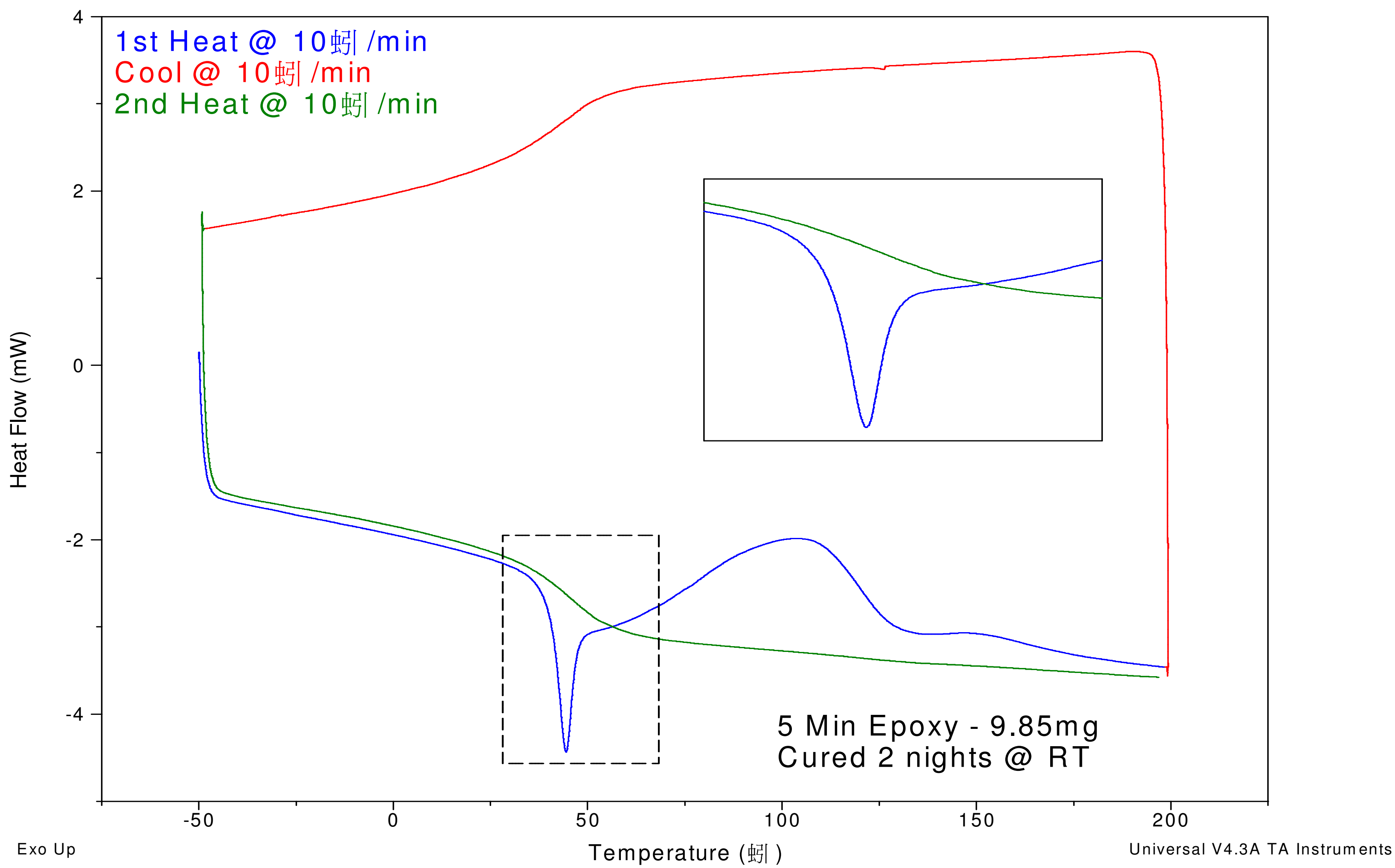
Epoxy Cured 48 Hours: Heat Cool Heat



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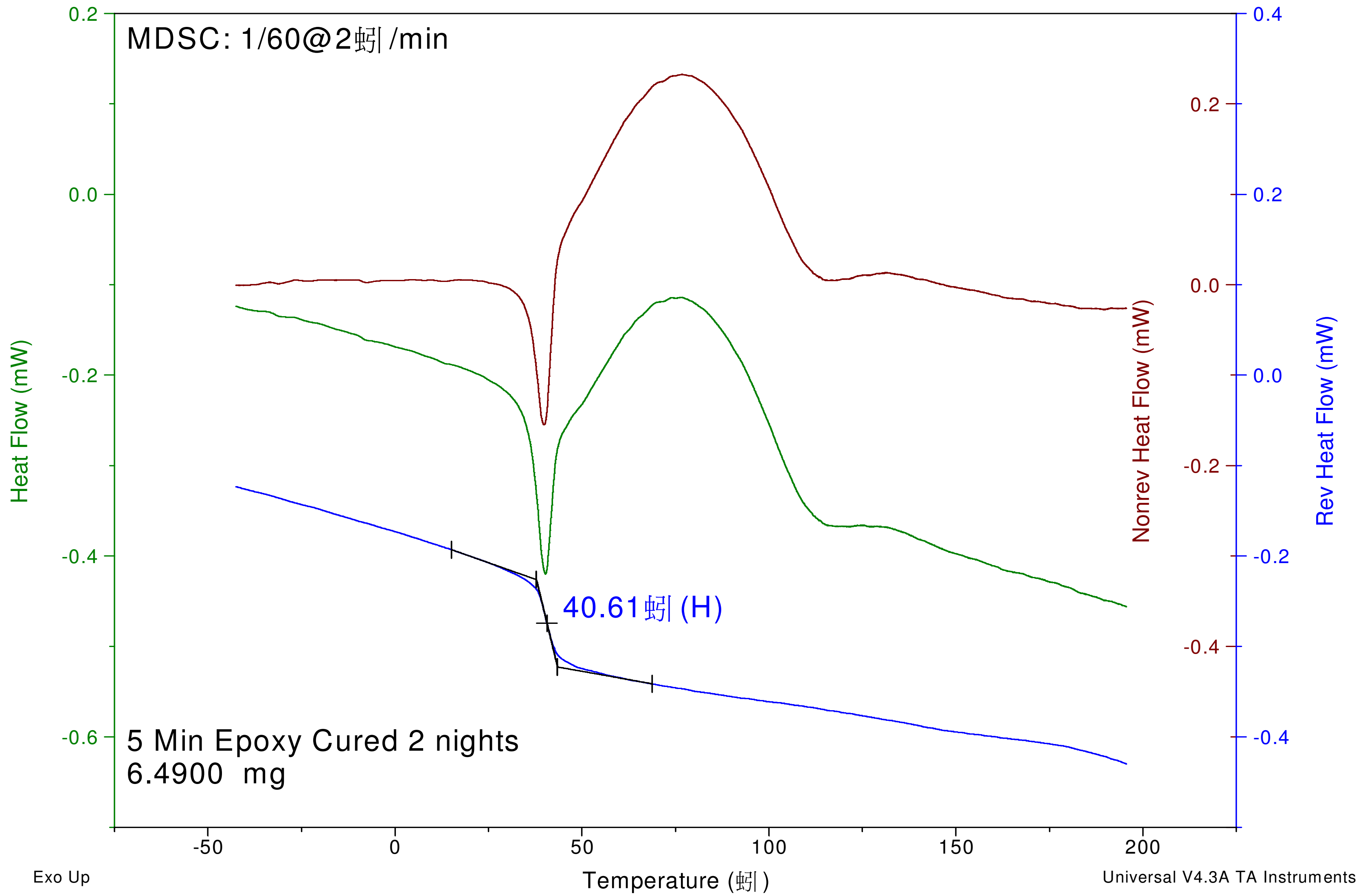
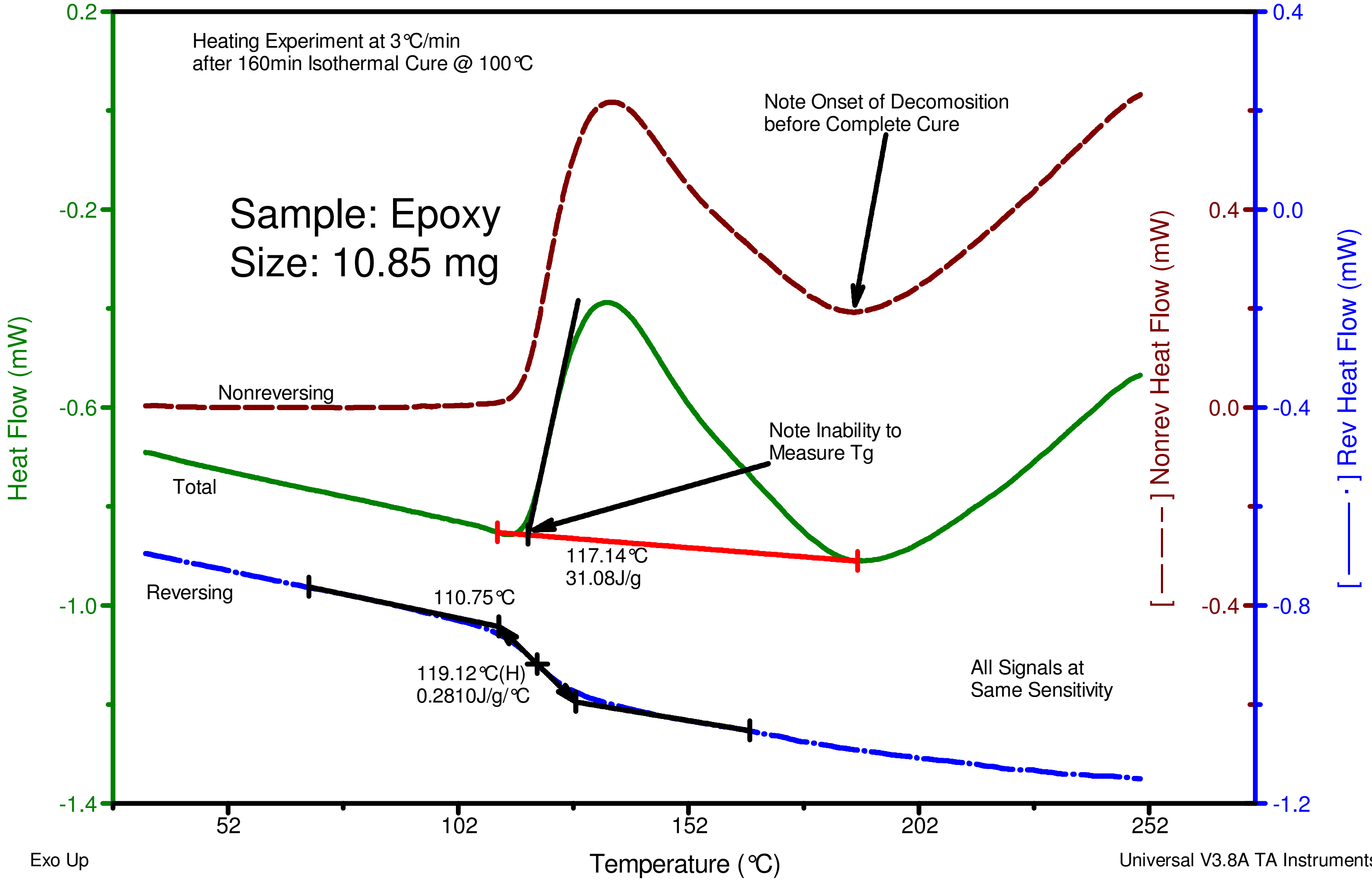
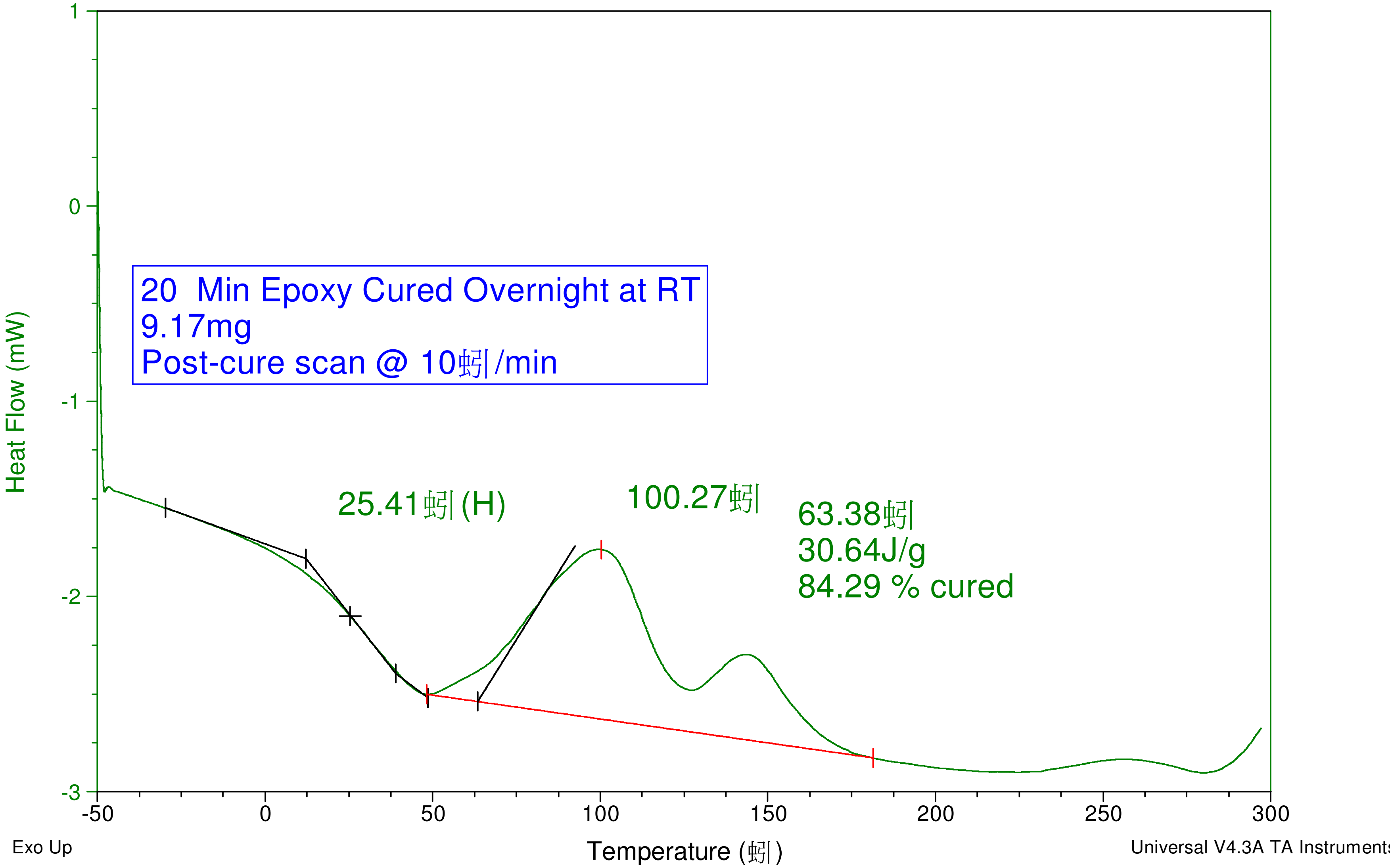
Rev-Heat Flow Easily Shows Tg



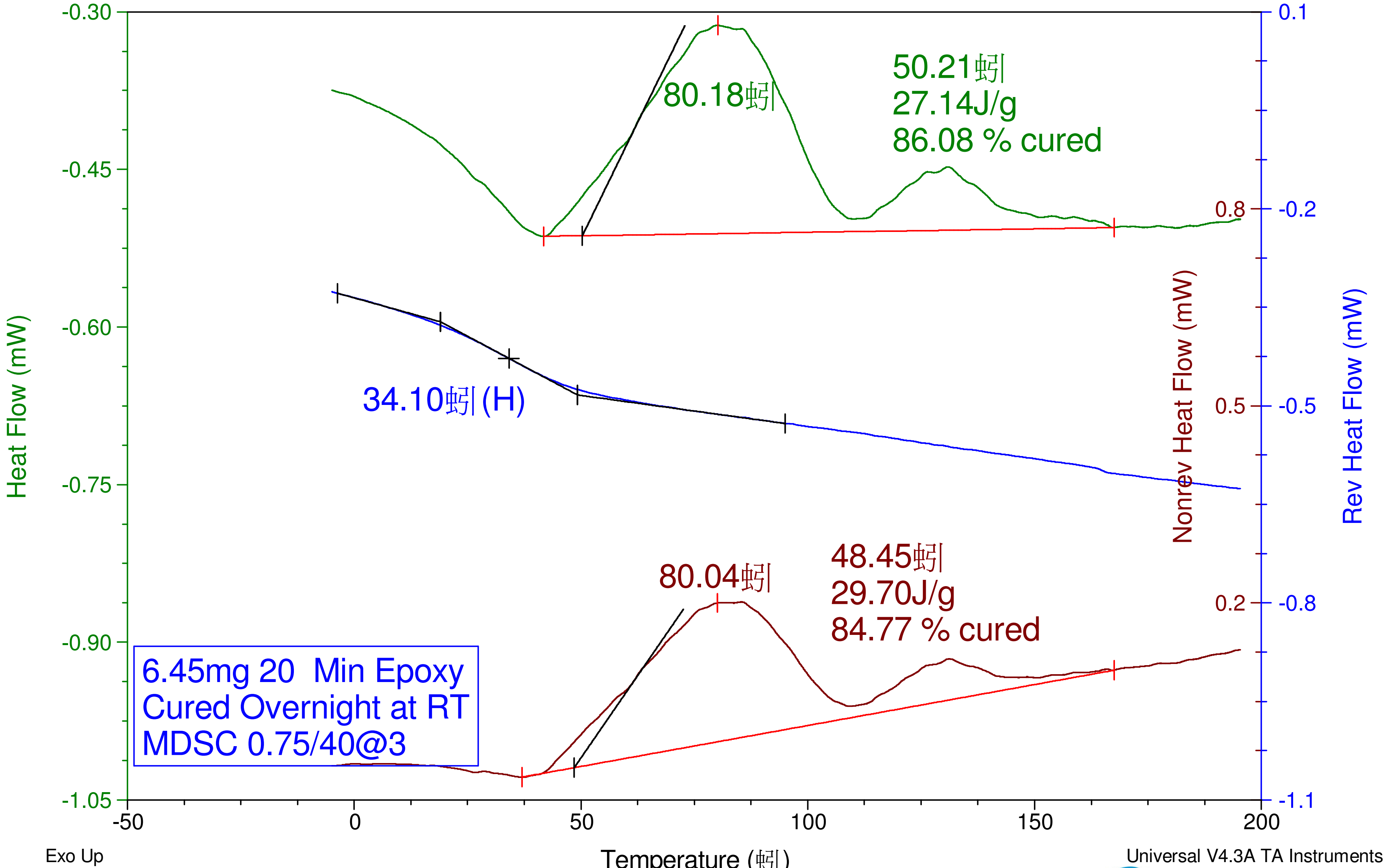
Advantage of MDSC for Post Cure Scan



Epoxy Cured Overnight at Room Temp



Epoxy Cured Overnight at Room Temp - MDSC



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Use of Kinetic modeling for characterization of curing reactions

- Predict how long a reaction takes to go to completion
- Optimize polymerization, curing
- Quantify parameters that characterize time-temperature-dependent process behavior under conditions that may not always be experimentally feasible.

Fundamental equation for kinetics

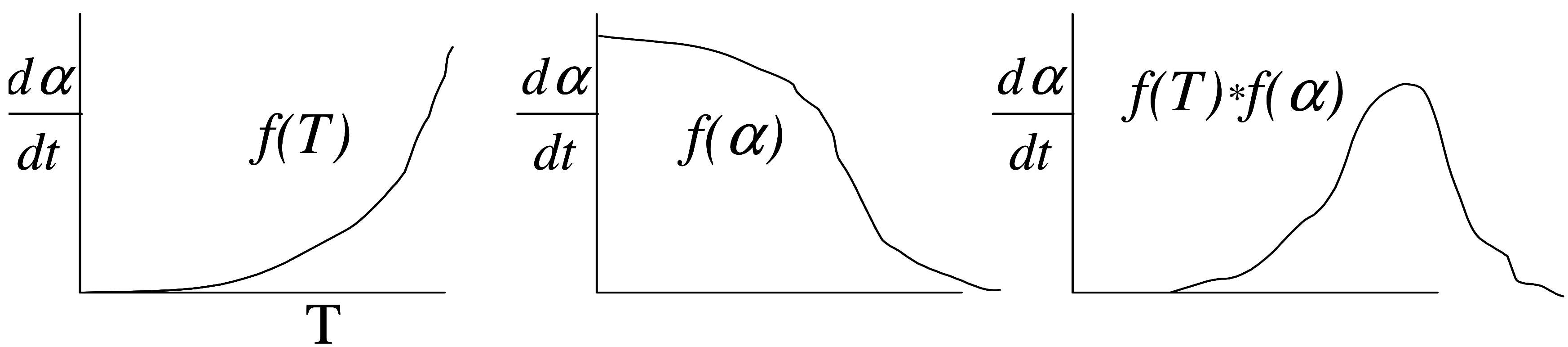
$$\frac{d\alpha}{dt} = f(T) \bullet f(\alpha)$$

α = fraction reacted or converted

$\frac{d\alpha}{dt}$ = reaction rate

$f(T)$ = a function of Temp.

$f(\alpha)$ = a function of α



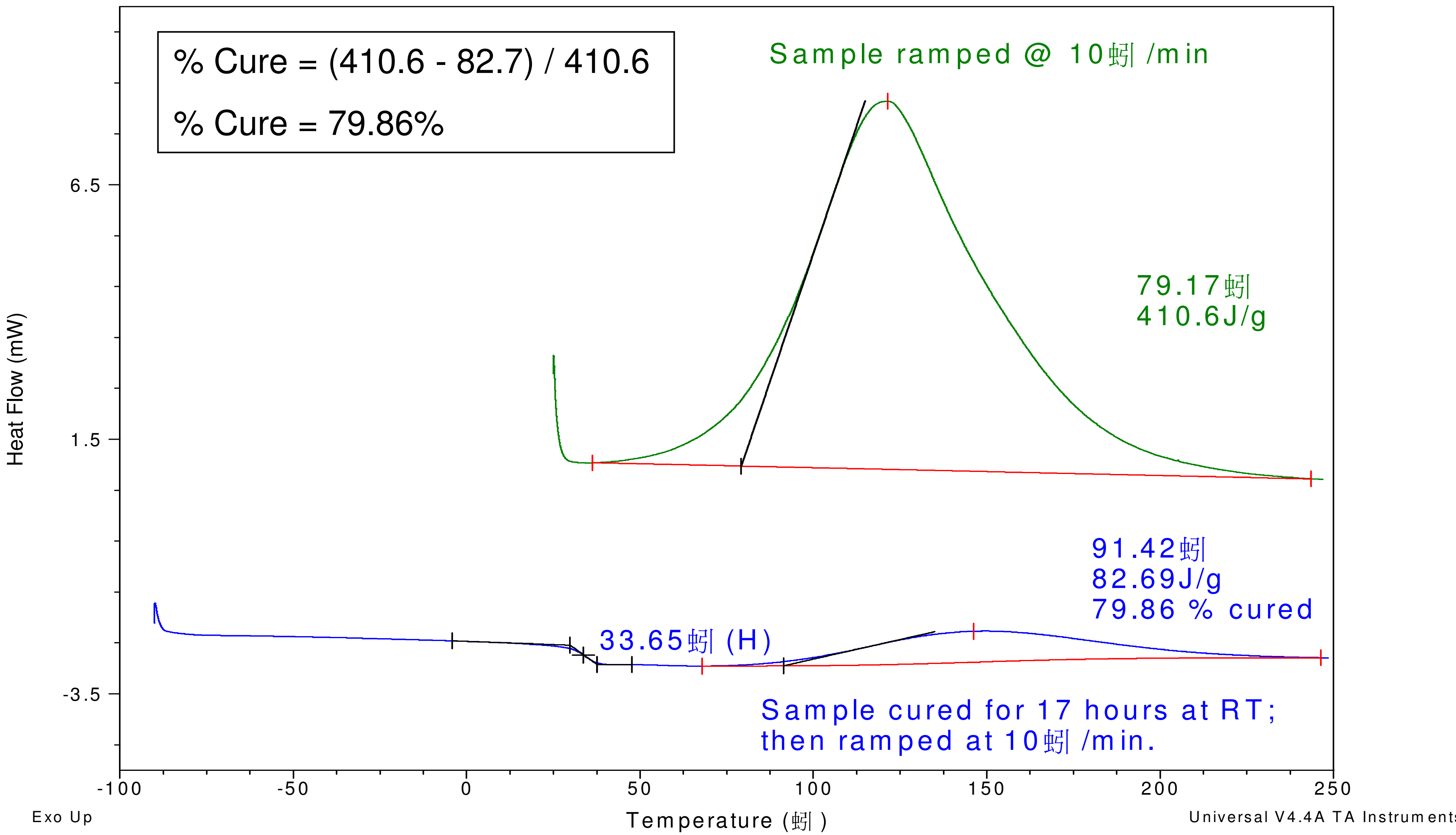
Percent Cure Calculation by DSC

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

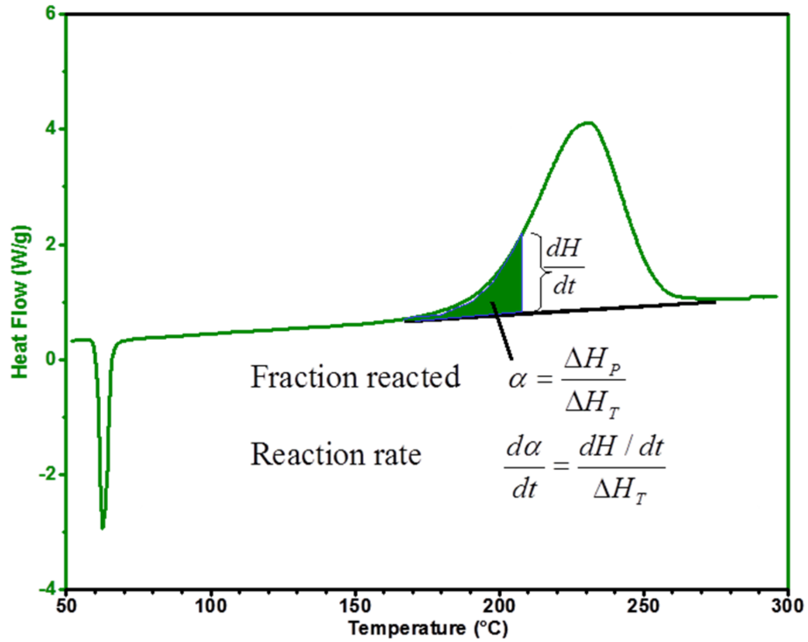
% Cure = 1 - (ΔH Residual Cure / ΔH Full Cure) * 100

% Uncured = (ΔH Residual Cure / ΔH Full Cure) * 100

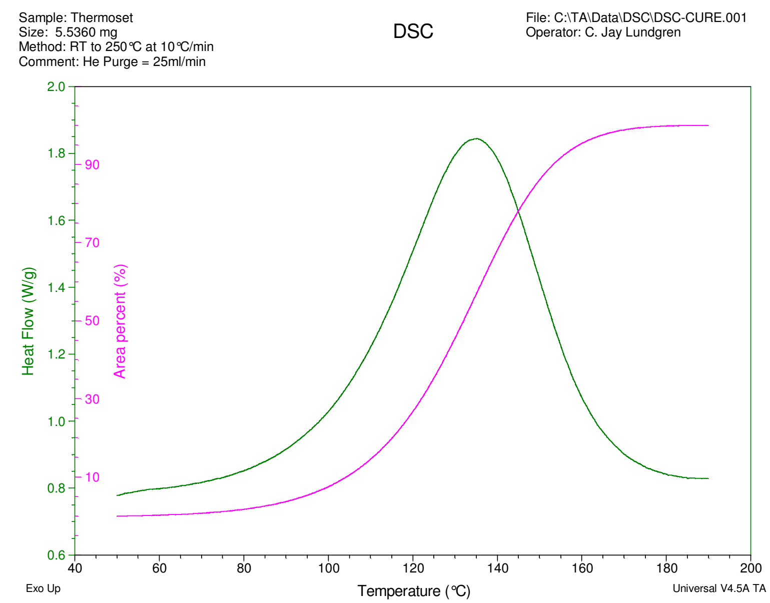
Calculation of % Cure: An Epoxy



Obtaining kinetics information from a DSC experiment

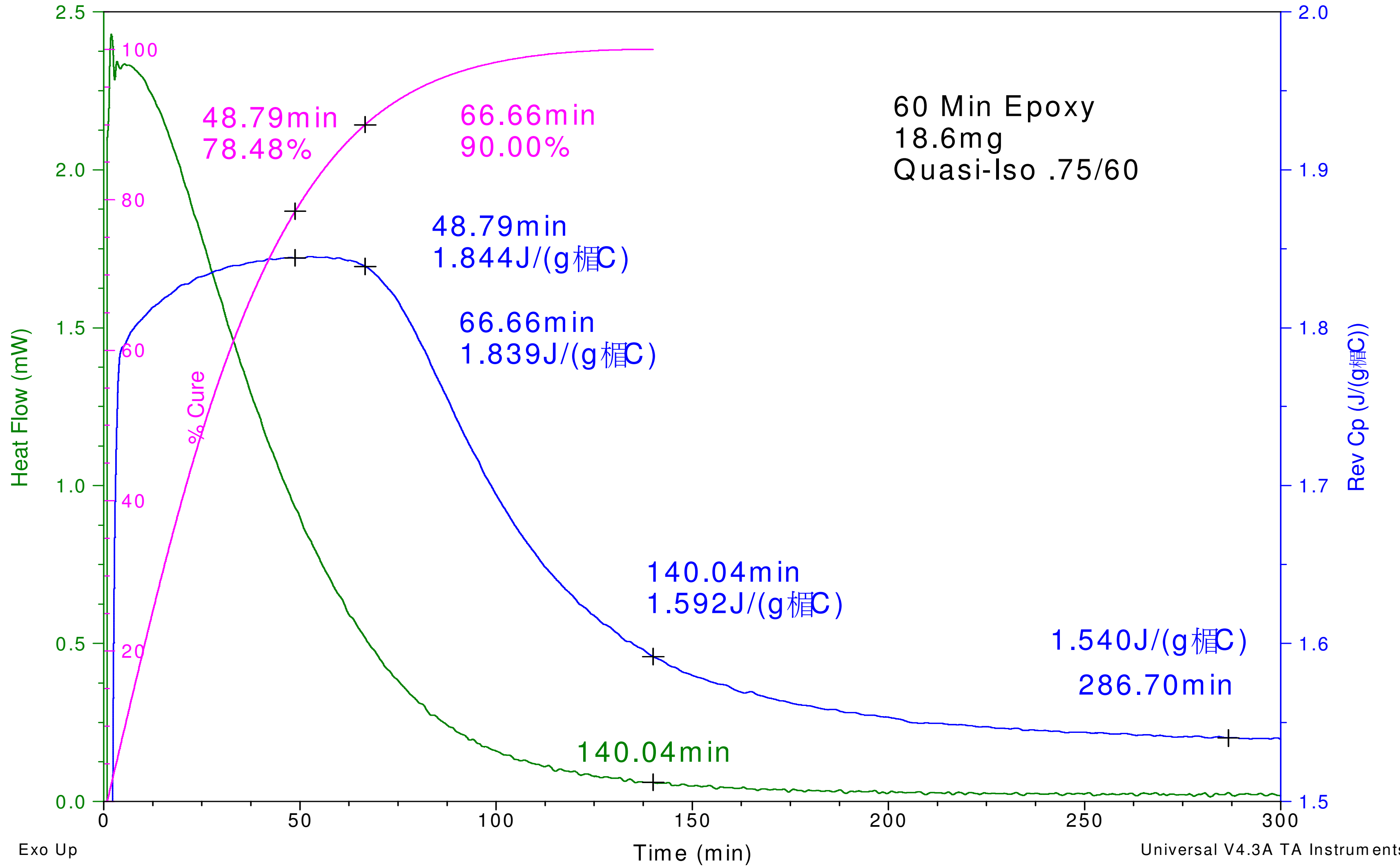


DSC gives us α and dα/dt vs time and temperature



Running integral option provides α as a direct function of time/temperature

Quasi-Isothermal Cure of an Epoxy



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Fundamental equation for kinetics – the temperature factor

- Fundamental equation for kinetics

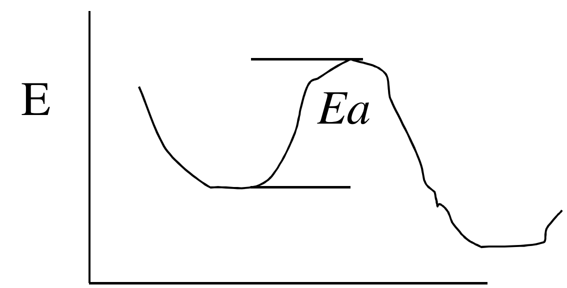
$$\frac{d\alpha}{dt} = \boxed{f(T)} \bullet f(\alpha)$$

- Arrhenius temperature dependence

$$f(T) = Ze^{-Ea/RT}$$

Where Ea is activation energy
Z is the “frequency factor”
R is the gas constant
T in kelvin

- Derived from dilute gas or solution, refined for solids
- Physical significance: Molecules colliding with sufficient kinetic energy to overcome Ea cause a reaction
- Pre-exponential factor, Z, “frequency factor” accounts for steric effects



Selection of appropriate model – the "α" factor

- Fundamental equation

$$\frac{d\alpha}{dt} = f(T) \bullet \boxed{f(\alpha)}$$

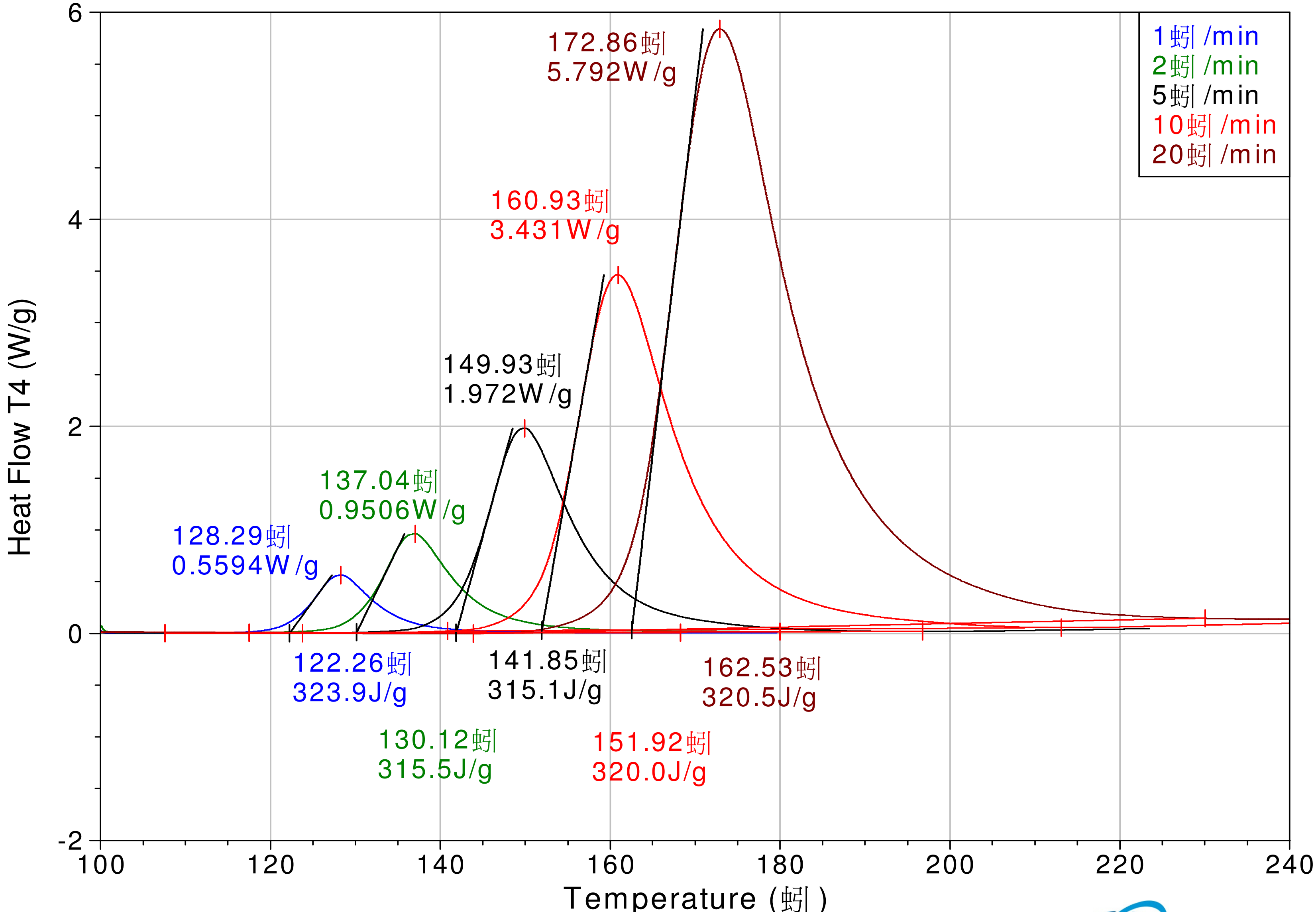
- Many models, three simple ones
  - n^{th} order reaction:
  - Modelling technique: $f(\alpha) = (1-\alpha)^n$ n is reaction order
    - n = 1: ASTM E698[1]/Ozawa, Wall and Flynn method[2]
    - n ≠ 1: ASTM E2041[3]/Borchardt and Daniels method[4]

  - Autocatalyzed reaction:
  - Modelling technique: $f(\alpha) = \alpha^m (1-\alpha)^n$ n and m are reaction orders
    - ASTM E2070[5]/Sestak and Berggren method (Isothermal kinetics)[6]

- TA Application note TA-073 gives detailed information on the assumptions, merits and limitations of each model

[1]ASTM E698, ASTM Annual Book of Standards 2005 volume 14.02
[2]Ozawa, T.J. J. Thermal Analysis, 1970, v2, p301
[3]ASTM E2041, ASTM Annual Book of Standards 2005 volume 14.02
[4]Borchardt, H.J., and Daniels, F.J., Am. Chem. Soc. 1956, v79, pg 41
[5]ASTM E2070, ASTM Annual Book of Standards 2005 volume 14.02
[6]Sestak, J., and Berggren, G., Thermochim. Acta, 1971, vol 3, pg 1

Curing reactions are kinetic in nature



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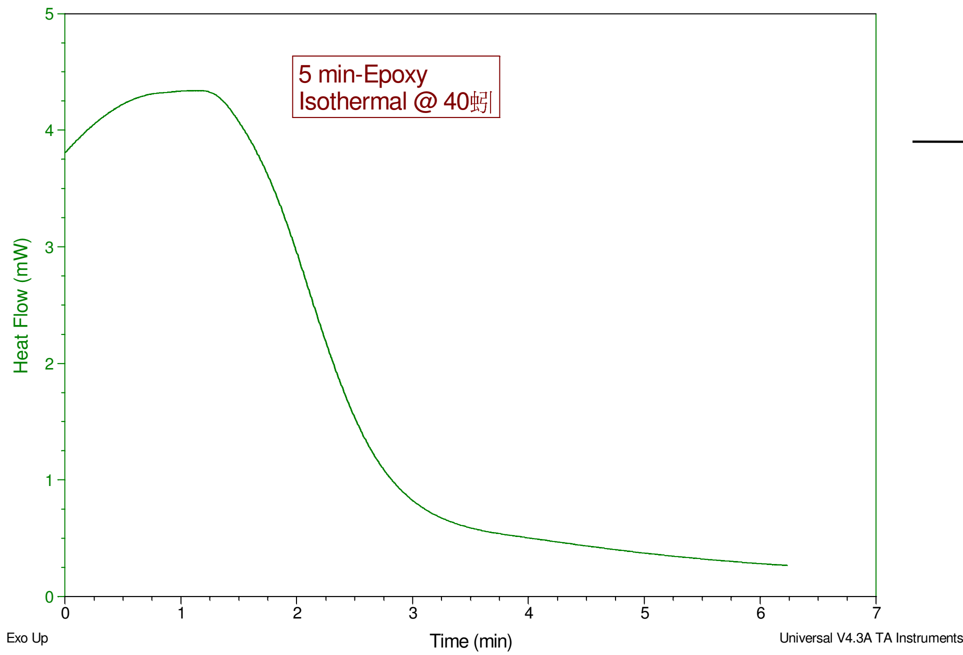
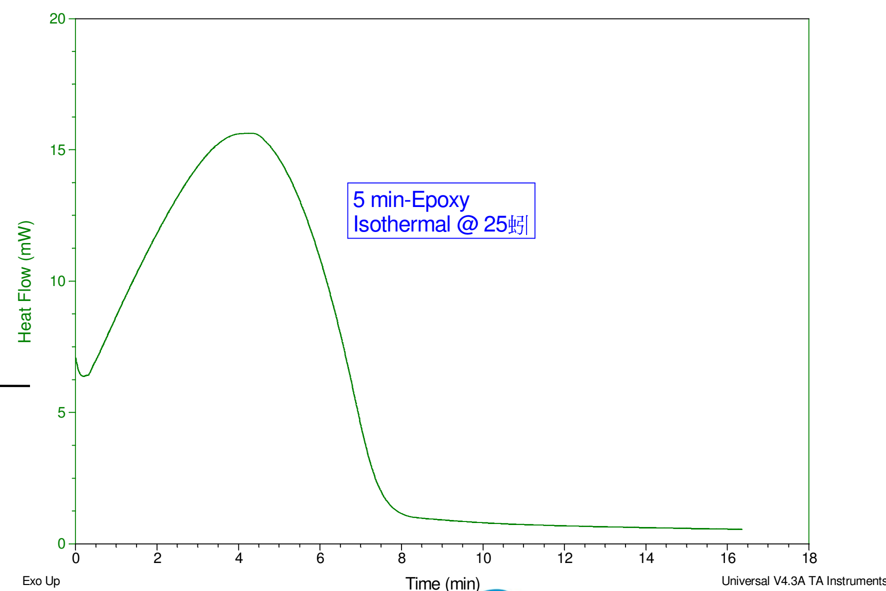
Isothermal curing of a Thermosetting Material



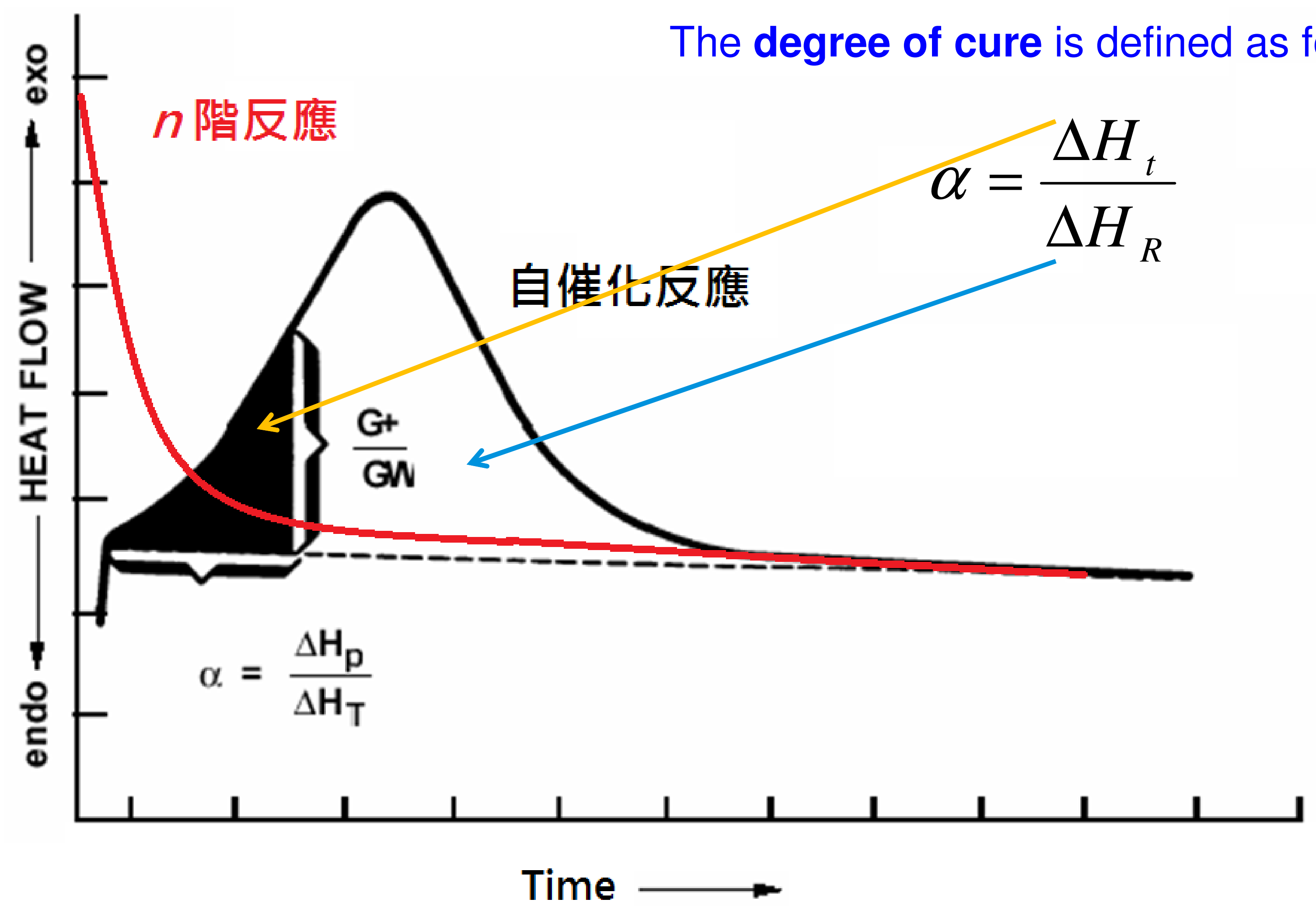
Temperature is too high
Missed most of the reaction



Temperature is better

Need to either go even lower in temperature or work faster

N^{th} Order Reaction vs Autocatalyzed Reaction



The **degree of cure** is defined as follows:

$$\alpha = \frac{\Delta H_t}{\Delta H_R}$$

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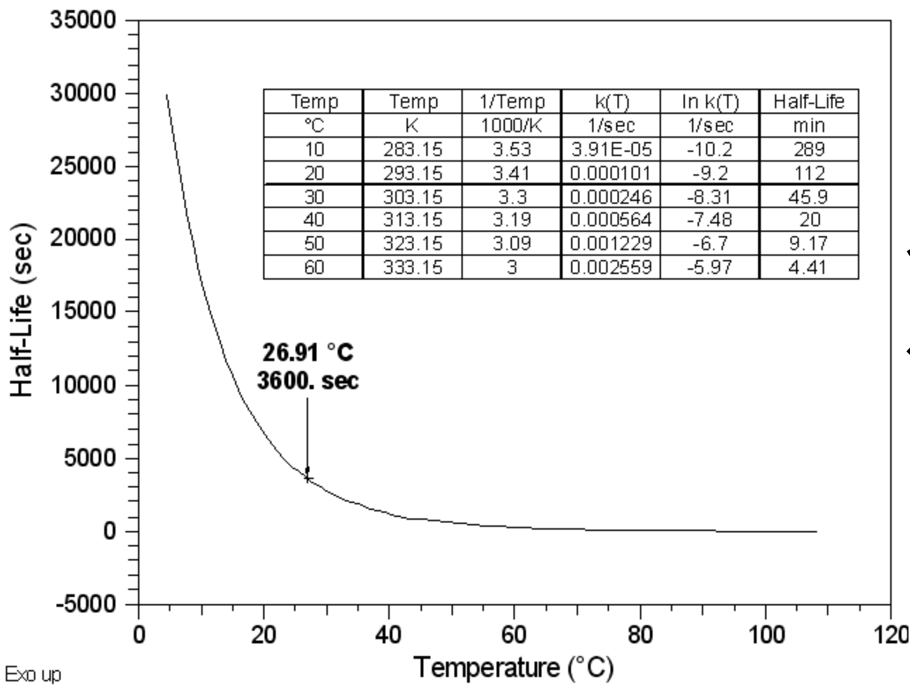
Kinetic analyses can provide valuable information

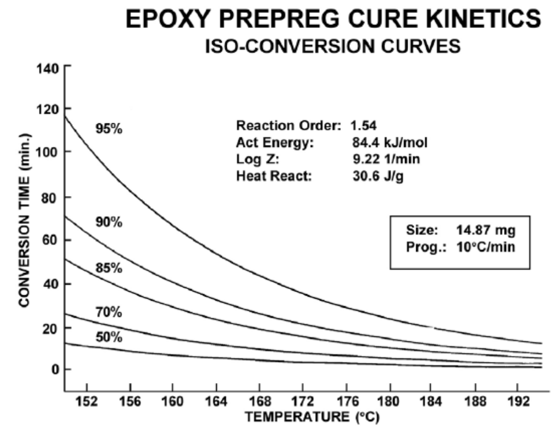
Half-life of the reaction: Use as litmus test for validity of kinetic model



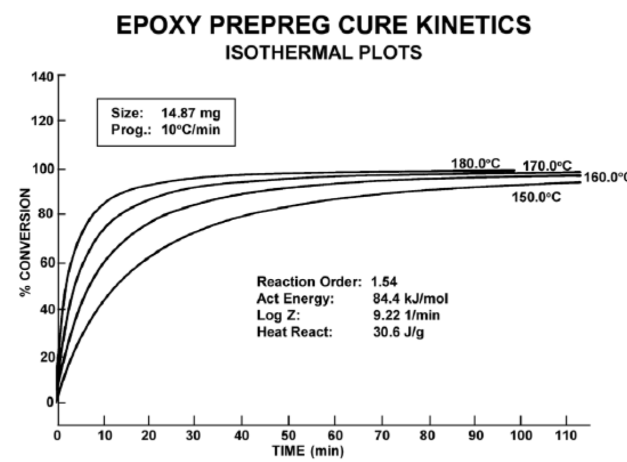
Temp	Temp	1/Temp	k(T)	ln k(T)	Half-Life
°C	K	1000/K	1/sec	1/sec	min
10	283.15	3.53	3.91E-05	-10.2	289
20	293.15	3.41	0.000101	-9.2	112
30	303.15	3.3	0.000246	-8.31	45.9
40	313.15	3.19	0.000564	-7.48	20
50	323.15	3.09	0.001229	-6.7	9.17
60	333.15	3	0.002559	-5.97	4.41

Predict the cure temperature for one hour half life and carry out the iso cure in the DSC. Cool the sample after 1 hour and rerun. Was the residual reaction ½ the total heat of reaction?

If verifies



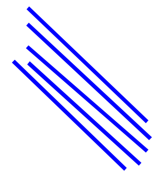
If verifies



Thermoplastics

Thermoplastic Polymers

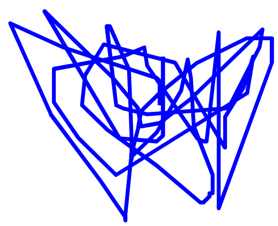
Semi-Crystalline or Amorphous



Crystalline Phase

melting temperature Tm

(endothermic peak)



Amorphous Phase

glass transition temperature (Tg)

(causing ΔCp)

Tg < Tm

Study of melting/crystallization using a DSC

- Melting is the process of converting solid, crystalline structure (lower energy) to a liquid amorphous structure (higher energy).

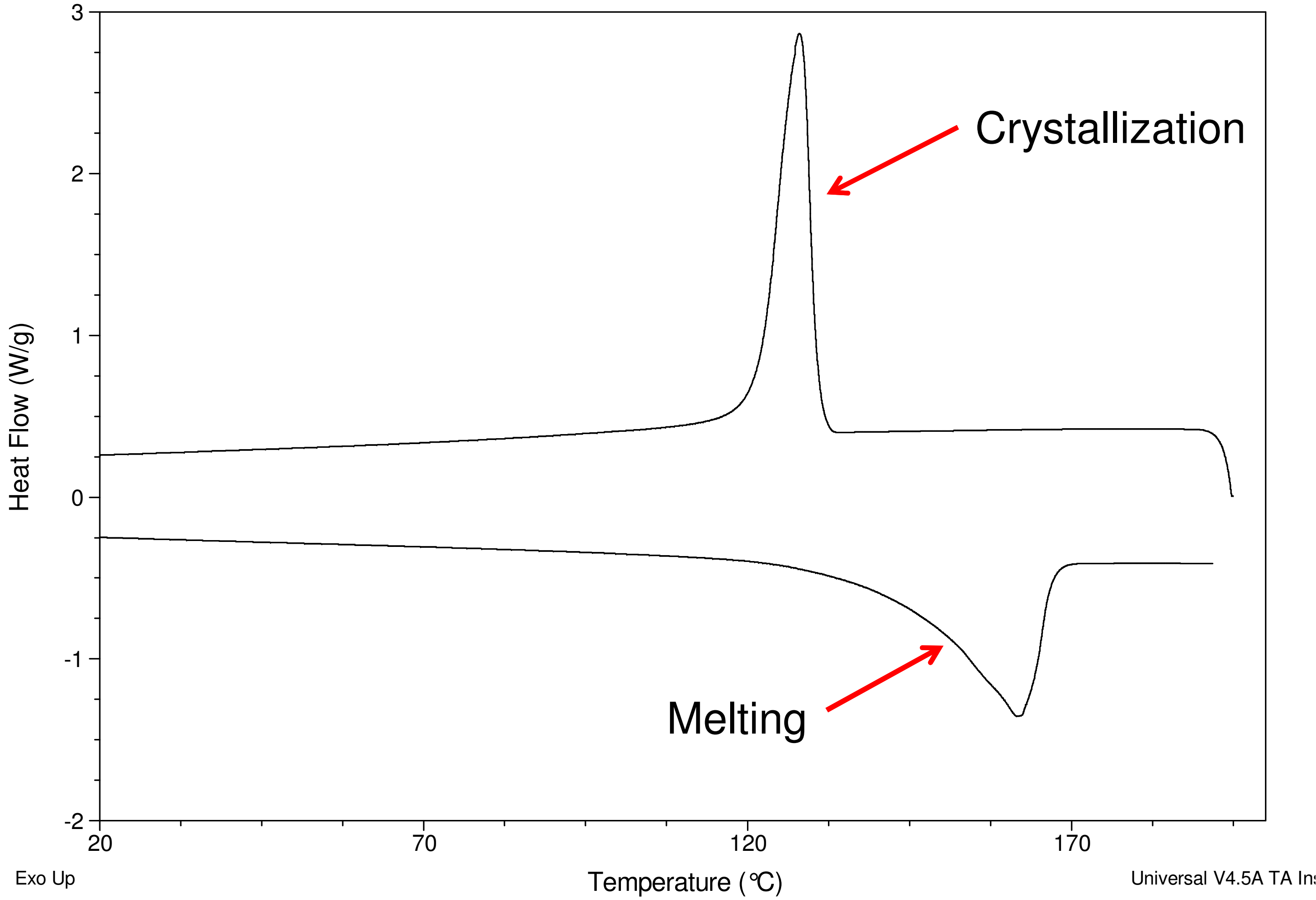
- Crystallization – The process of converting either solid amorphous structure (cold crystallization on heating) or liquid amorphous structure (cooling) to a more organized solid crystalline structure

- Melting:
  - low energy state → high energy state; requires input of energy; Endothermic peak

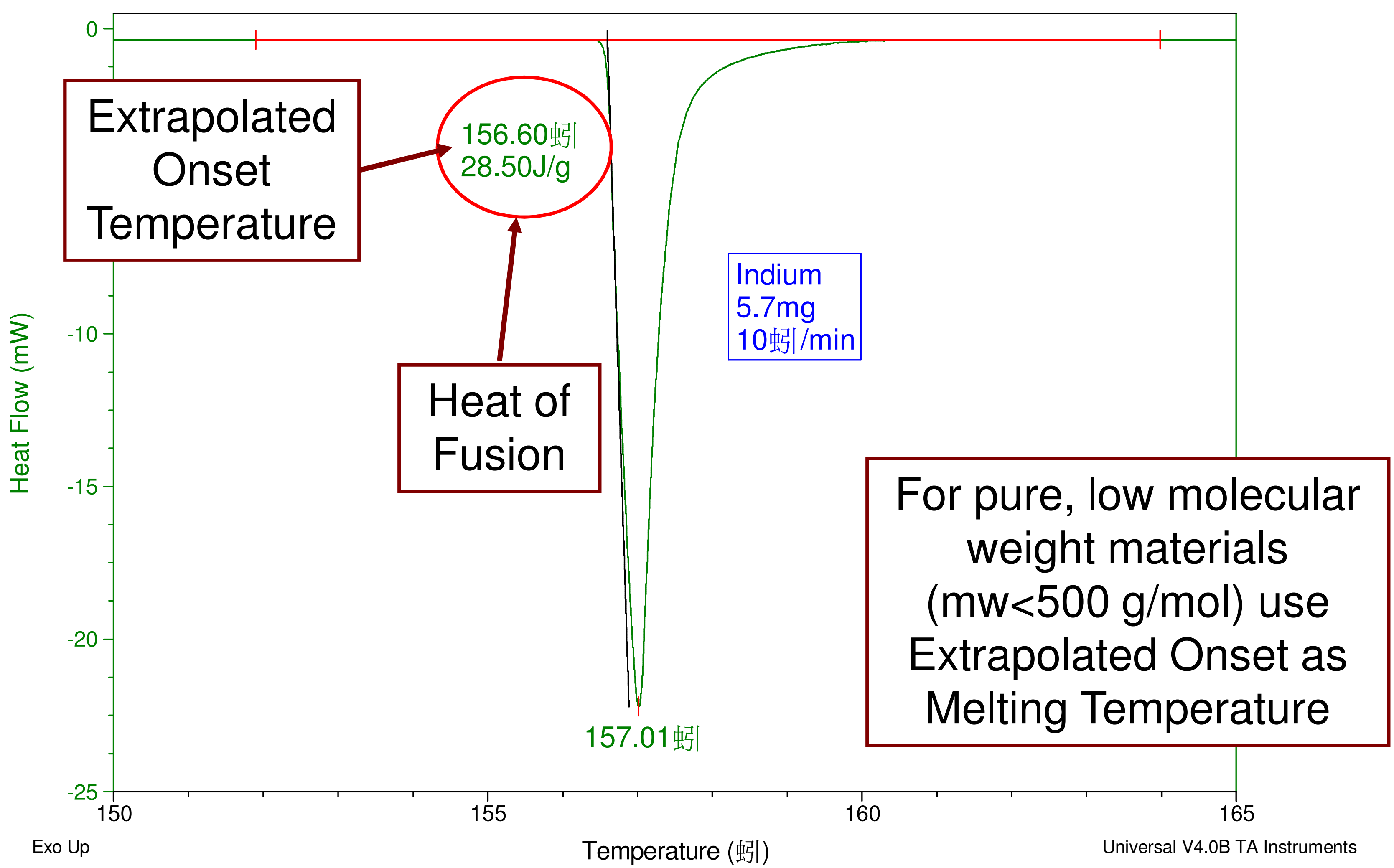
- Crystallization:
  - high energy state → low energy state; releases energy; Exothermic peak

- We integrate these peaks, <u>on a time basis</u> to determine the Heat of Fusion (melting) and Heat of crystallization

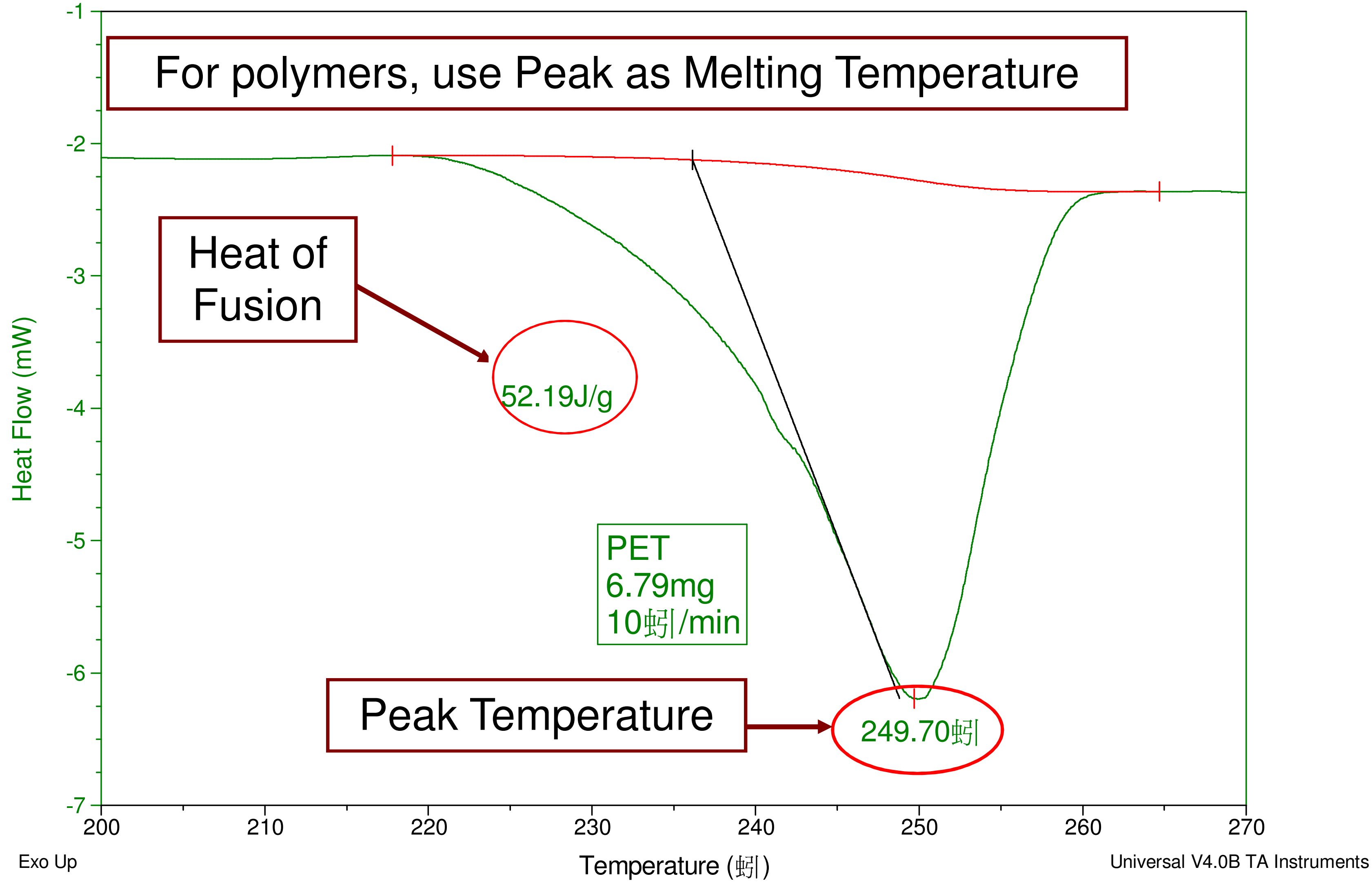
Appearance of melting and crystallization on a DSC thermogram



Melting of Indium



Melting of PET



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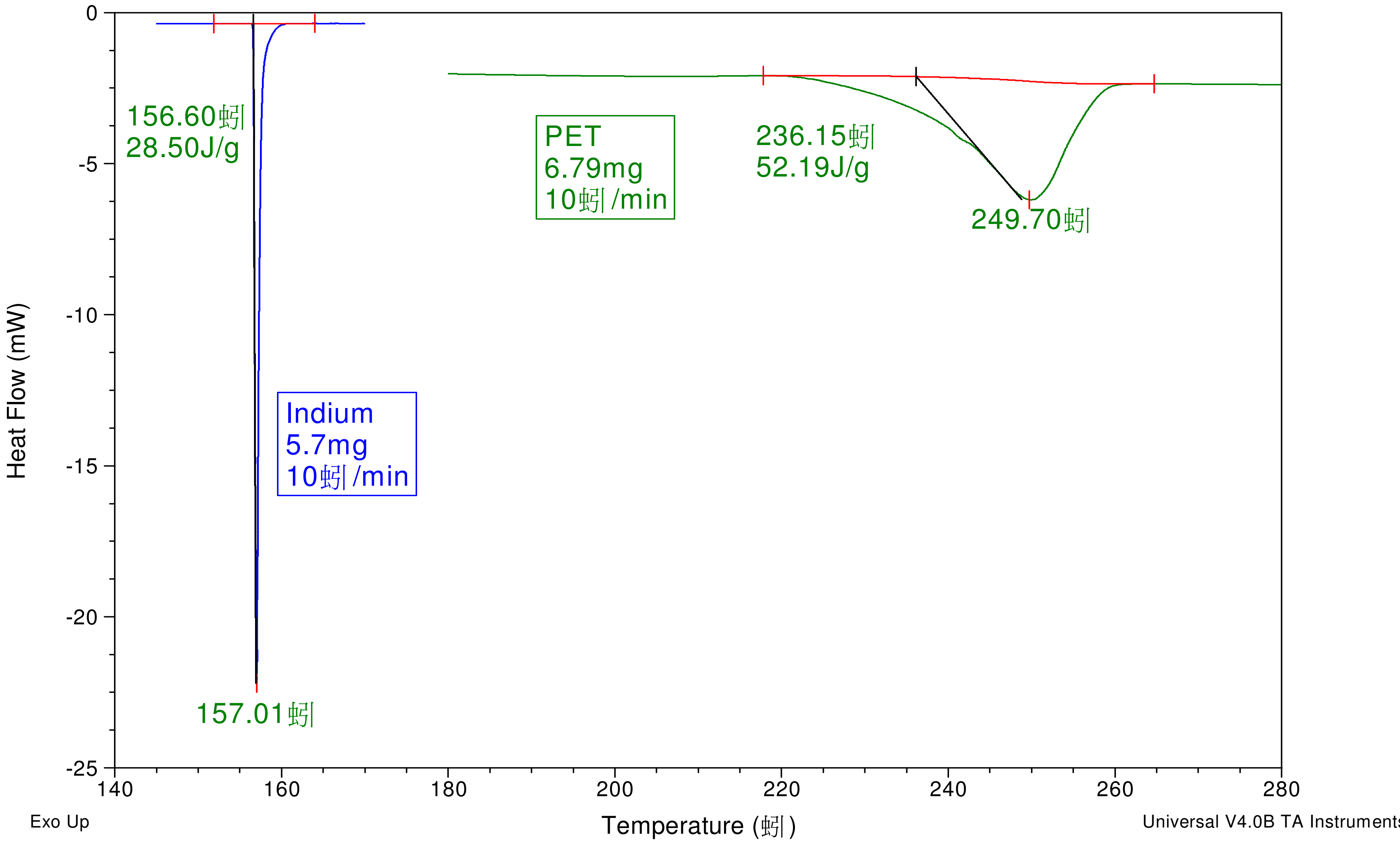
Comparison of Melting



Definitions of some terms commonly used in crystallinity analyses

- Amorphous Phase - The portion of material whose molecules are randomly oriented in space.
  - Liquids and glassy or rubbery solids.
  - Thermosets and some thermoplastics
- Crystalline Phase - The portion of material whose molecules are regularly arranged into well defined structures consisting of repeat units.
  - Very few polymers are 100% crystalline
- Semi-crystalline Polymers - Polymers whose solid phases are partially amorphous and partially crystalline.
  - Most common thermoplastics are semi-crystalline

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Definitions of some terms commonly used in crystallinity analyses

- Thermodynamic Melting Temperature – The temperature where a crystal would melt if it had a perfect structure (crystal with no defects)
- Metastable Crystals – Crystals that melt at lower temperature due to small size (high surface area) and poor quality (large number of defects)
- Crystal Perfection – The process of less perfect crystals (metastable) melting at a temperature below their thermodynamic melting point and then (re) crystallizing into more perfect crystals that will melt again at a higher temperature.

Crystal Structure Analysis

- Crystal structure is typically broken down during the process of melting
- The formation of crystalline structure or crystallization can occur during heating or cooling
  - Cold crystallization occurs on heating when a solid amorphous material becomes ordered
  - Crystallization on cooling occurs when the liquid amorphous material solidifies into an ordered structure
- Typically, the same amount of energy required to create the structure during crystallization is also required to break down the crystal structure during melting

Selecting Experimental Conditions

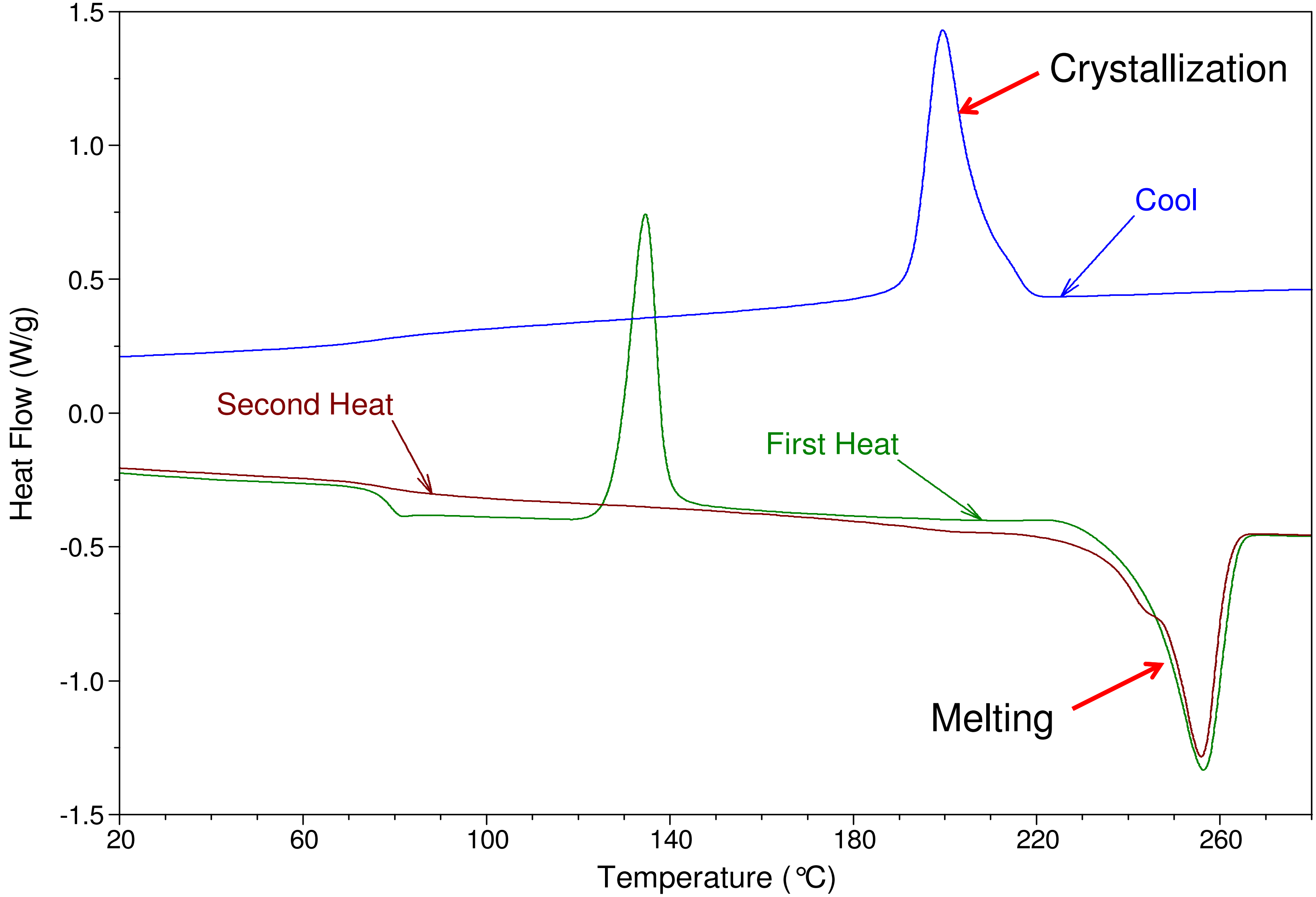
- Thermoplastic Polymers
  - Perform a Heat-Cool-Heat Experiment at 10°C/min.
  - First heat data is a function of the material and an unknown thermal history
  - Cooling segment data provides information on the crystallization properties of the polymer and gives the sample a known thermal history
 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

- General Recommendations
  - 10-15mg
  - Heat - cool - reheat cycles @ 10°C/min

Selecting Experimental Conditions

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

A typical Heat/Cool/Heat thermogram



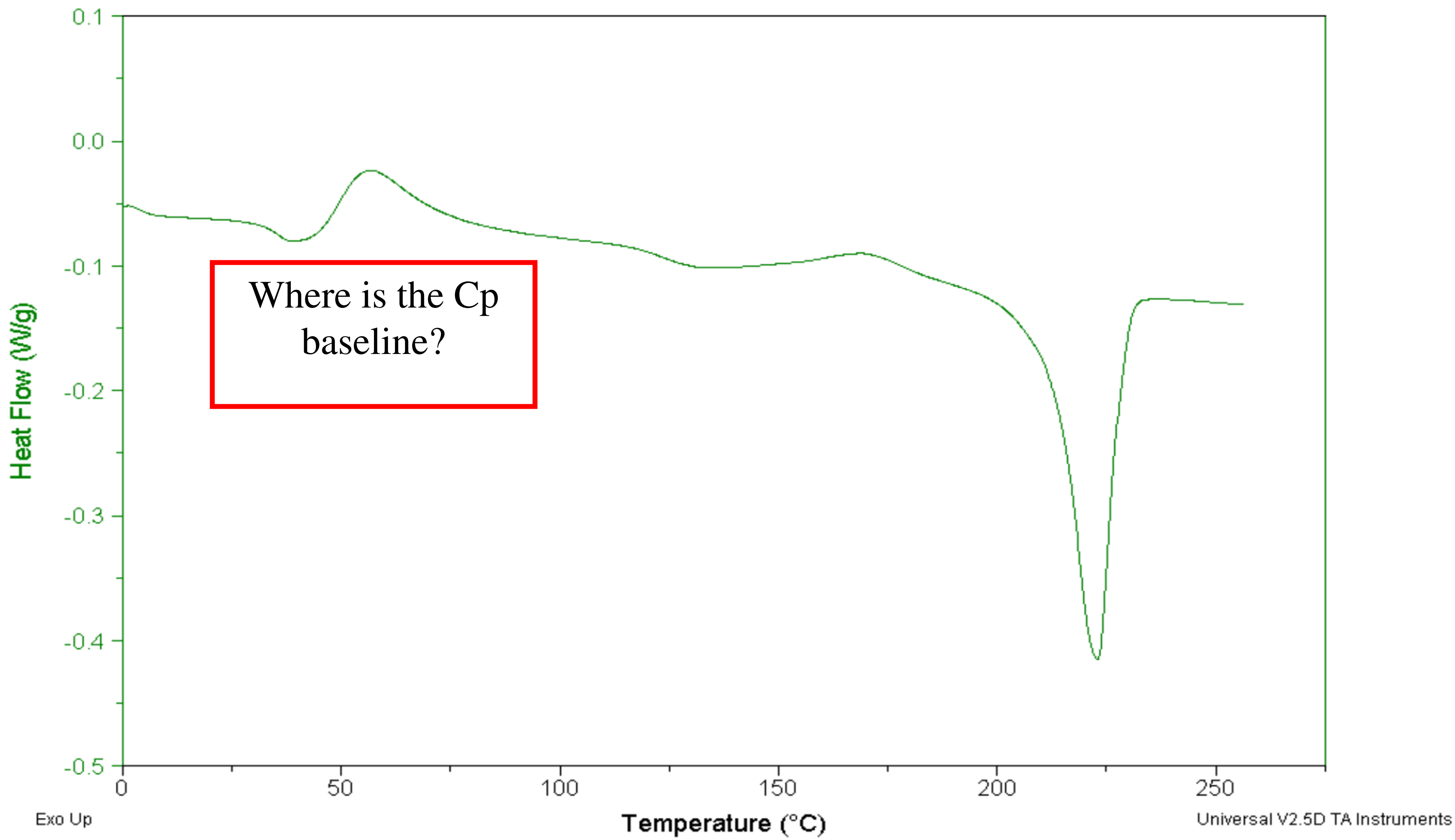
Heat capacity baseline: the definition

- True Heat Capacity Baseline – Often called the thermodynamic baseline, it is the measured baseline (usually in heat flow rate units of mW) with all crystallization and melting removed.
  - Assumes no interference from other latent heat such as polymerization, cure, evaporation etc. over the crystallization/melting range.

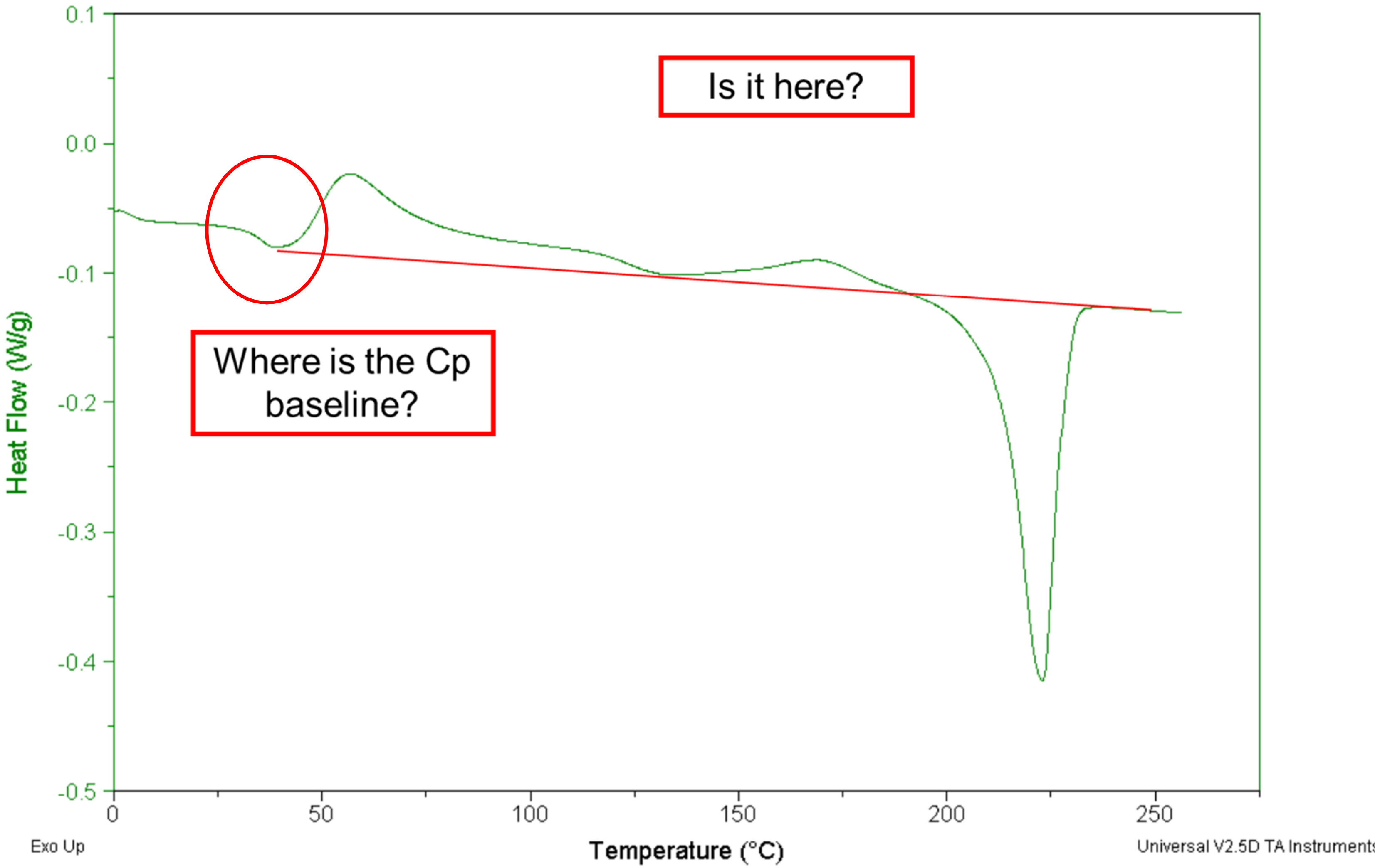
Analyzing/Interpreting Results – selecting integration limits on the heat capacity baseline

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

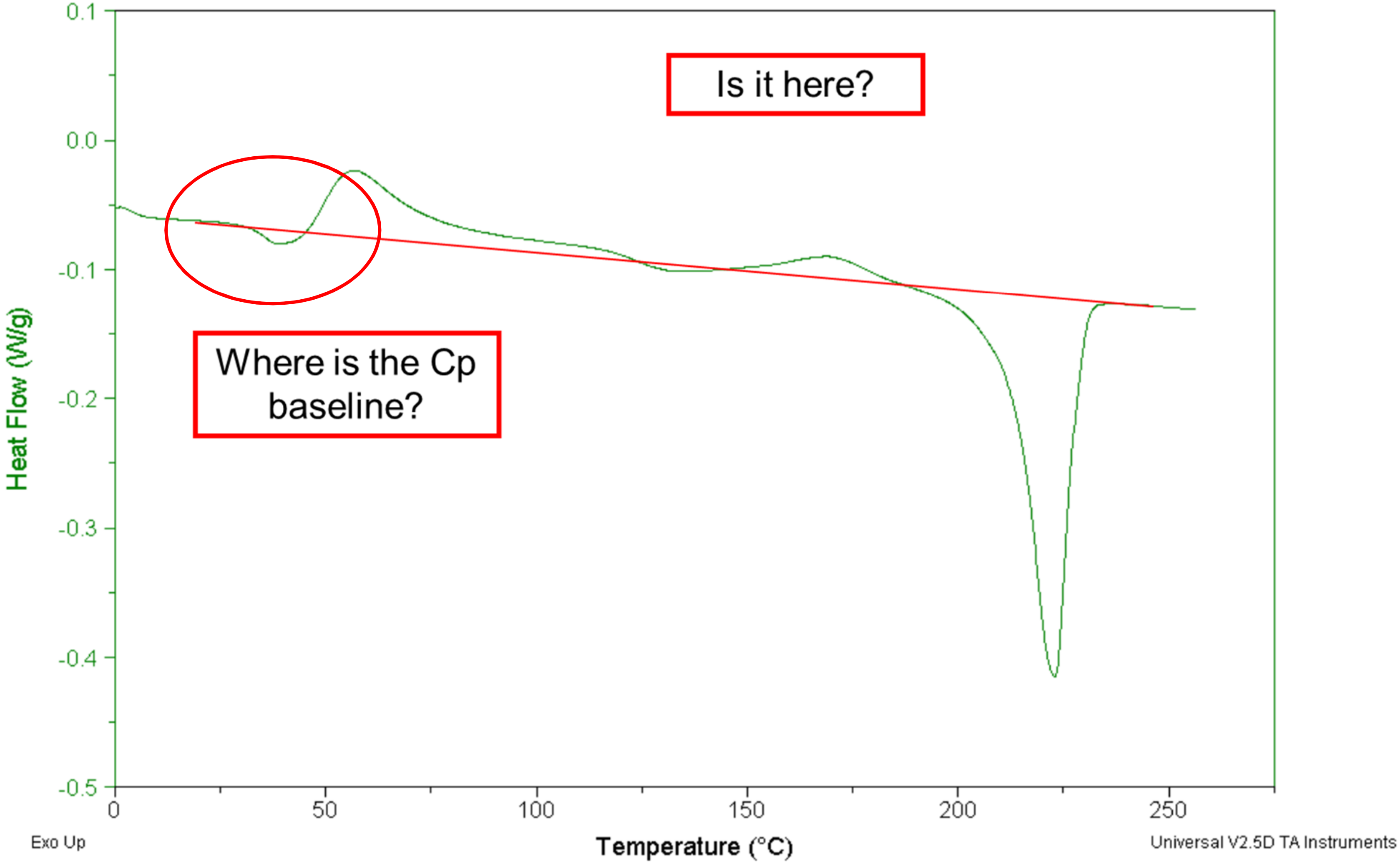
Example: DSC of Polymer Blend



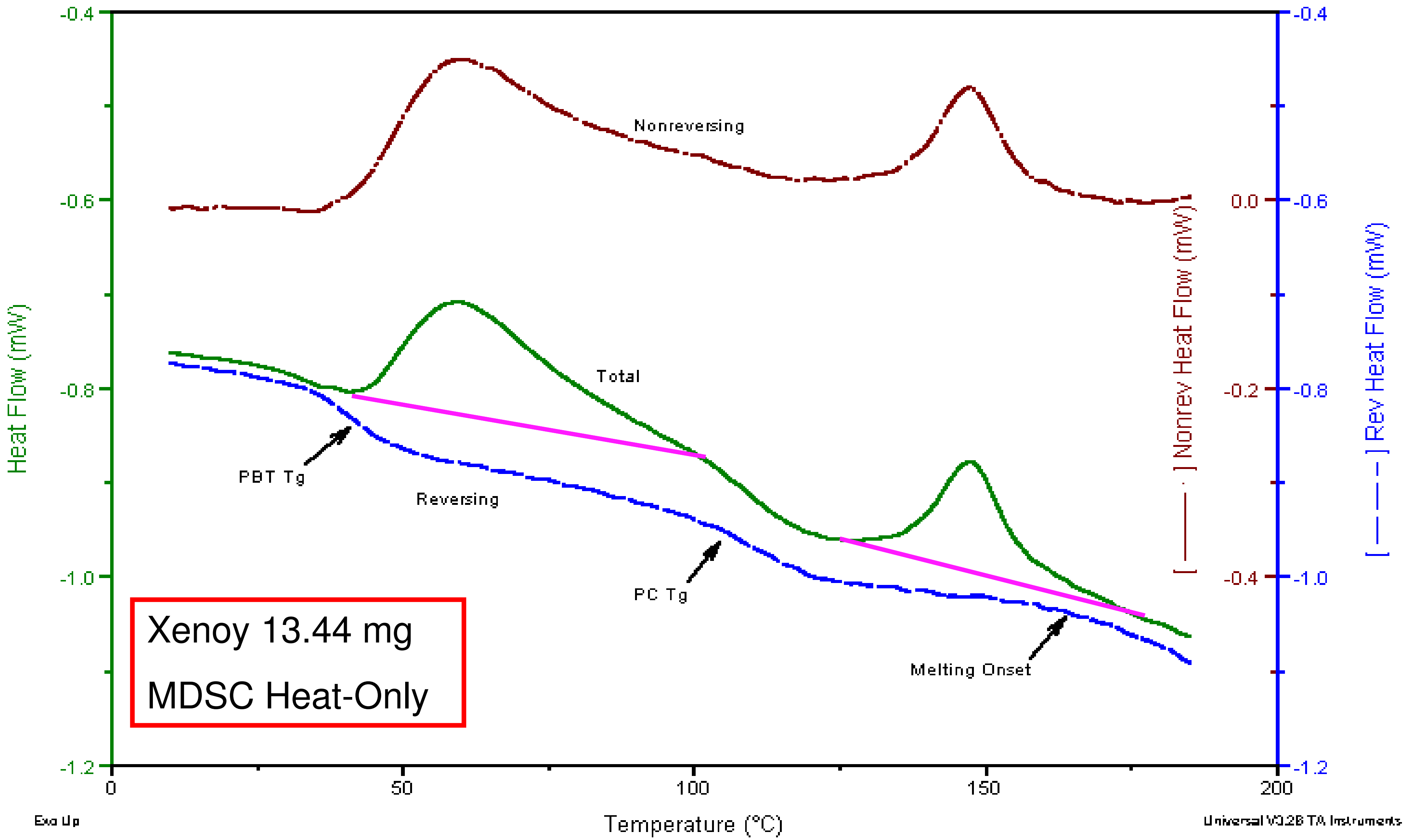
Example: DSC of Polymer Blend



Example: DSC of Polymer Blend



MDSC® Aids Interpretation



Calculation of % Crystallinity

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

For standard samples:

$$\% \text{ crystallinity} = 100^* \, \Delta H_m / \Delta H_{lit}$$

For samples with cold crystallization:

$$\% \text{ crystallinity} = 100^* \, (\Delta H_m - \Delta H_c) / \Delta H_{lit}$$

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- Semiconductivity
- Superconductivity
- Crystallography

Preface to the ATHAS Data Bank in SpringerMaterials

The ATHAS (Advanced THermal Analysis System) Data Bank offers the equilibrium thermal properties of macromolecules (polymers) and relatively small molecules materials. The ATHAS Data Bank contains three major parts:

1. A table of thermal properties (glass and melting temperatures, heats of fusion if crystallization is possible, auxiliary data on molecular motion, and phase structure).
2. A Data Bank of the experimental and calculated heat capacities.
3. Recommended Data of thermodynamic properties of macromolecules and related small molecules (C_p from approximate and exact vibrational spectra, enthalpy H, entropy S, and free enthalpy (Gibbs function) G).

The goal of generating the equilibrium thermal properties of macromolecules was to help analyze nonequilibrium behaviors of polymeric materials.

The ATHAS data bank, for example, contains such equilibrium information on heat capacities from 0 to 1000 K, vibrational spectra, transition parameters, enthalpies, free enthalpies, and entropies for a number polymers and related materials. All these equilibrium thermodynamic quantities and parameters can serve as references for the quantitative thermal analysis of experimental data of semi-crystalline, metastable states and non-equilibrium processes of materials.

The collection of data, in the form of ATHAS data bank, began in the mid 1970s by Prof. Berhard Wunderlich and co-workers. In 2005, data bank moved to Prof. Marek Pyda's Laboratory. At present, the ATHAS data bank is available by SpringerMaterials on their internet page.

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

PET Data from ATHAS

Poly(ethylene terephthalate) (PET)

Crystalline Calculated Data

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

```
Name :                Poly(ethylene terephthalate)

File Name :           PET

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

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

< Crystalline >

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

ATHAS Summary Page for PET

ΔH_f in kJ/mol

Poly(ethylene terephthalate) (PET)

Summary

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

- Explanations

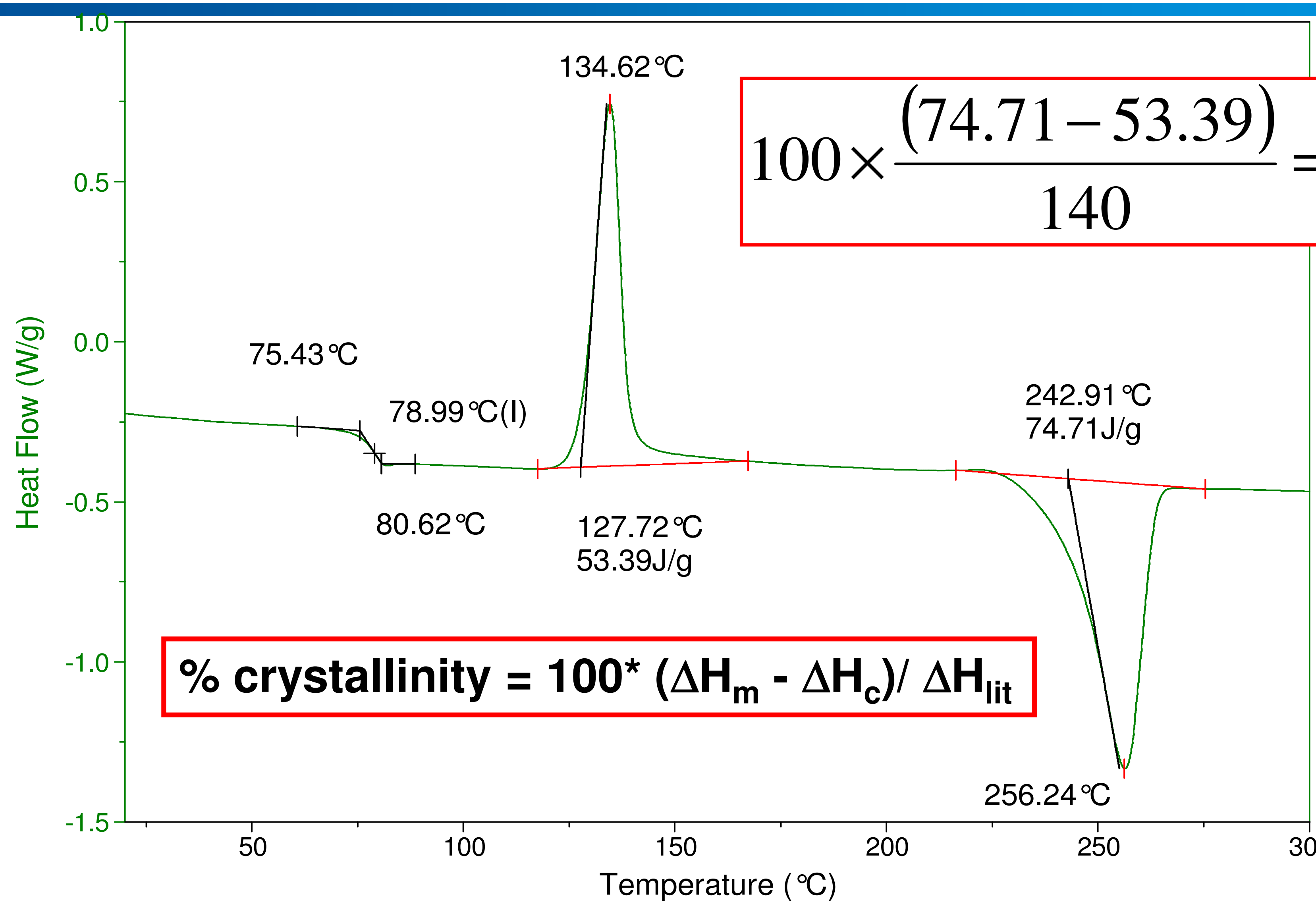
The data are separated into

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

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

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

Quench-cooled PET – calculation of initial crystallinity



$$100 \times \frac{(74.71 - 53.39)}{140} = 15\%$$

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

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Quench-cooled PET – calculation of initial crystallinity

- 15% Crystalline
  - Does that sound right?
- The sample is quenched cooled PET
- We know that quenched cooled PET is 100% amorphous

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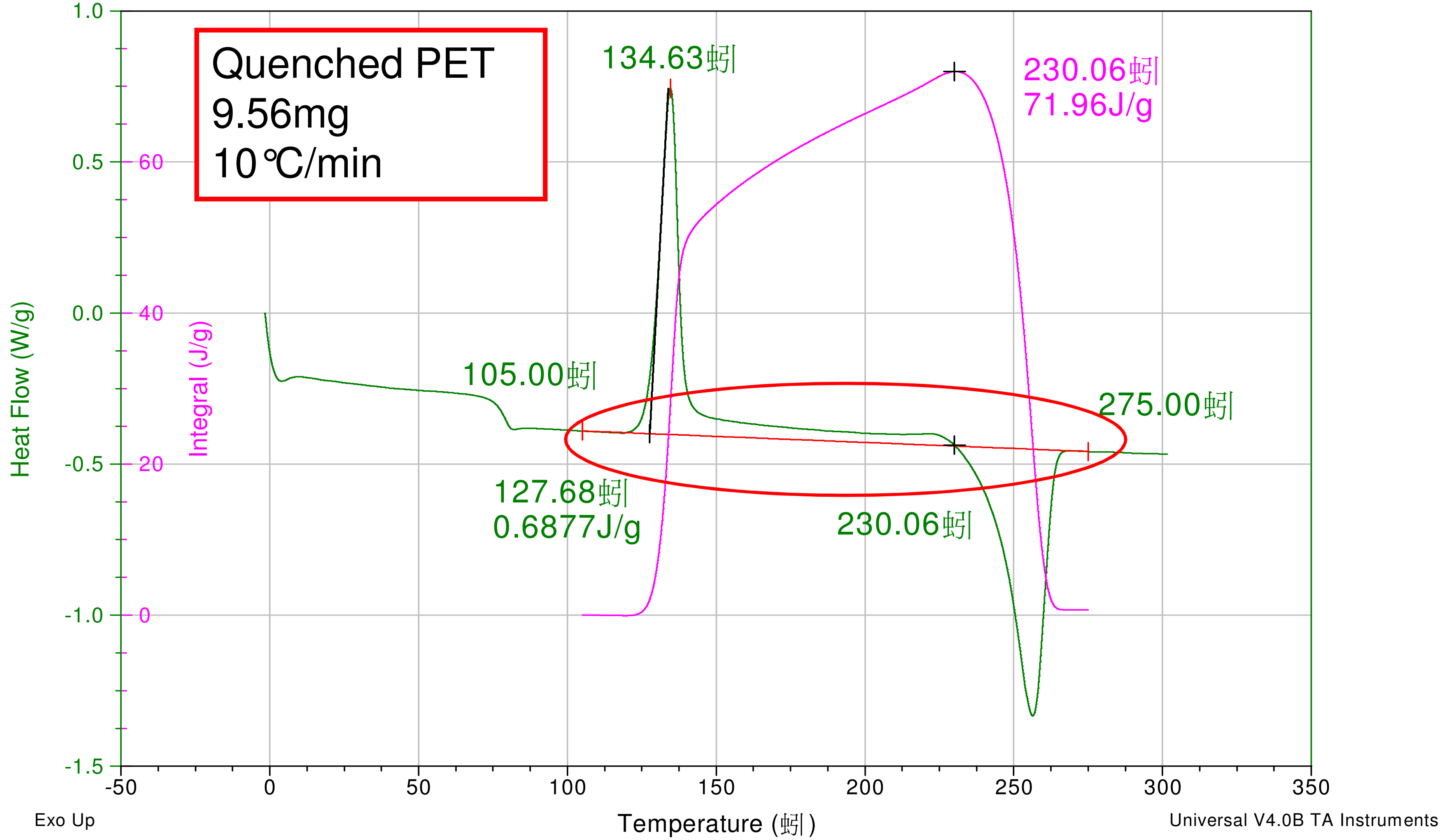
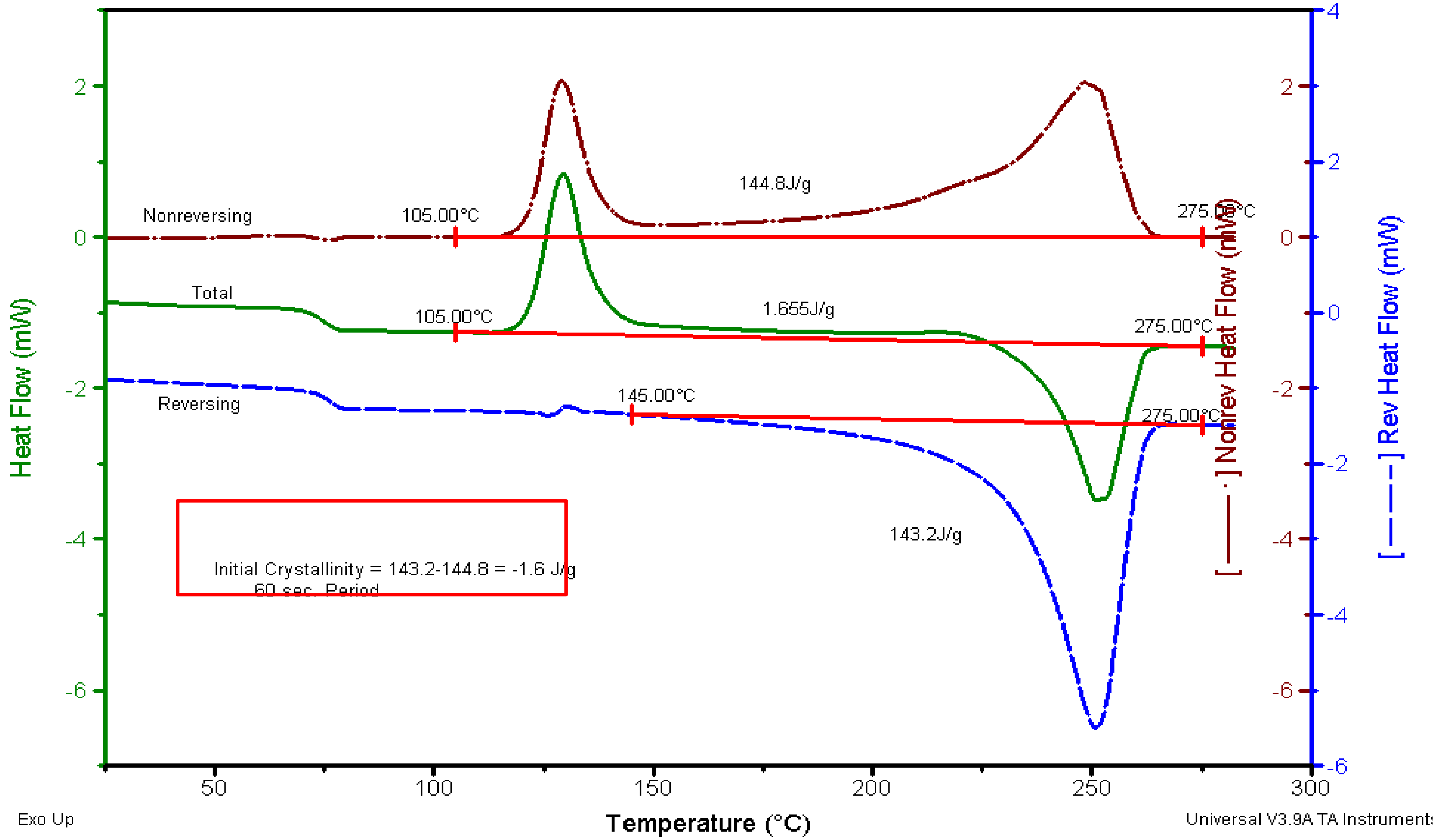
Cold crystallization and crystal perfection can impact % crystallinity calculations

- The question is: “How can DSC provide such a wrong answer?”
  - The answer is that it does not.
  - The error is due to the integration limits selected by the operator.
- Total signal of DSC is often misleading because it measures only the sum of all exothermic and endothermic processes.
- This causes crystal perfection to manifest subtly in the thermogram by a small shift in the baseline (see next slide).
- Cold crystallization also needs to be considered in calculating the crystallinity of the sample.

Change in Crystallinity While Heating



MDSC Experiment on PET



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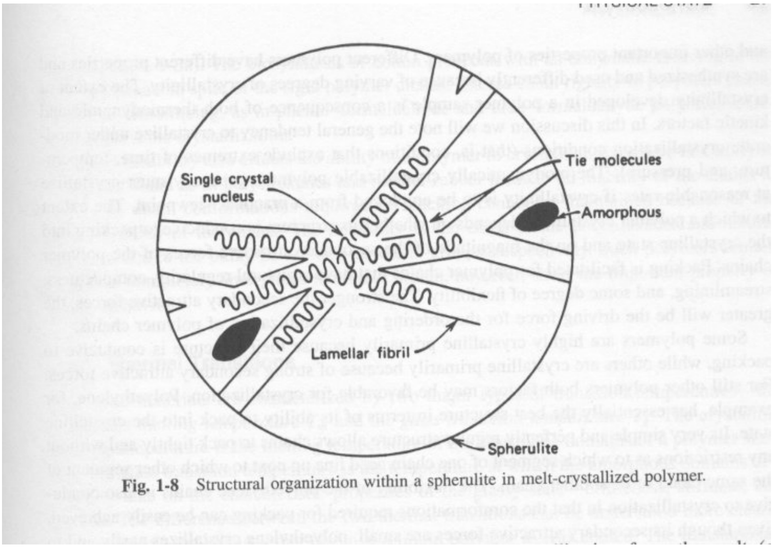
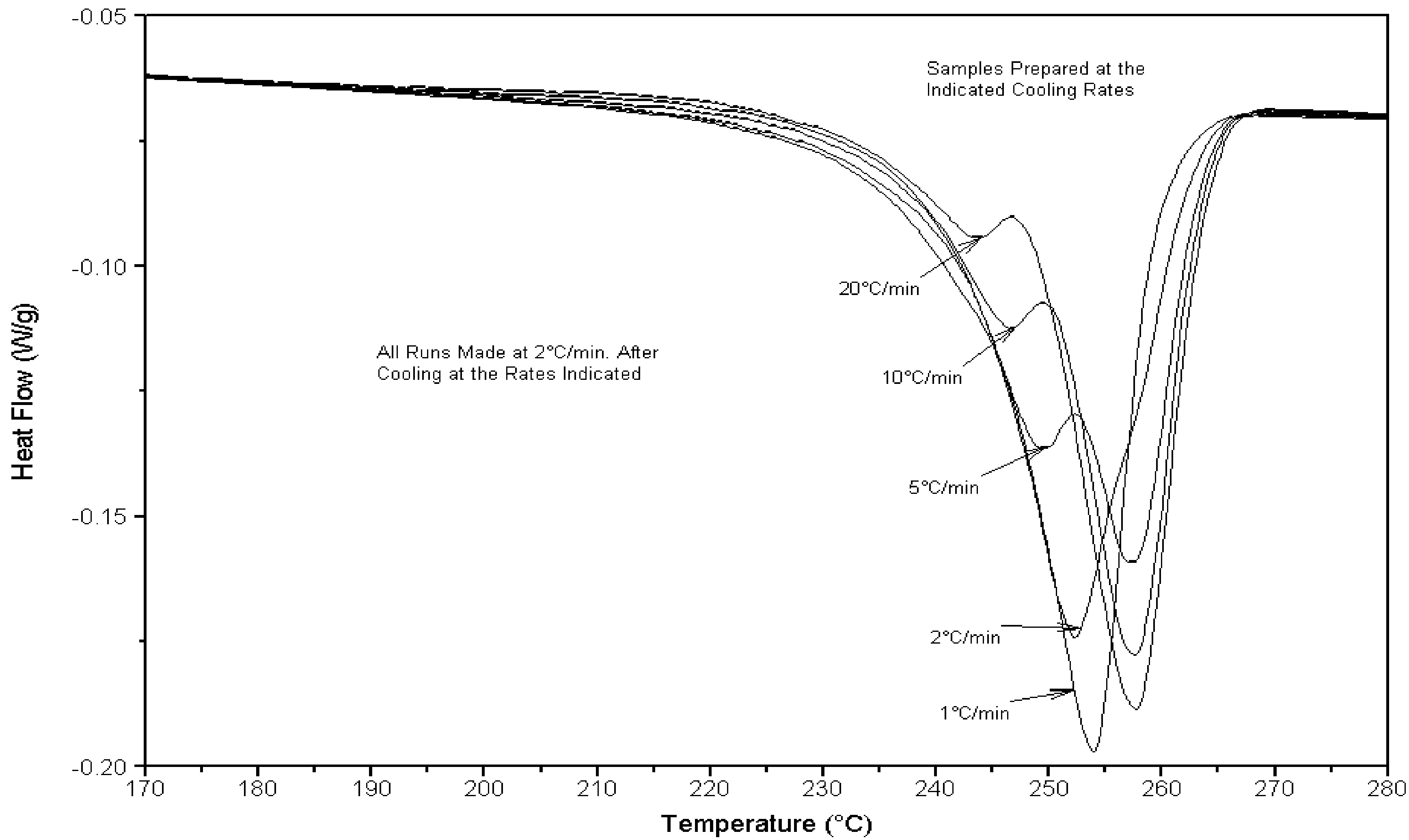
Impact of crystal perfection on the melting peak

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

The next slide compares the shape of the melting process on the same sample of PET after it had been cooled at different rates from above its melting point.



PET Melting after Cooling at Different Rates



Thermoplastics continued: Crystallization kinetics

Crystallization

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

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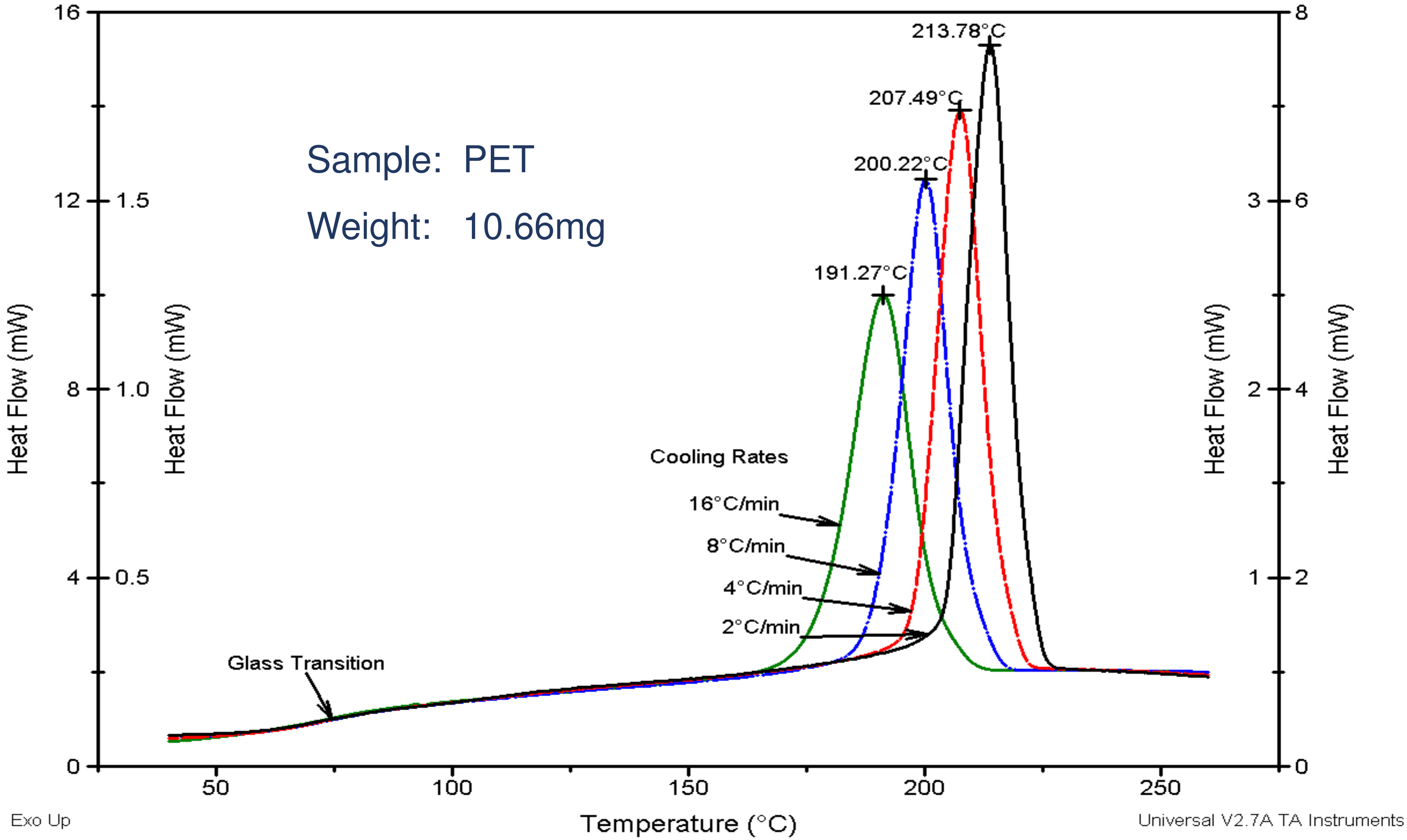
Effect of Cooling Rate on Crystallization



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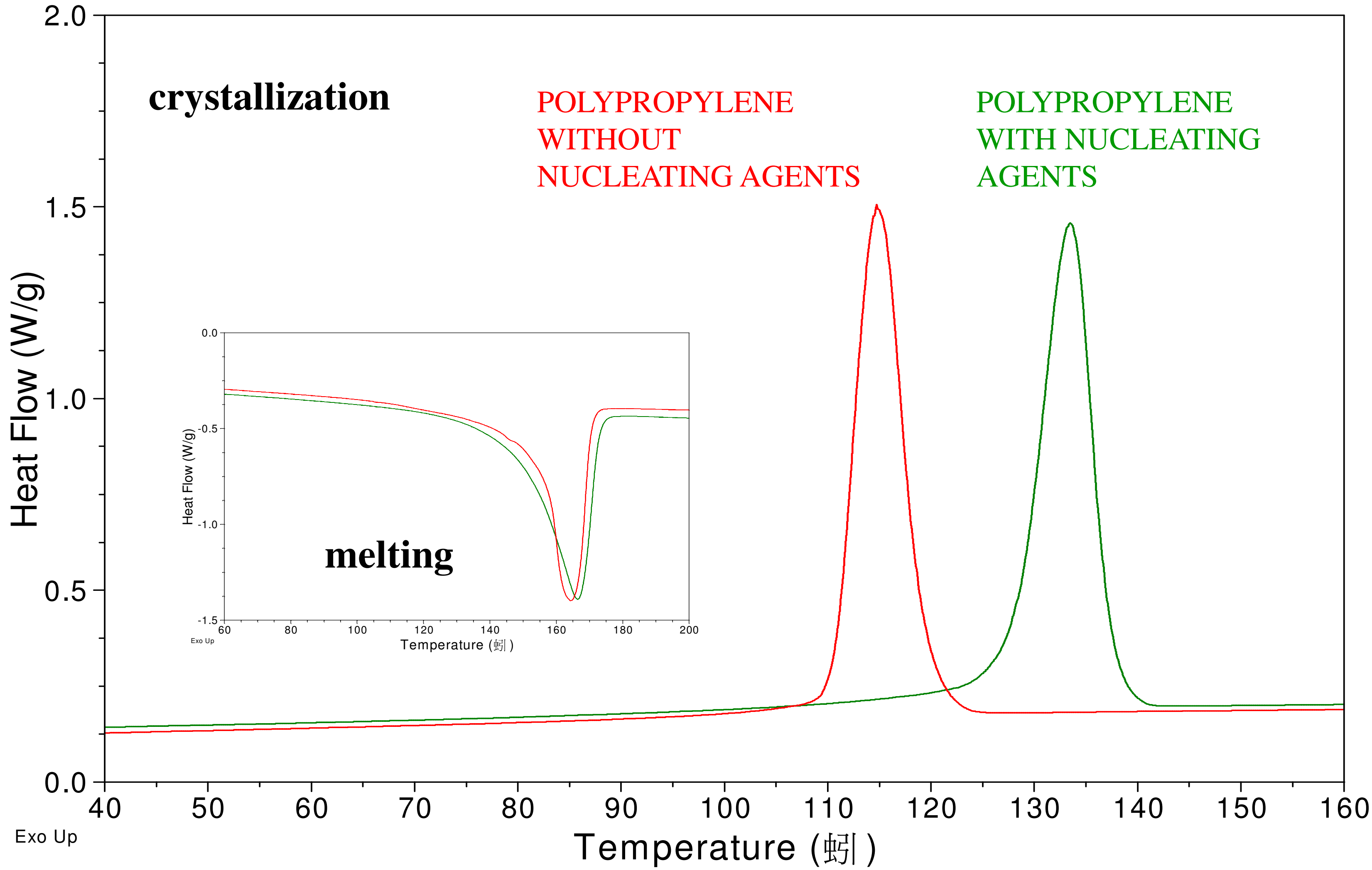
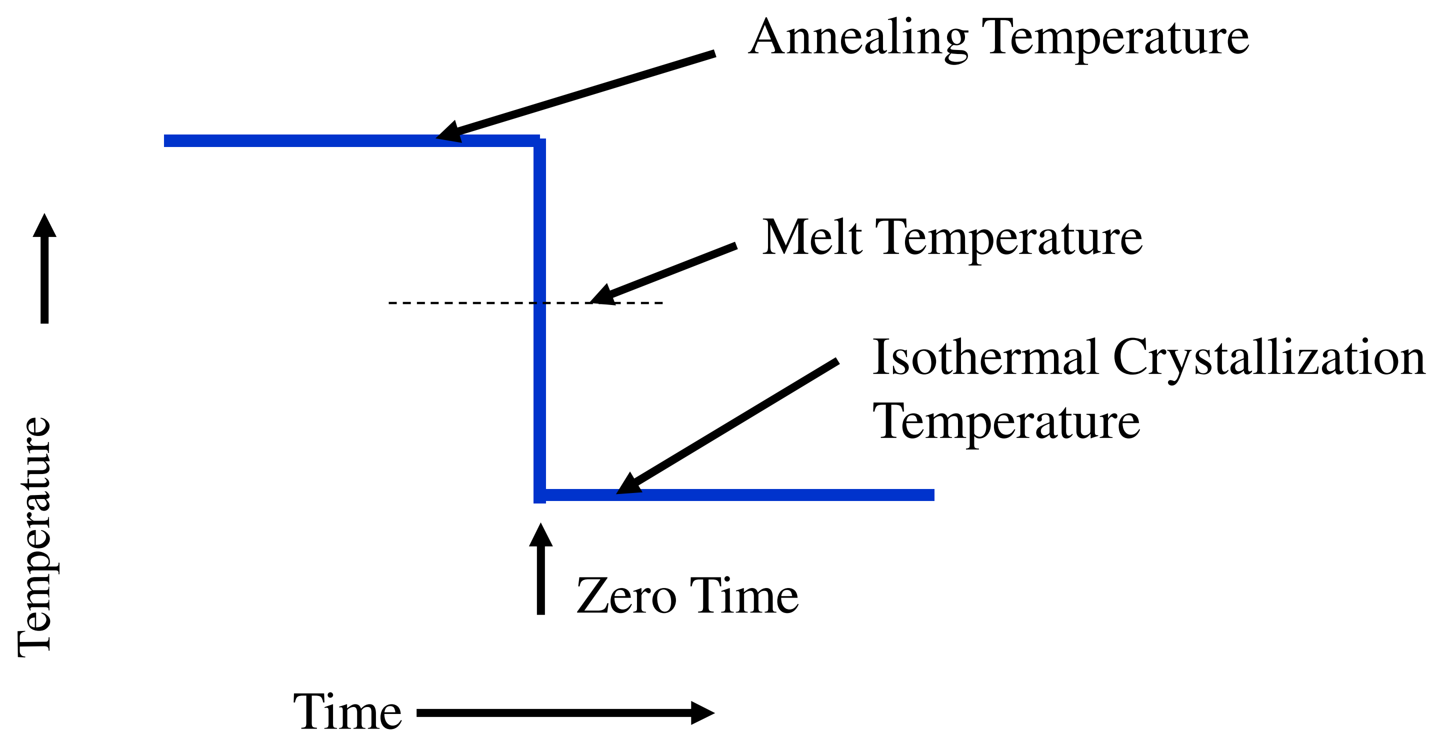
Effect of Nucleating Agents

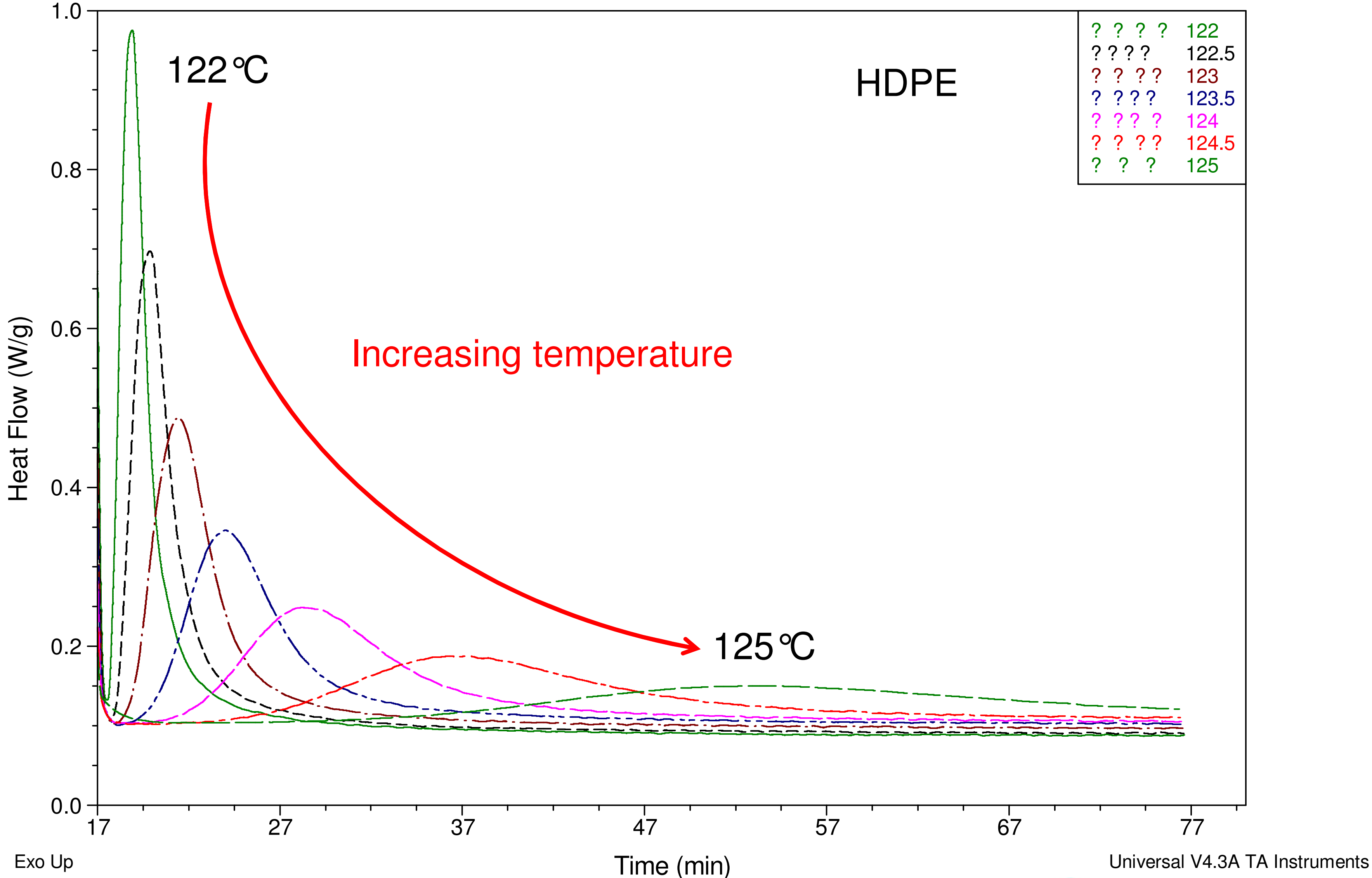


What is Isothermal Crystallization? *Method I*

- A Time-To-Event Experiment – Direct Cooling

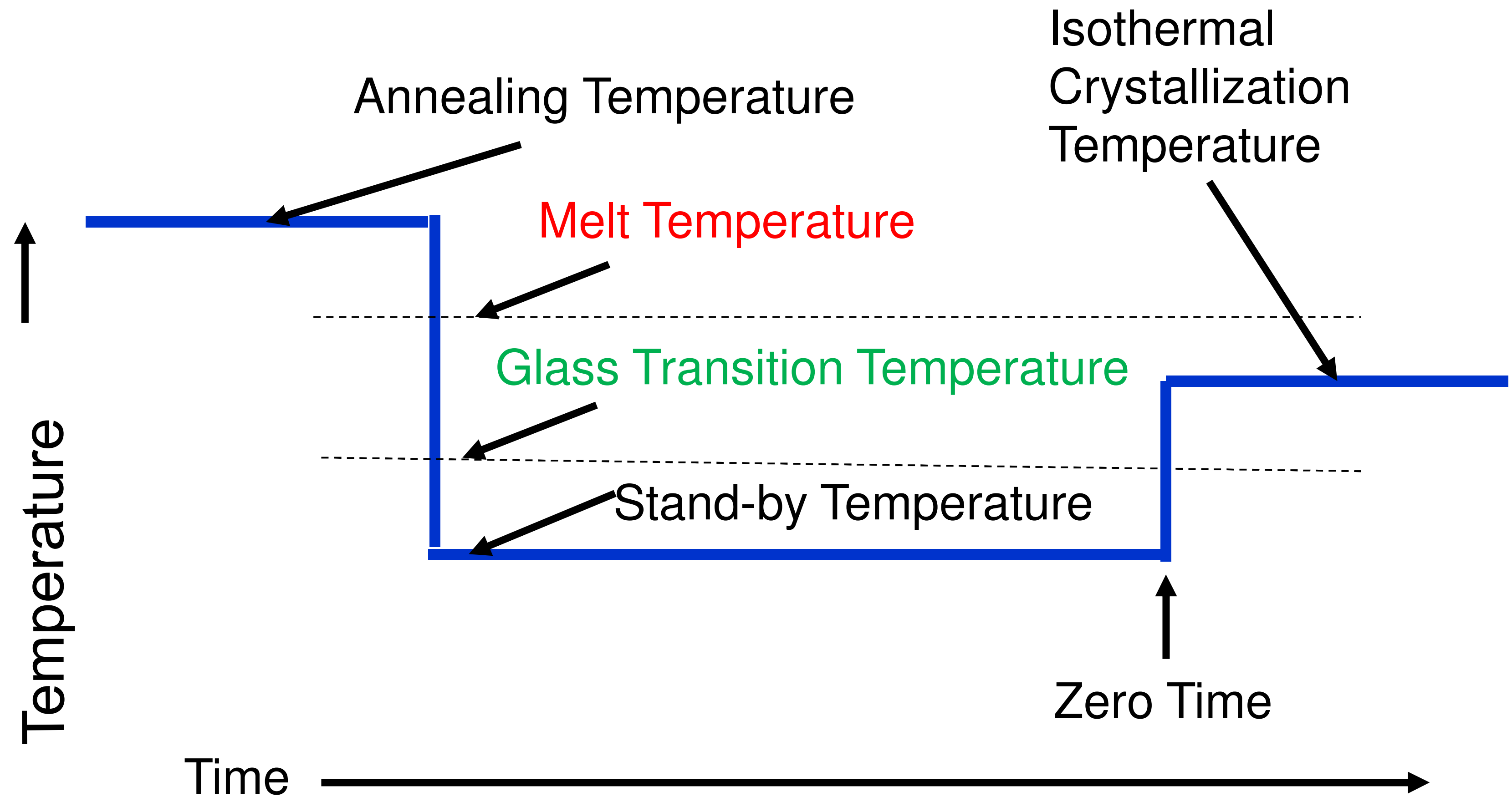


Isothermal Crystallization



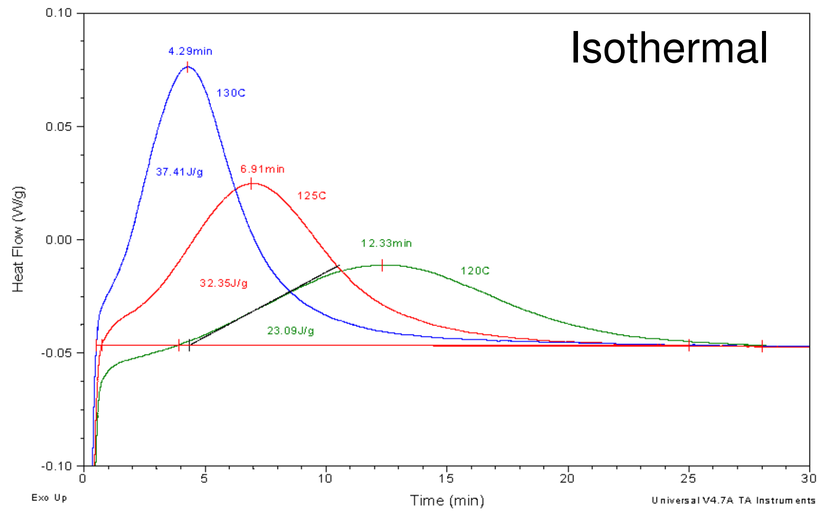
What is Isothermal Crystallization? *Method II*

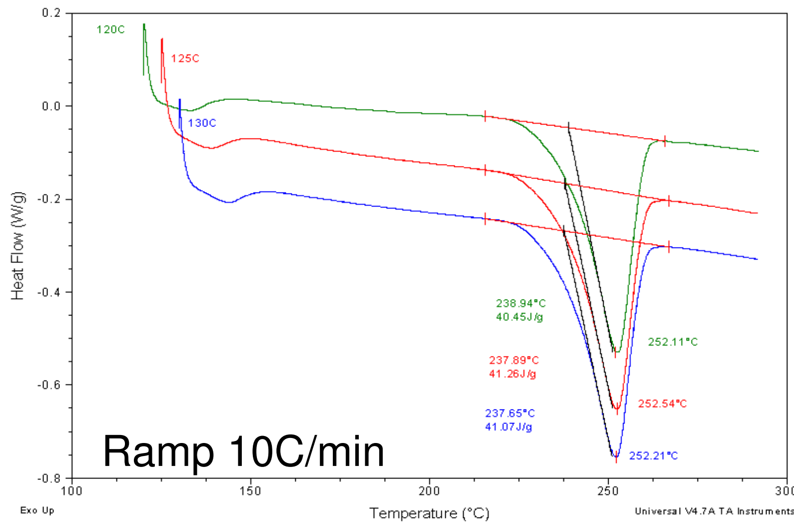
- A Time-To-Event Experiment – Quench & Reheating



DSC Applications: Quench-Isothermal-Crystallization

Method Log:
1: Initial temperature: 高於Tm
2: Initial temperature: Tm與Tg之間
3: Mark end of cycle 1
4: Isothermal 恆溫結晶一段時間
5: Mark end of cycle 2
6: Ramp 10.00C/min to高於Tm
7: Mark end of cycle 3





Isothermal Kinetics

- Many models are available; such as Avrami, Malkin, Sestak& Berggeren etc.
- The following slides demonstrate the ASTM Standard Method E2070[1] based on the method of Sestak and Berggren[2]
- Consists of heating (or in the case of crystallization, cooling) a series of samples to a series of isothermal temperatures, equilibrating and recording the rate of reaction (or crystallization) versus time.
- Each reaction exotherm is fitted to the n^{th} order kinetics equation with an additional term for autocatalysis
- Values of the Arrhenius parameters Ea and Z and the reaction orders, n and m, are calculated using *all* data.

[1]ASTM Annual Book of Standards 2005 volume 14.02 p818-826

[2]Sestak, J., and Berggren, G., Thermochim. Acta, 3, 1 (1971)

Isothermal Kinetics: Equation used for fit

- Starting with general equation

$$\frac{d\alpha}{dt} = f(T) \bullet f(\alpha)$$

$$= Ze^{-Ea/RT}\alpha^m(1-\alpha)^n$$

Where:
Ea is activation energy
Z is a frequency factor
R is the gas constant
T is temperature in kelvin
α is fraction reacted
n is the reaction order
m is the autocatalytic reaction order

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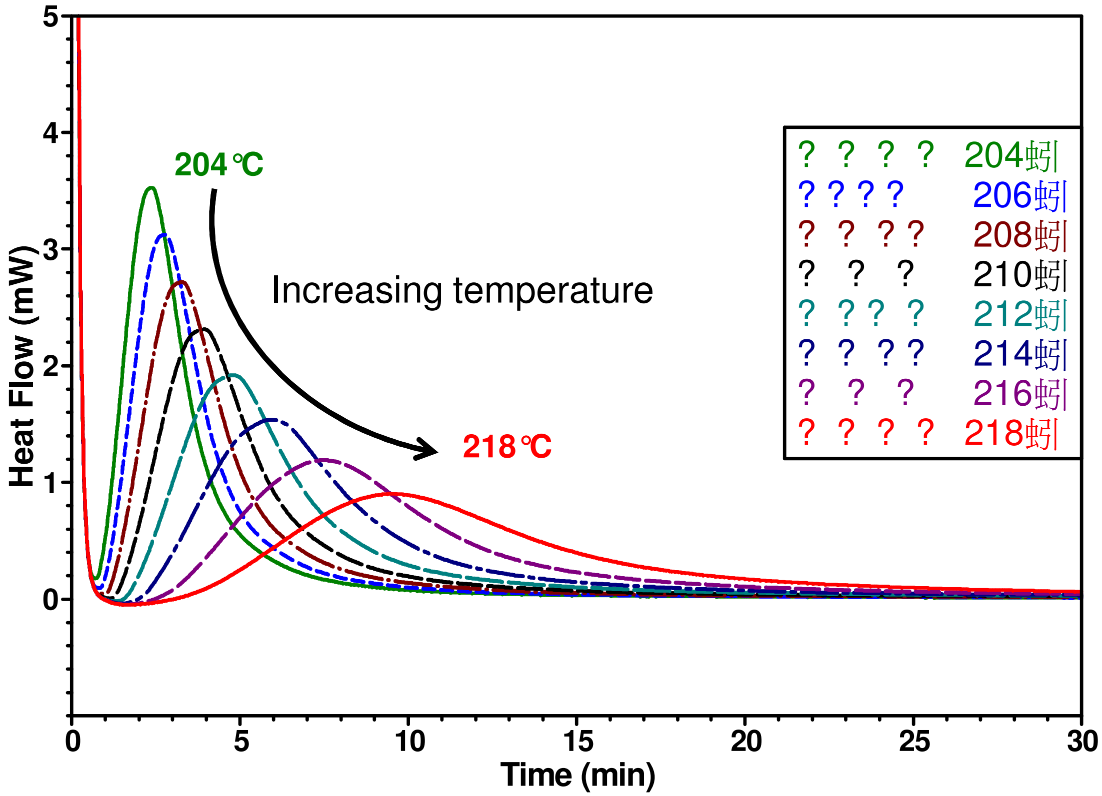
Crystallization Kinetics: Collecting the data

Polyethylene Terephthalate

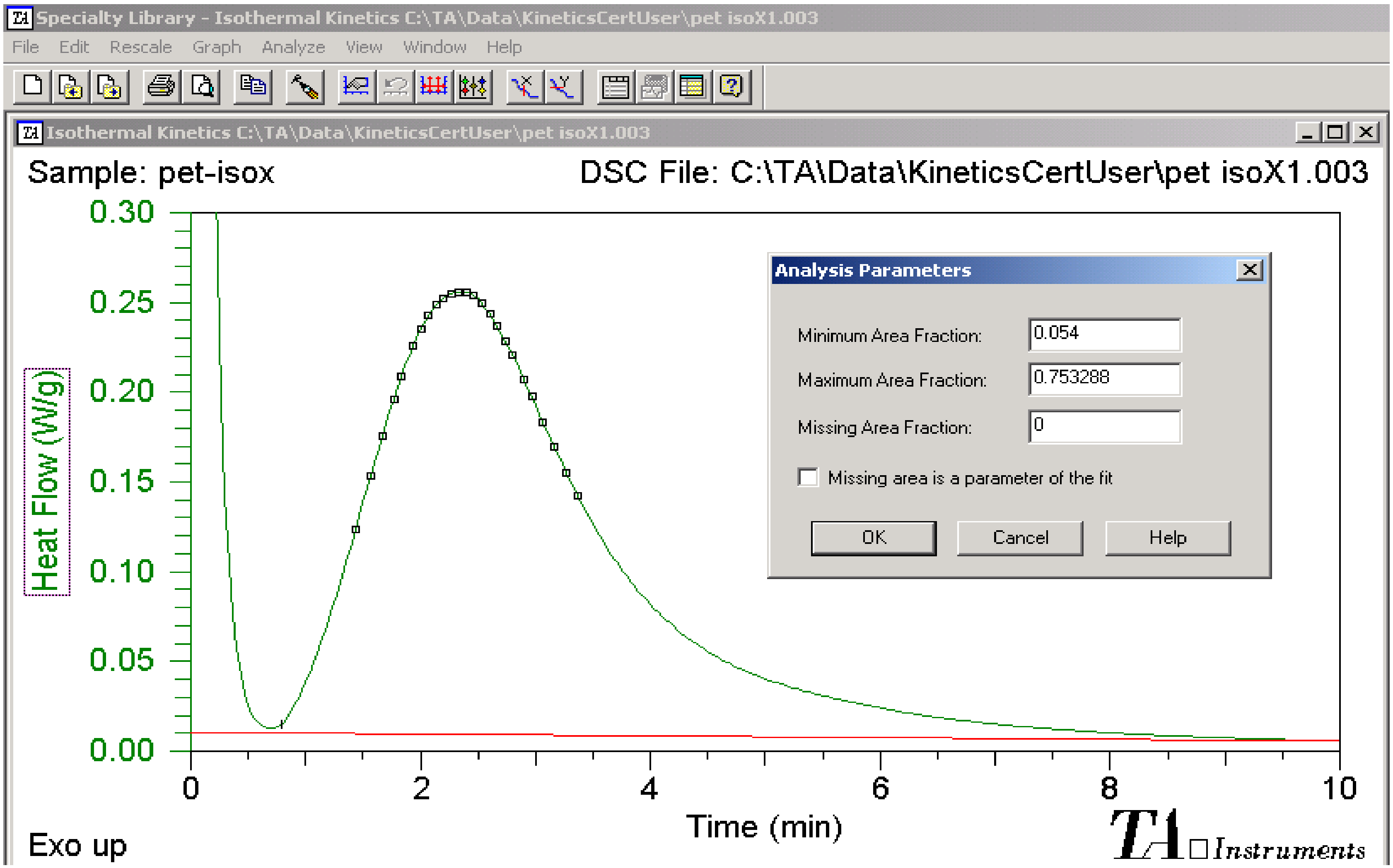


- Cooling from the melt at 50℃/min
- Equilibrating and running isothermally at a temperature
- Re-melting and re-crystallizing at another temperature
- Alternately could do “cold crystallization” kinetics

Method to Take Isothermal Crystallization Data from Single Run

- Method Log:
- 1: Sampling interval 2.0 sec/pt
- 2: Ramp 40.00 ℃/min to 295.00 ℃
- 3: Isothermal for 5.00 min
- 4: Ramp 40.00 ℃/min to 204.00 ℃
- 5: Mark end of cycle 0
- 6: Isothermal for 30.00 min
- 7: Mark end of cycle 0
- 8: Ramp 40.00 ℃/min to 295.00 ℃
- 9: Isothermal for 5.00 min
- 10: Ramp 40.00 ℃/min to 206.00 ℃
- 11: Mark end of cycle 0
- 12: Isothermal for 40.00 min
- 13: Mark end of cycle 0
- 14: Ramp 40.00 ℃/min to 295.00 ℃
- 15: Isothermal for 5.00 min
- 16: Ramp 40.00 ℃/min to 208.00 ℃
- 17: Mark end of cycle 0
- 18: Isothermal for 50.00 min
- 19: Mark end of cycle 0
- 20: Ramp 40.00 ℃/min to 295.00 ℃
- 21: Isothermal for 5.00 min
- 22: Ramp 40.00 ℃/min to 210.00 ℃
- 23: Mark end of cycle 0
- 24: Isothermal for 60.00 min
- 25: Mark end of cycle 0
- 26: Ramp 40.00 ℃/min to 295.00 ℃
- 27: Isothermal for 5.00 min
- 28: Ramp 40.00 ℃/min to 212.00 ℃
- 29: Mark end of cycle 0
- 30: Isothermal for 80.00 min
- 31: Mark end of cycle 0
- 32: Ramp 40.00 ℃/min to 295.00 ℃
- 33: Isothermal for 5.00 min
- 34: Ramp 40.00 ℃/min to 214.00 ℃
- 35: Mark end of cycle 0
- 36: Isothermal for 100.00 min
- 37: Mark end of cycle 0
- 38: Ramp 40.00 ℃/min to 295.00 ℃
- 39: Isothermal for 5.00 min
- 40: Ramp 40.00 ℃/min to 216.00 ℃
- 42: Mark end of cycle 0
- 43: Isothermal for 100.00 min
- 44: Mark end of cycle 0
- 45: Ramp 40.00 ℃/min to 295.00 ℃
- 46: Isothermal for 5.00 min
- 47: Ramp 40.00 ℃/min to 218.00 ℃
- 48: Mark end of cycle 0
- 49: Isothermal for 120.00 min
- 50: End of method

Partial Area Analysis



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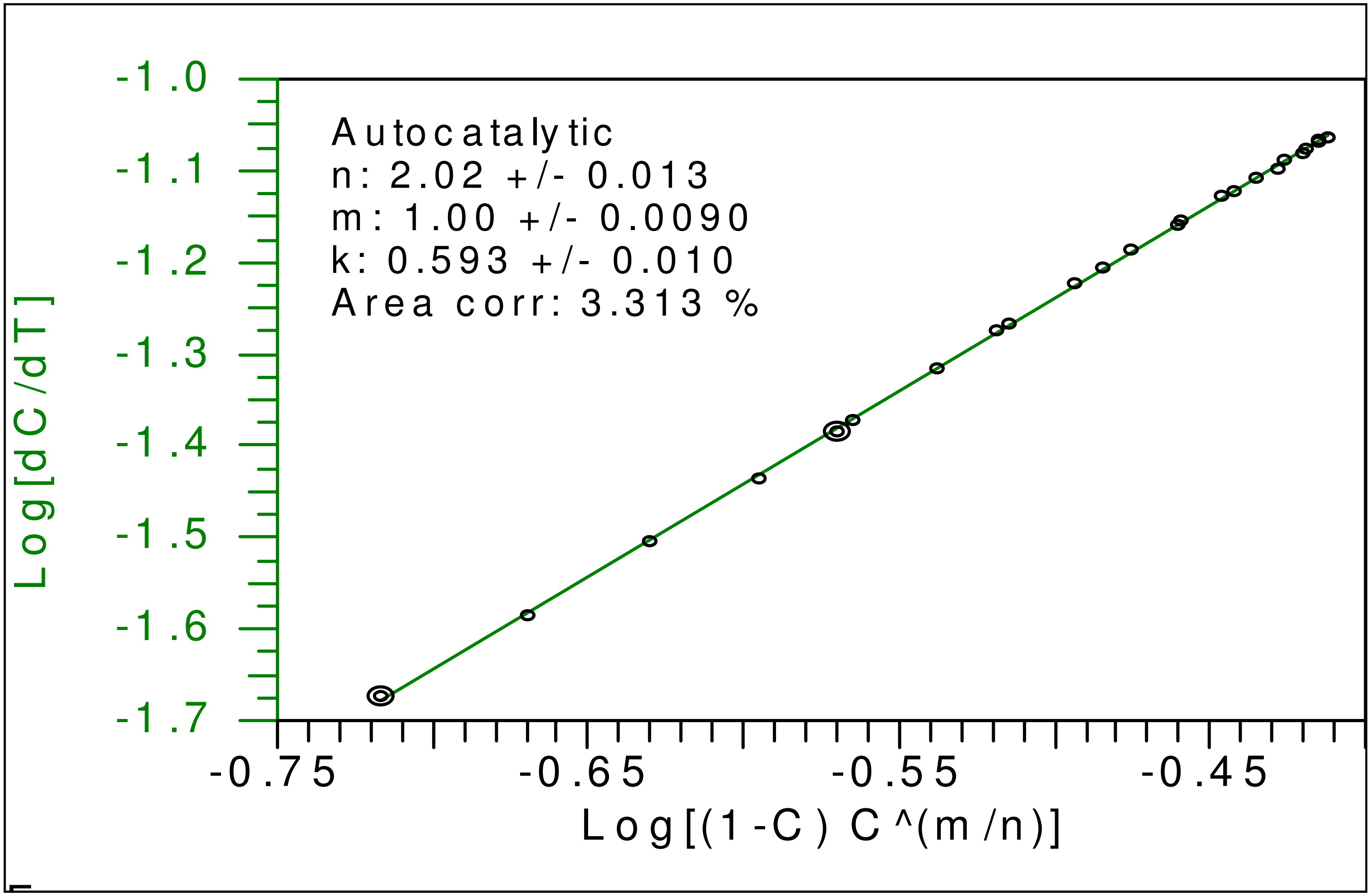
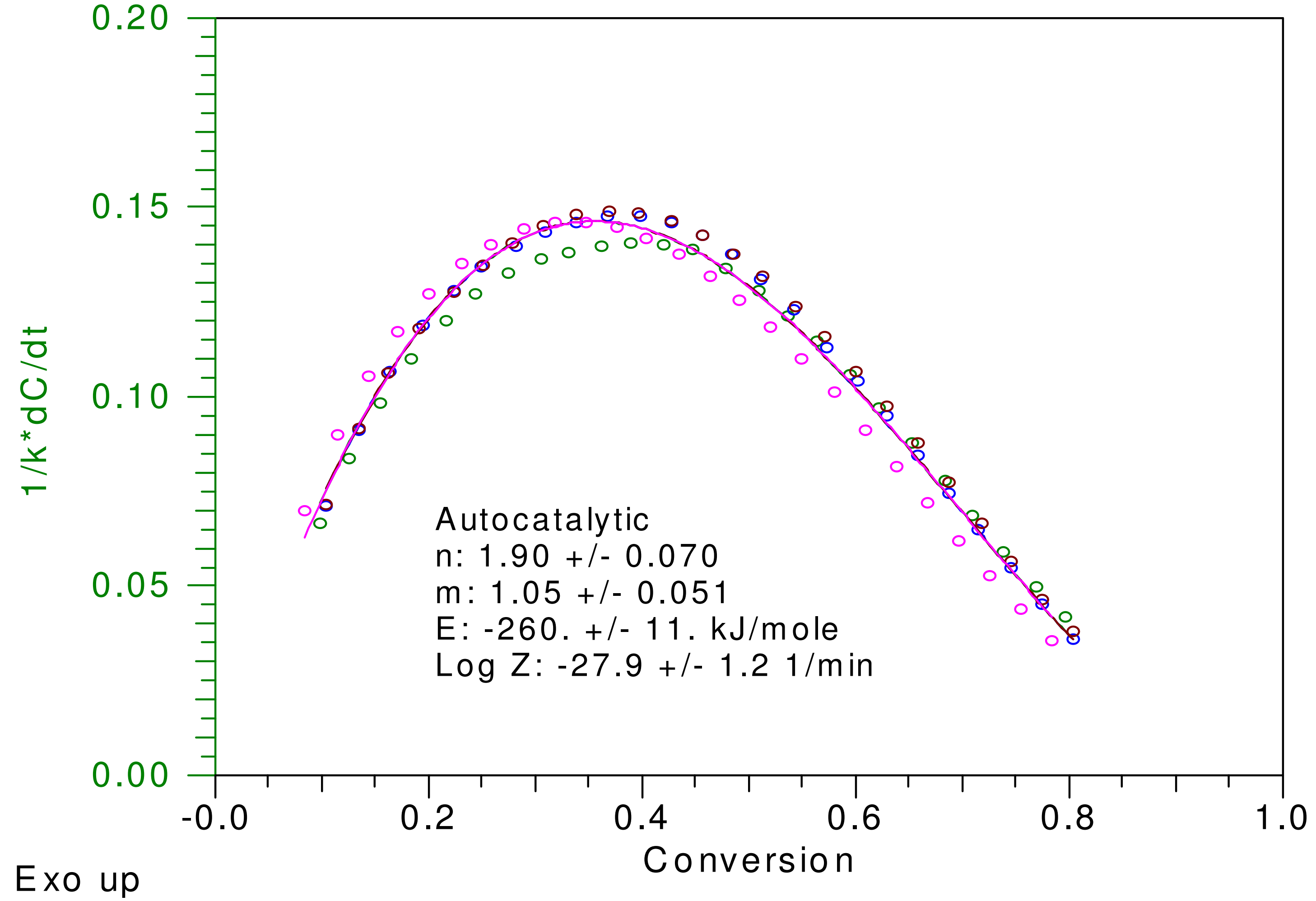
Single Run Log-Log of PET

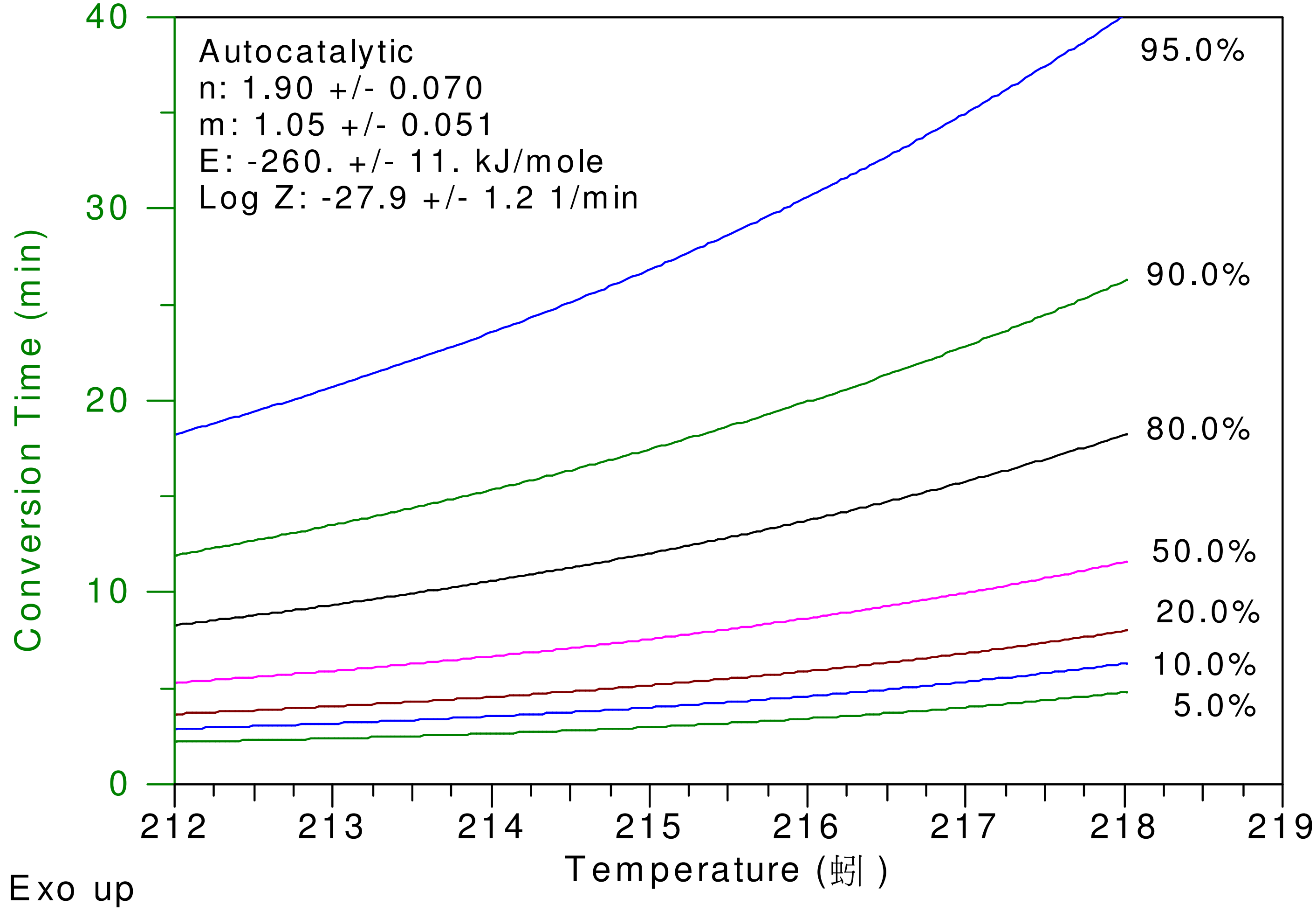


Linear fit

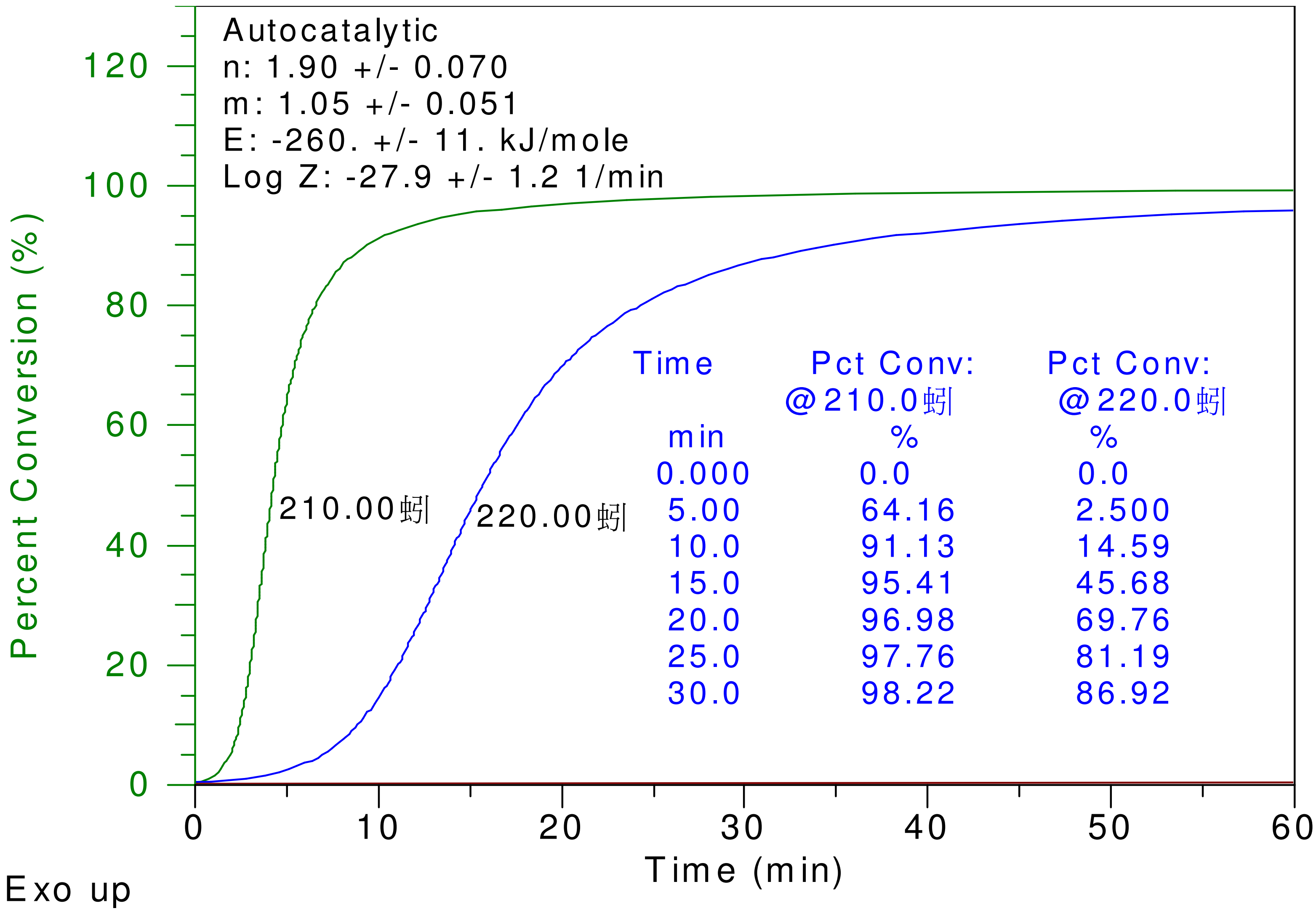
Multiple Run Analysis - PET



Conversion Time vs. T at Selected % Conversions



Percent Crystallized vs. Time at Selected temperatures



Tips and Precautions

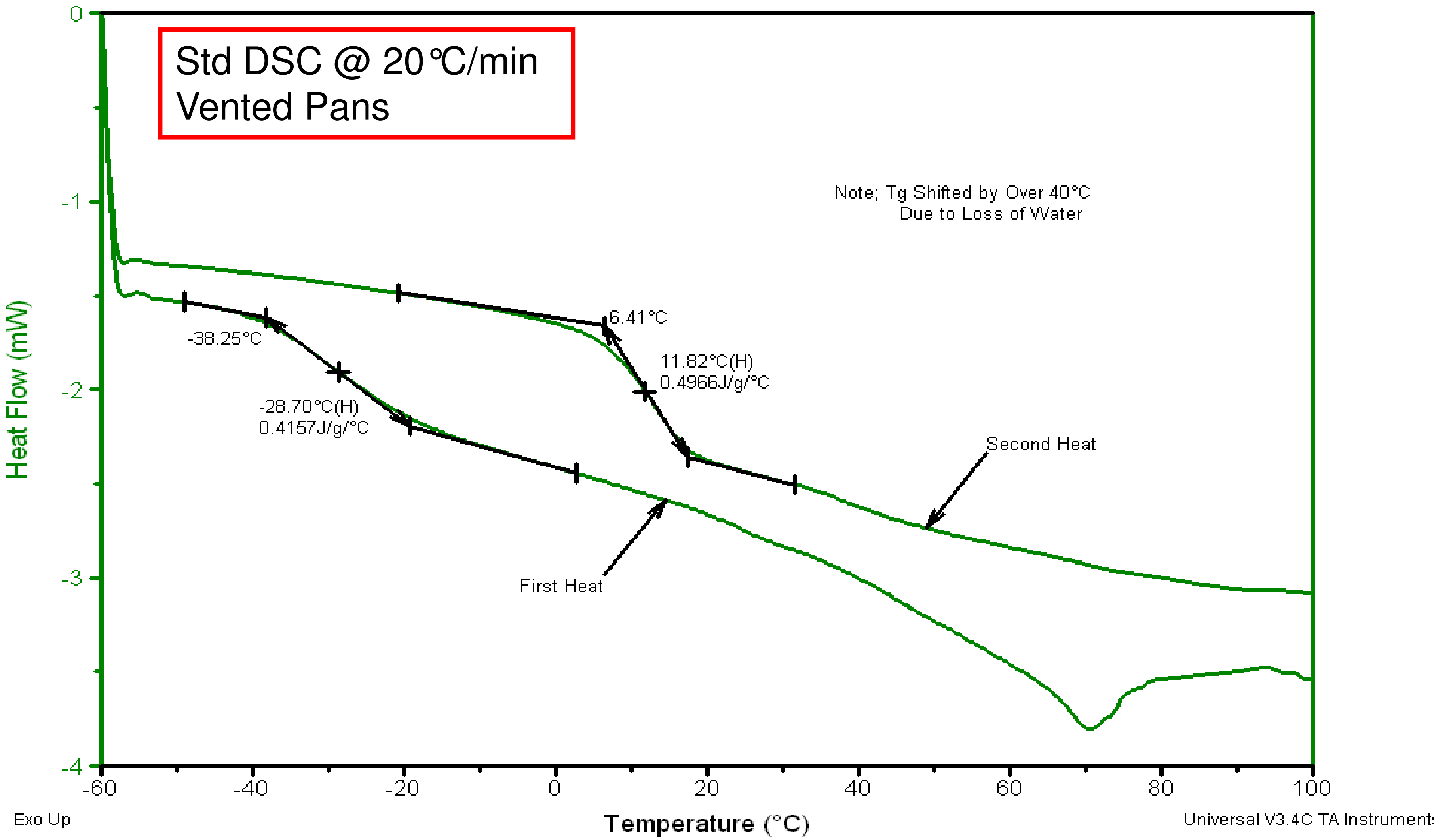
- Sample Prep – thin film
- Use same sample for each isothermal test
- Sample must be completely melted before cooling to crystallization (e.g., hold for 5 minutes above melt transition)
- Samples must not degrade in the melt
  - Purge out all oxygen before first melt
- Crimp or seal sample such that no material oozes out of pan
- Curve fitting Parameters are descriptive

Pharmaceuticals

Pharmaceuticals

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

Tg of Sucrose Varies with Moisture Content



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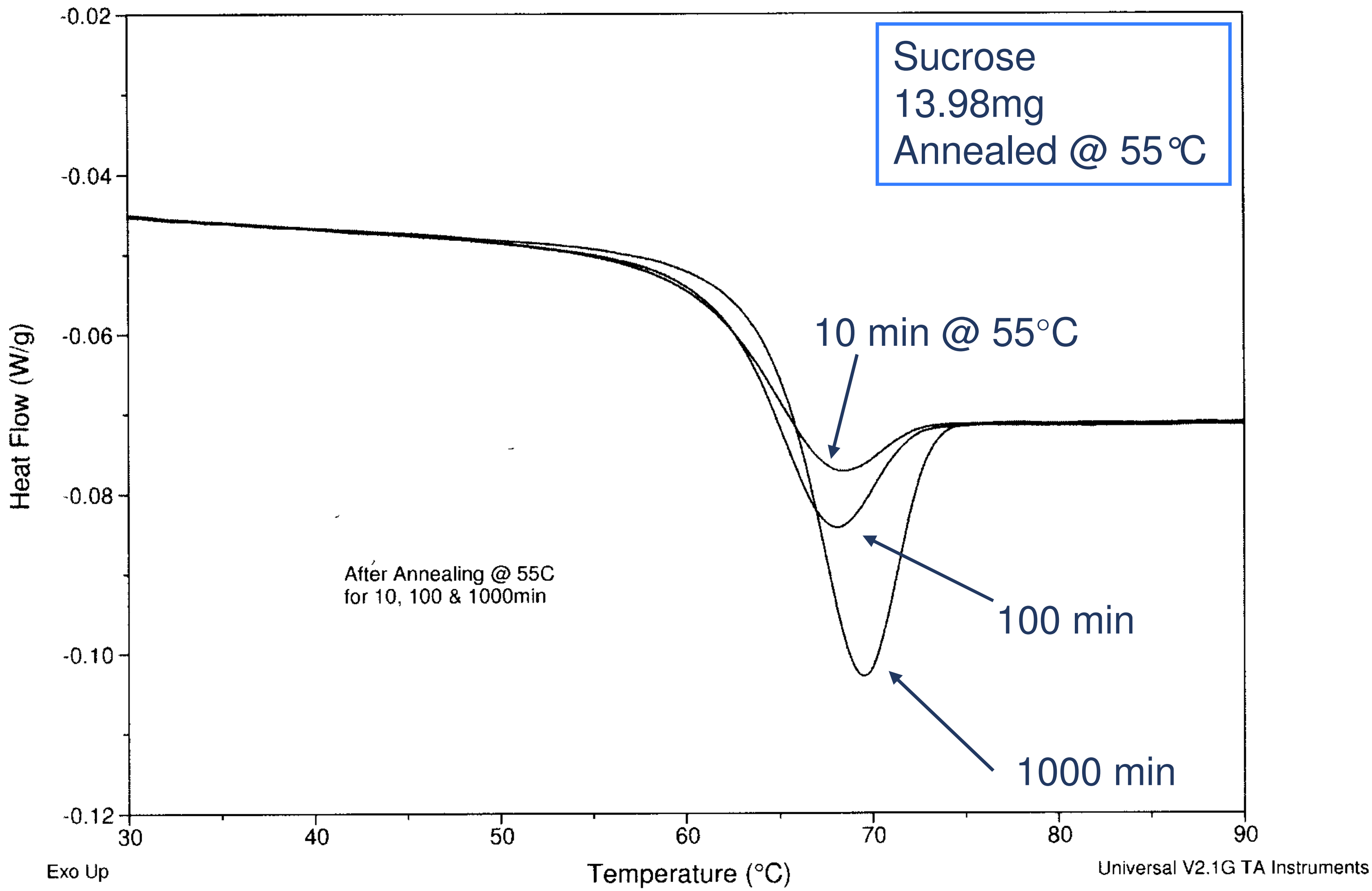
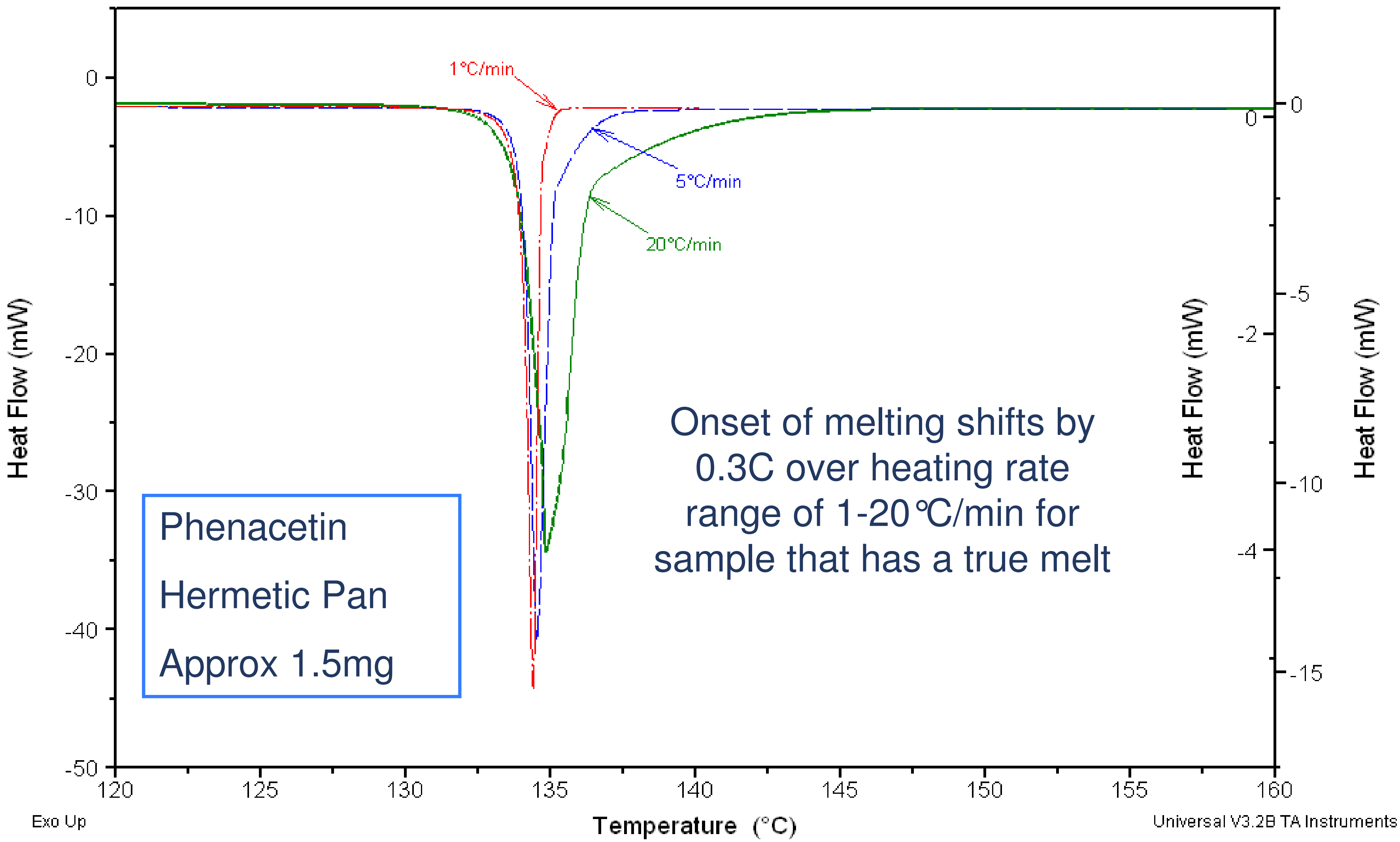
Structure Changes With Time

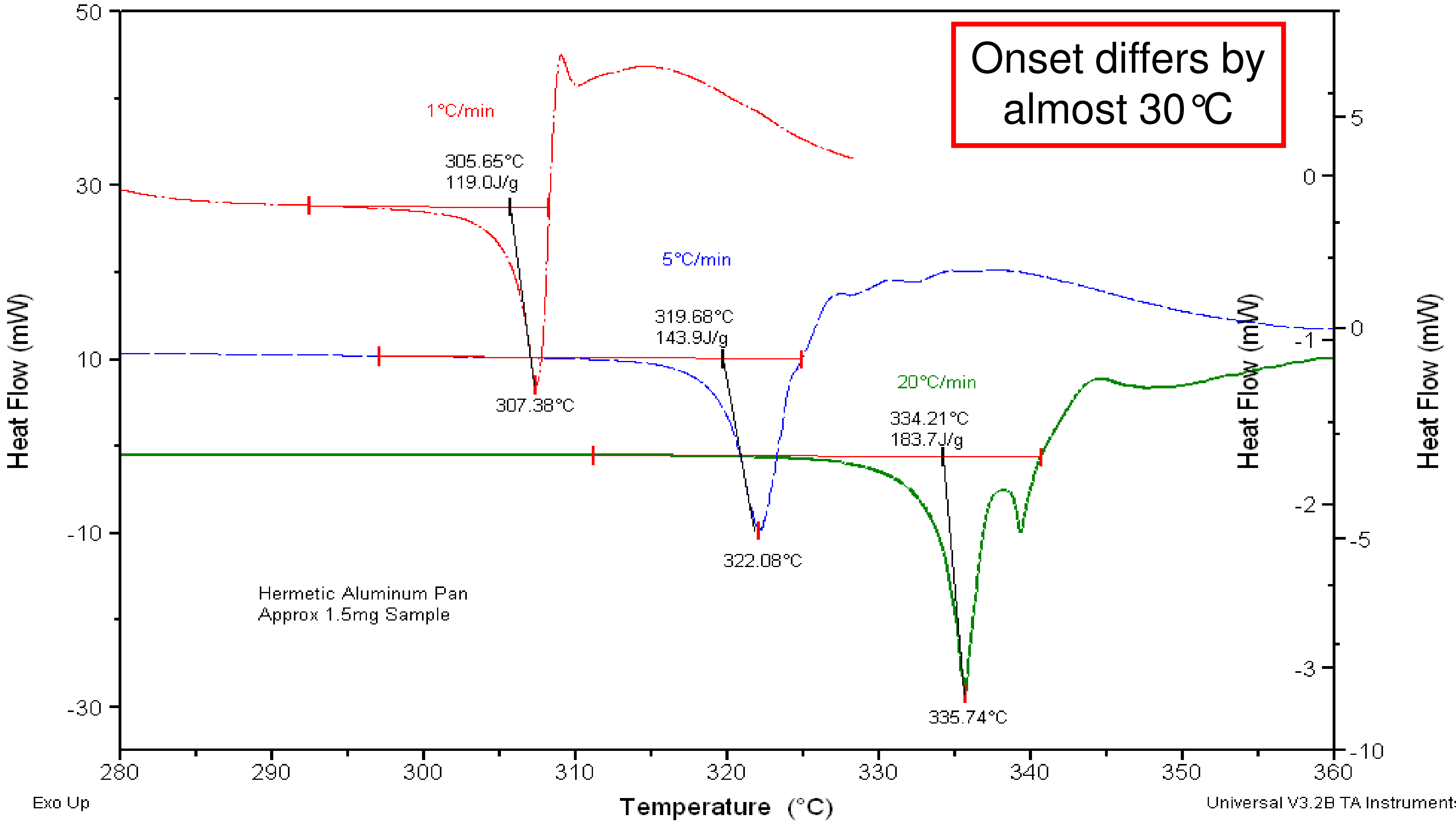


Melting is Not Heating Rate Dependent

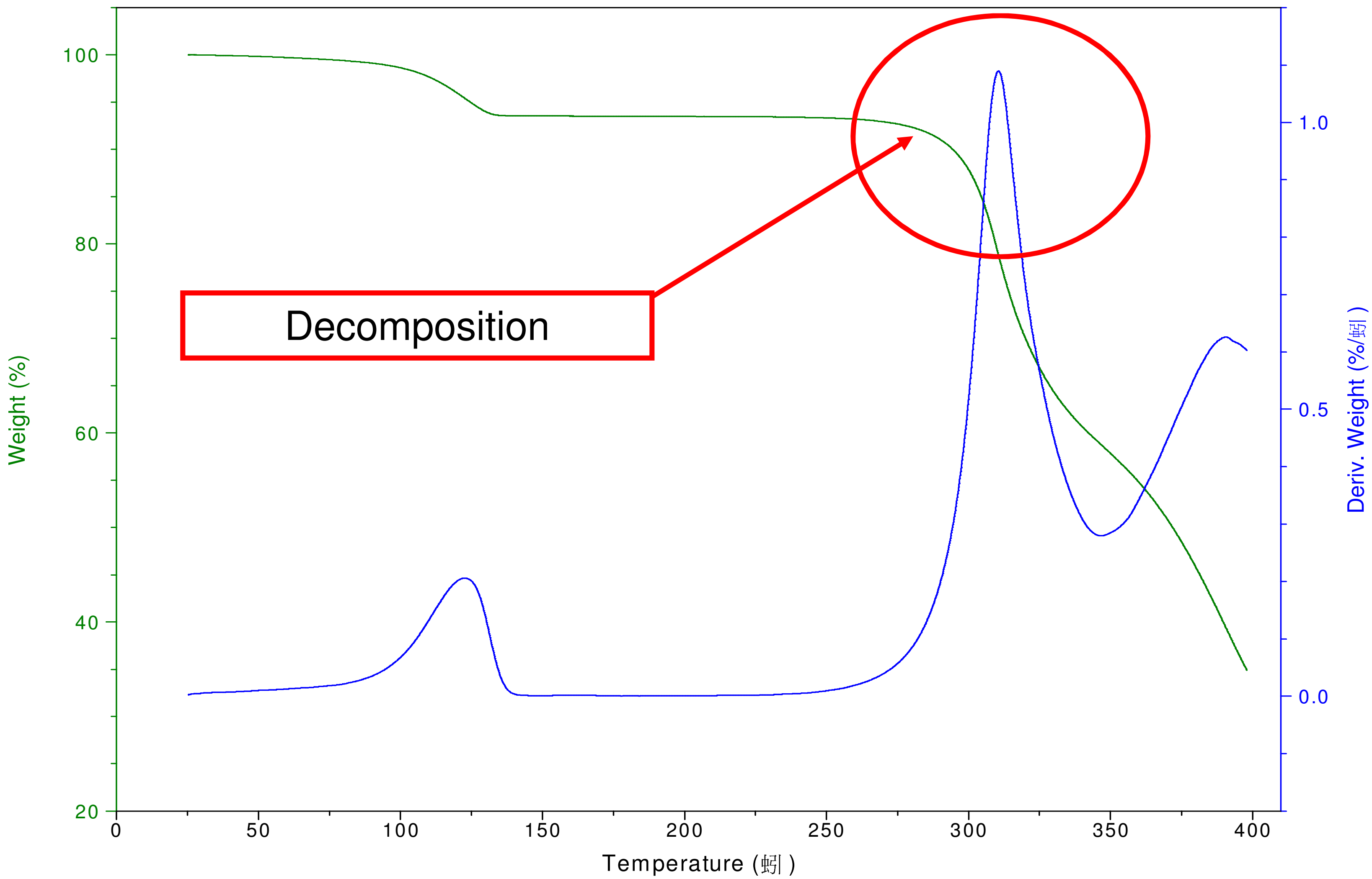


Ciprofloxacin Hydrochloride Decomposes

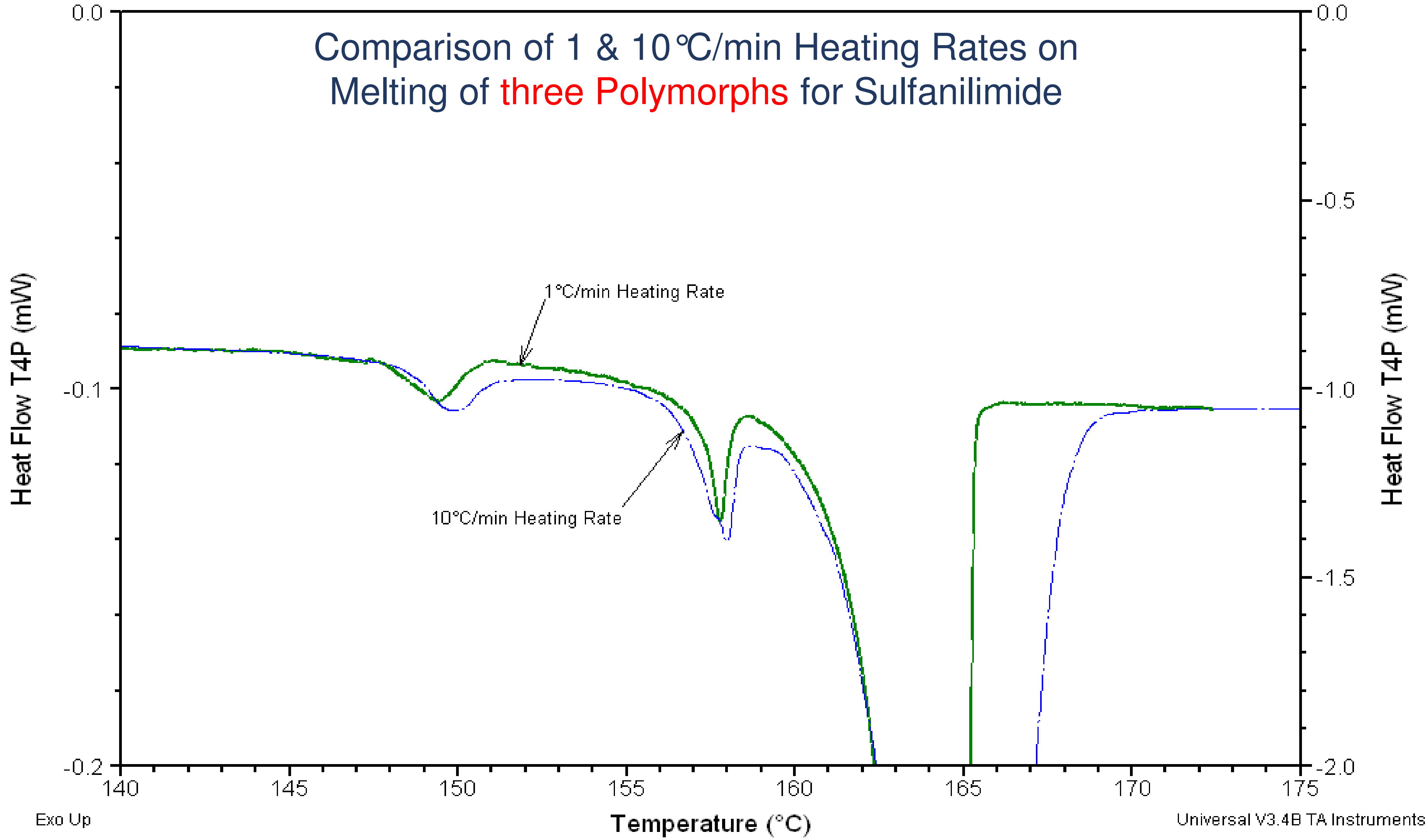
Decomposition is kinetic (heating rate dependent)



TGA of Ciprofloxacin Hydrochloride



Sulfanilimide



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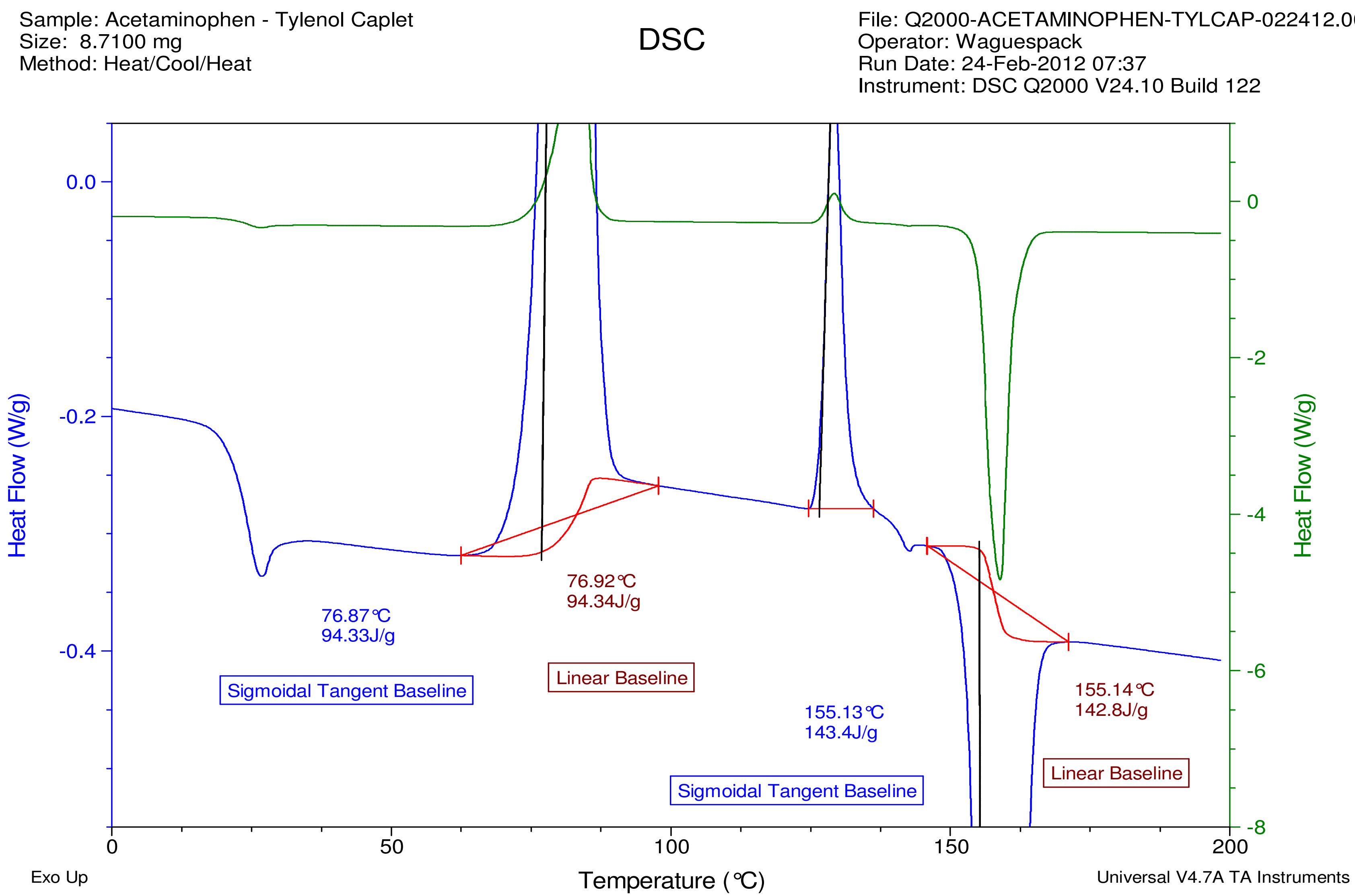
Linear or Sigmoidal Baseline?



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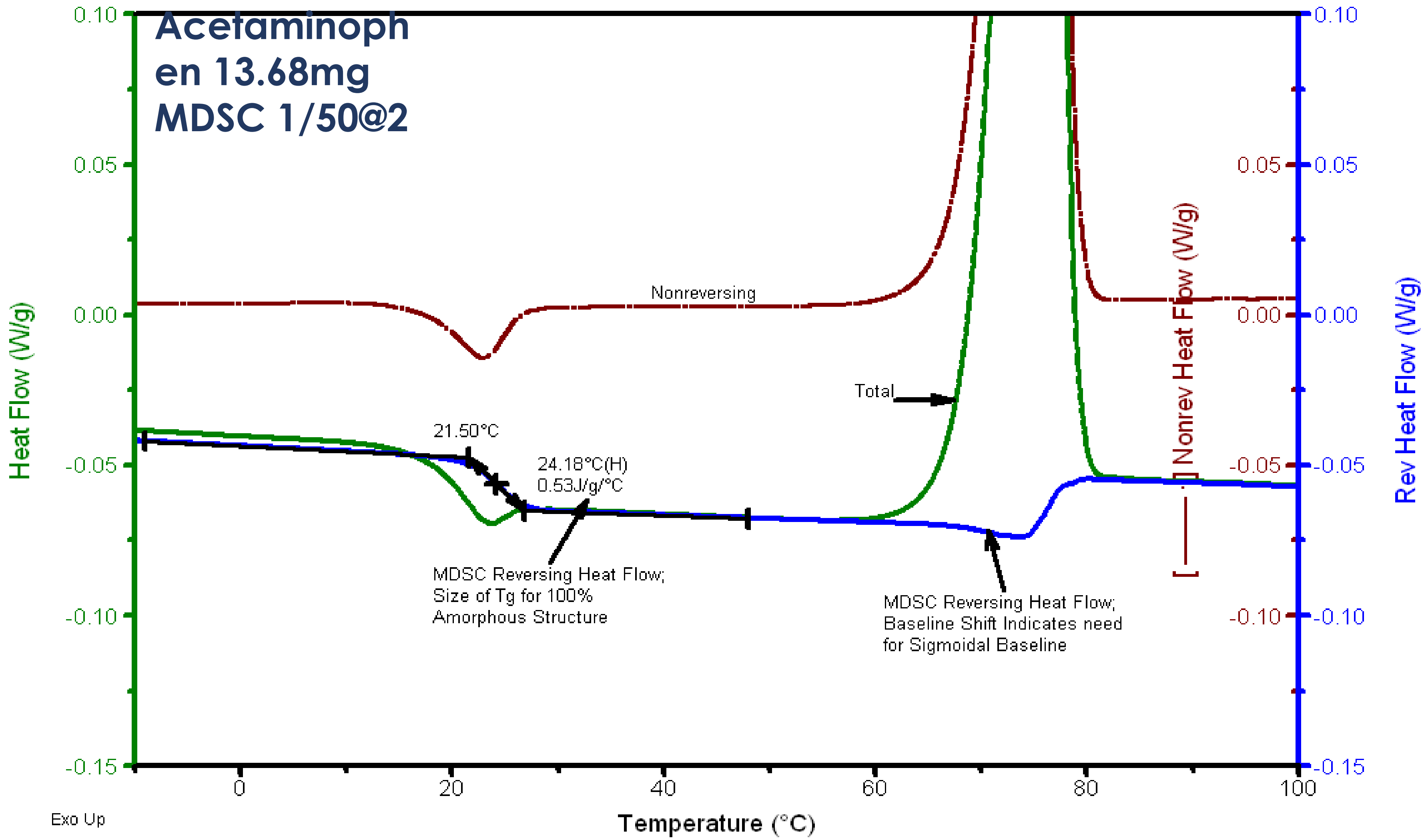
MDSC Analysis of Acetaminophen



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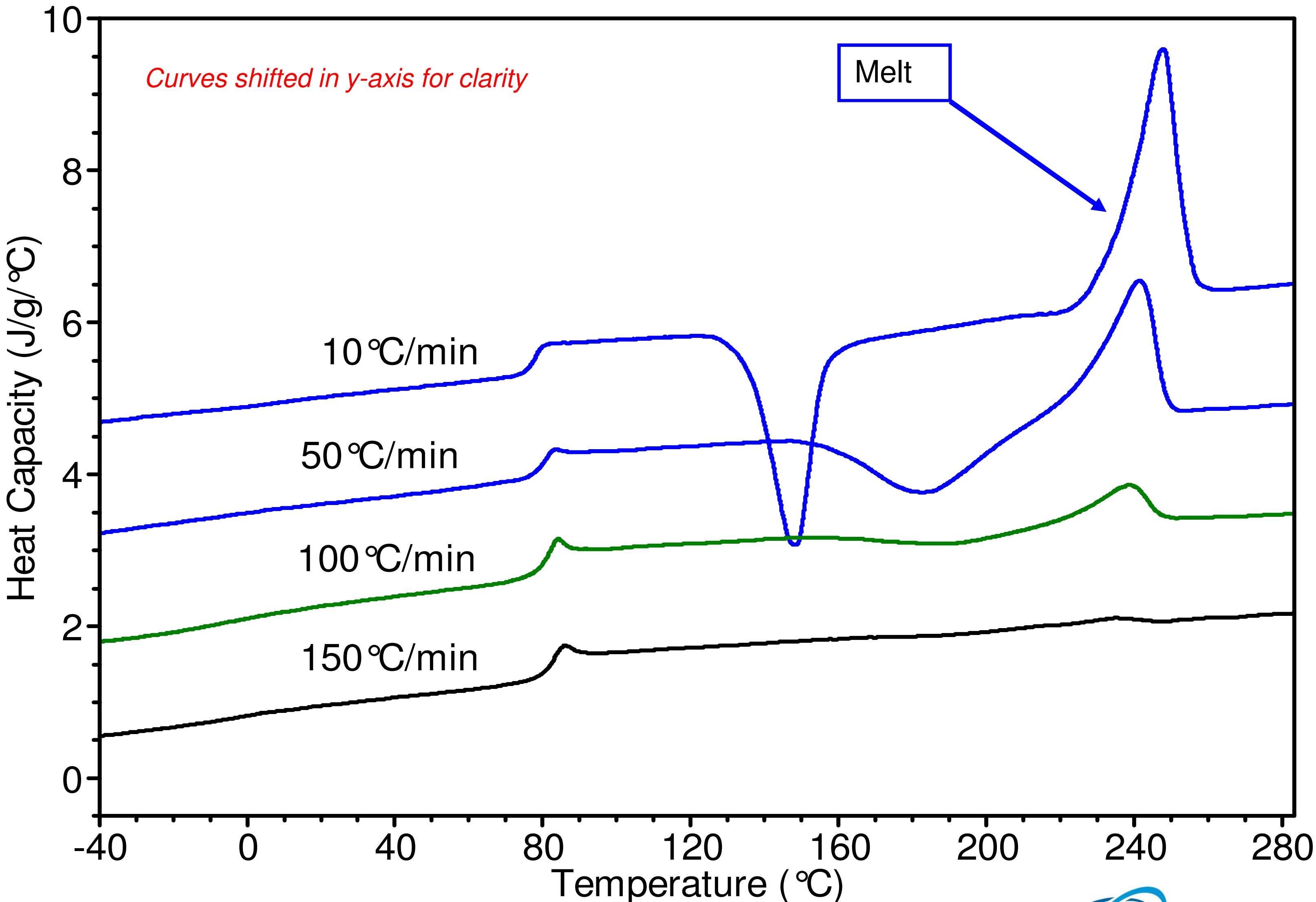
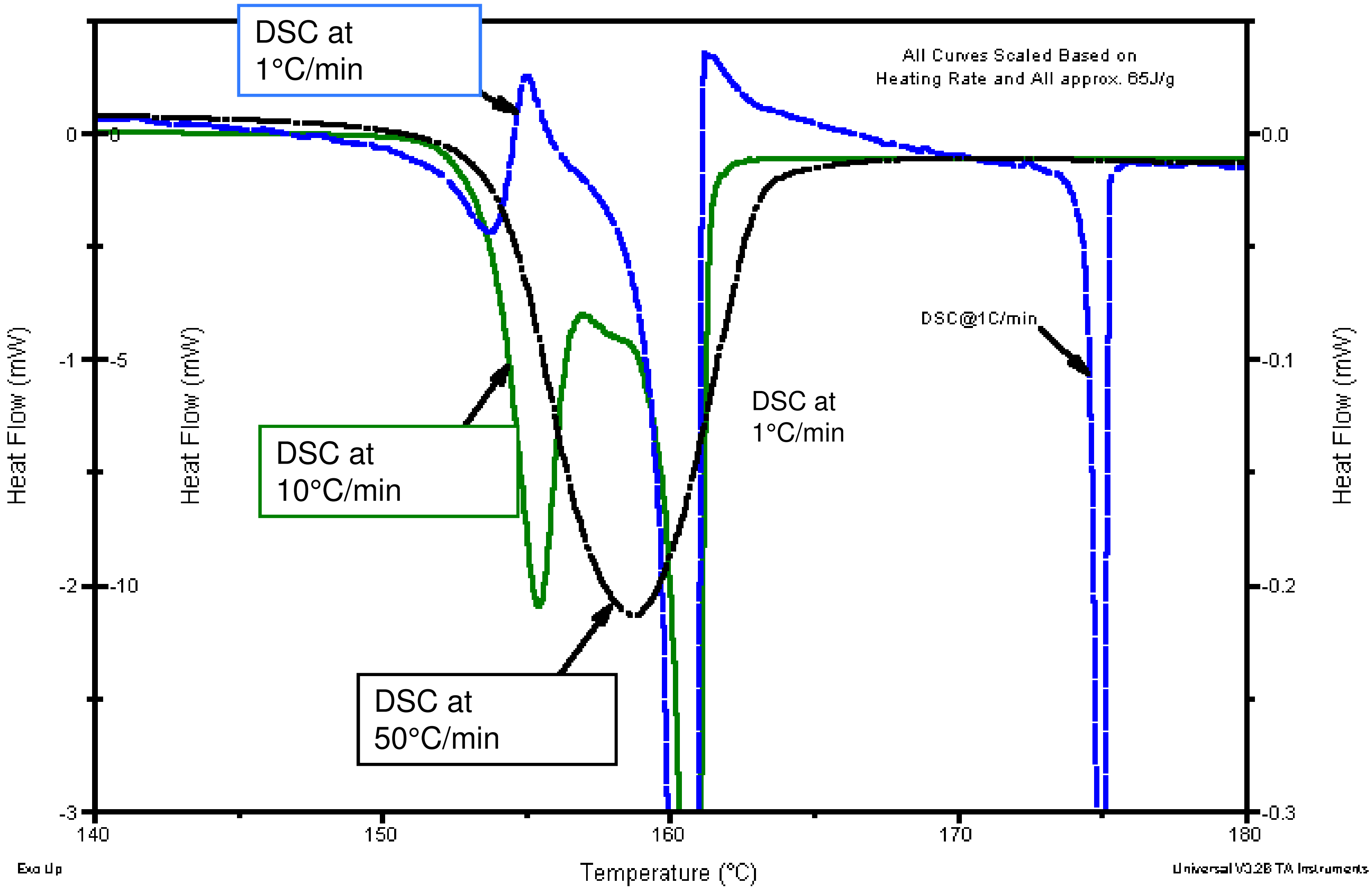
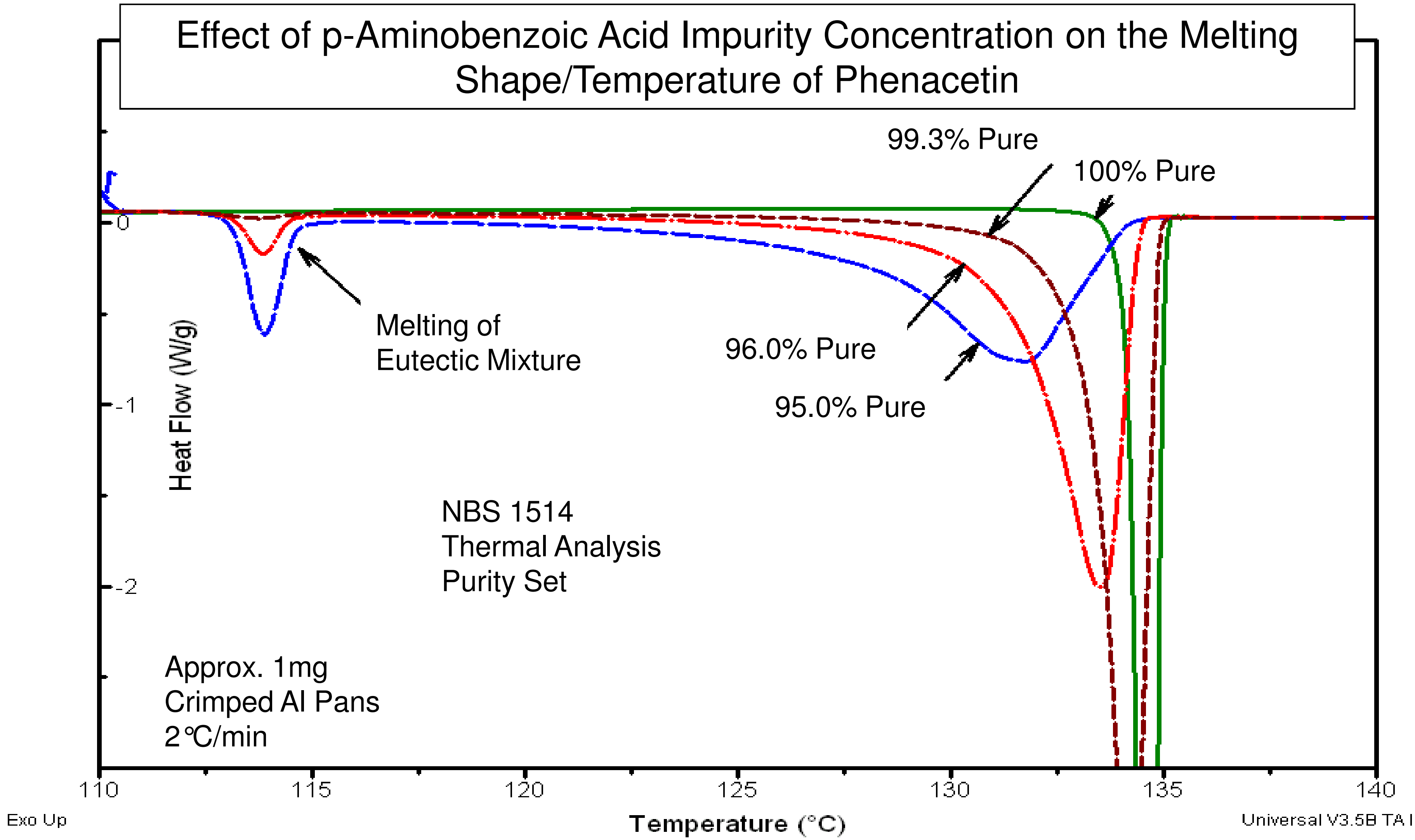
Effect of Heating Rate on Melting



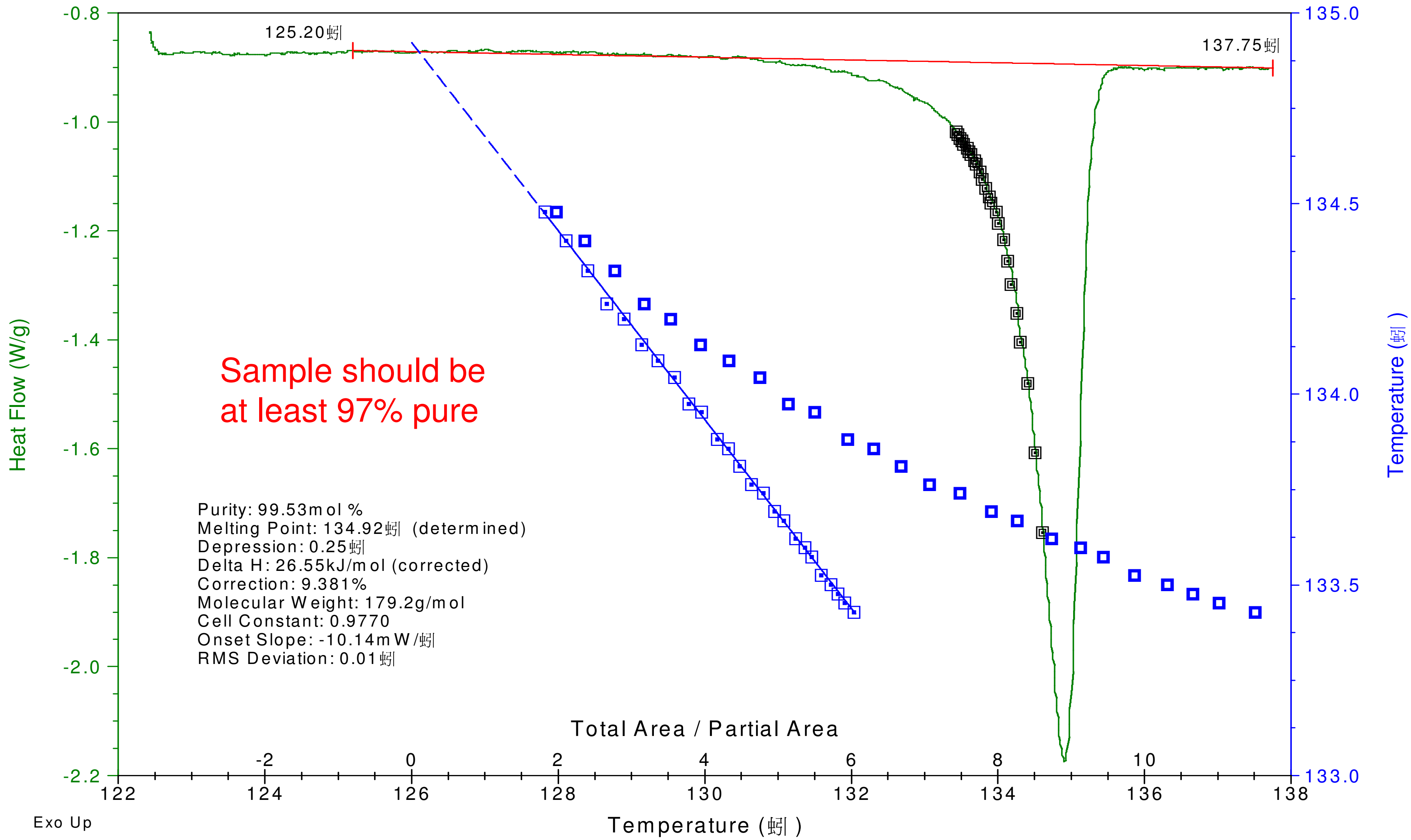
Effect of Heating Rate on Polymorph



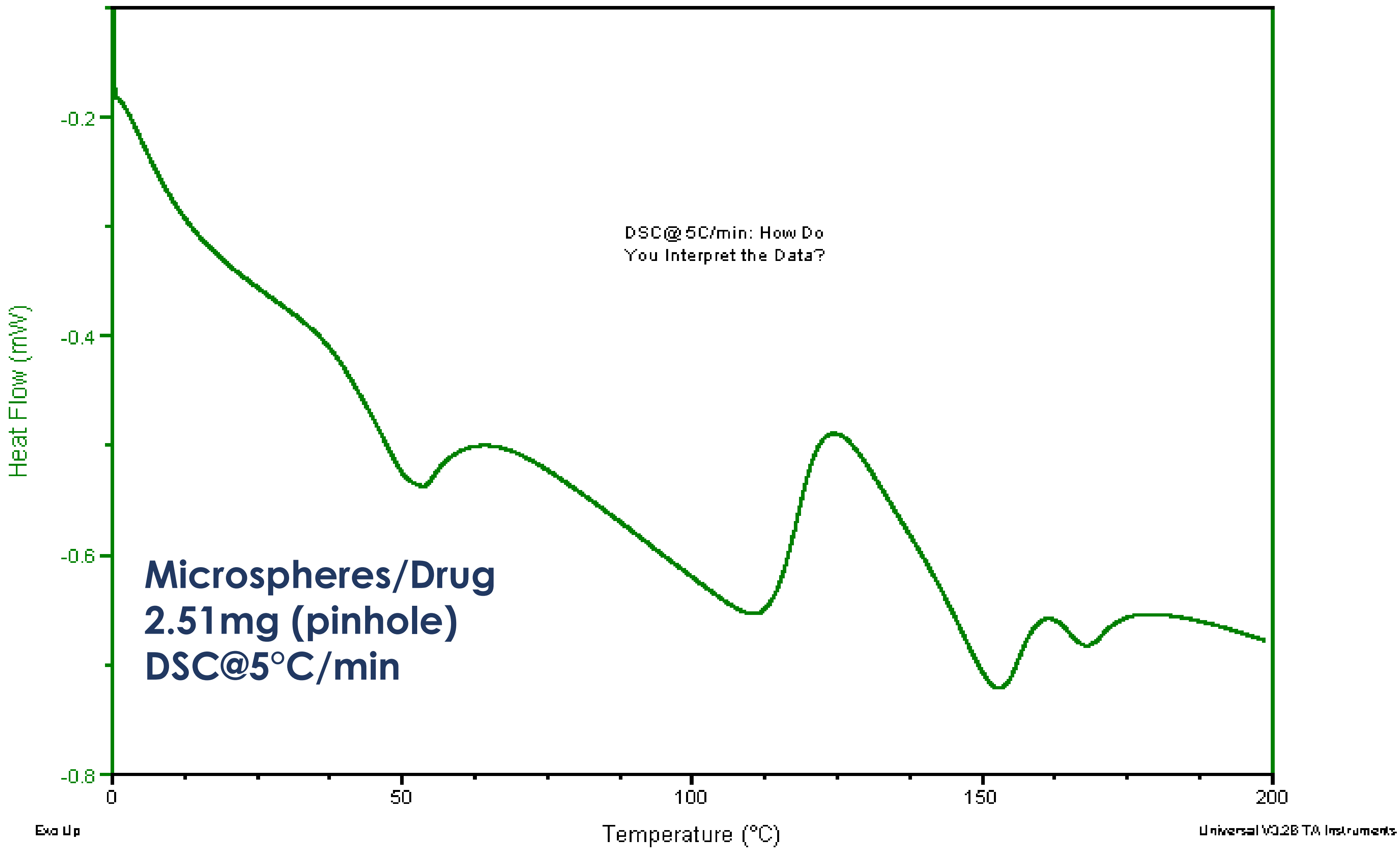
Effect of Impurities on Melting



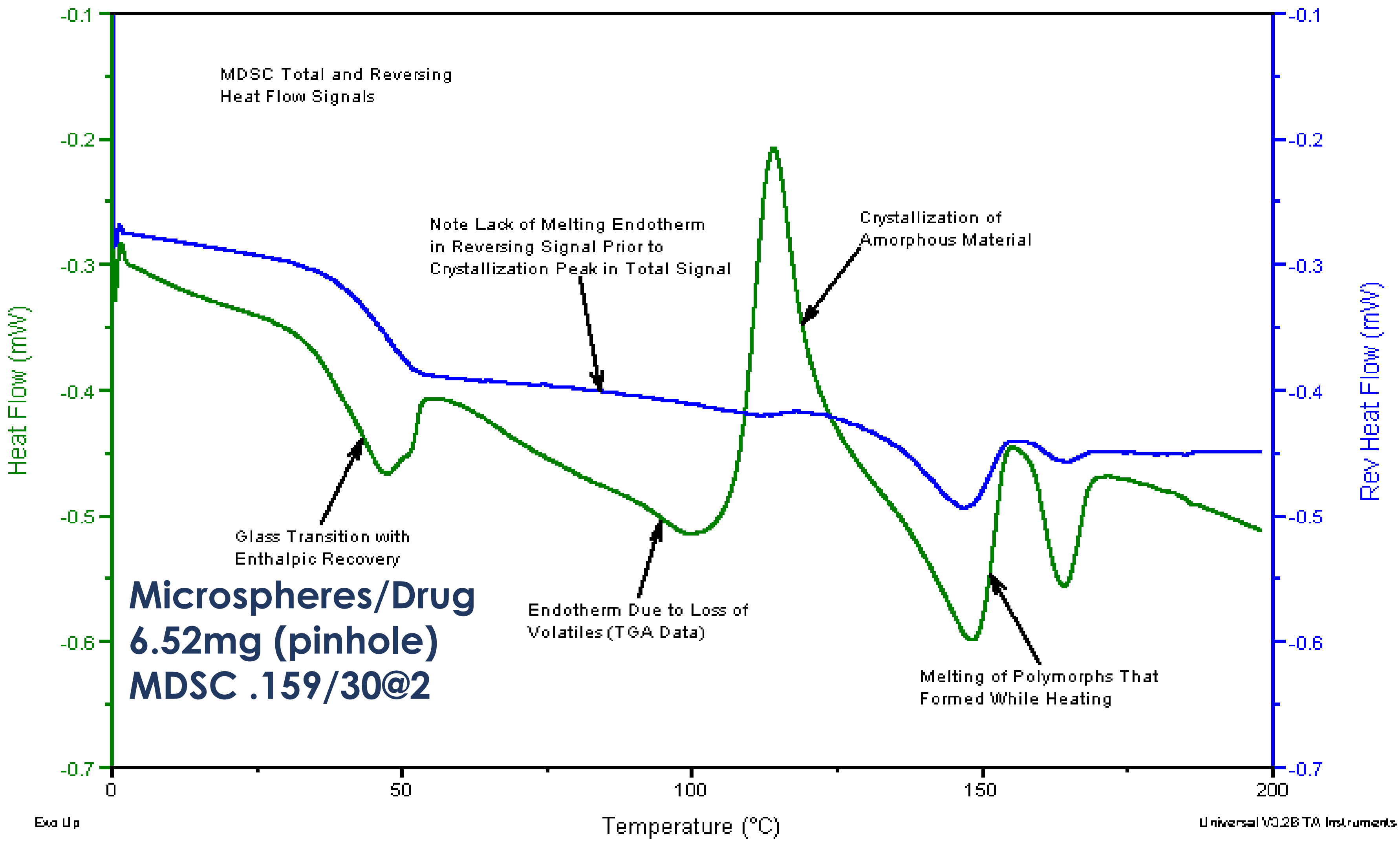
Van't Hoff Purity Calculation



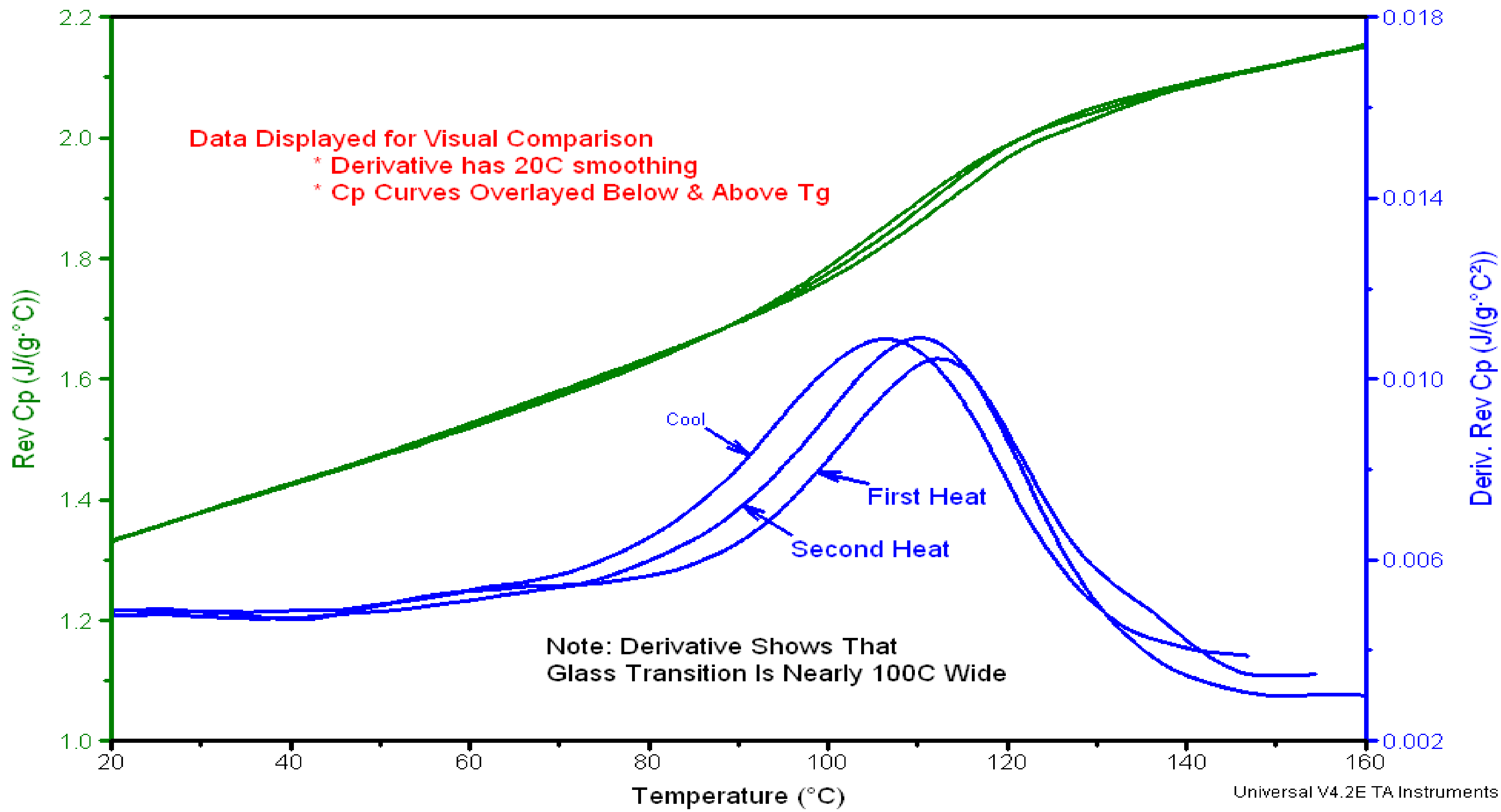
DSC @ 5°C/min for Drug Microspheres



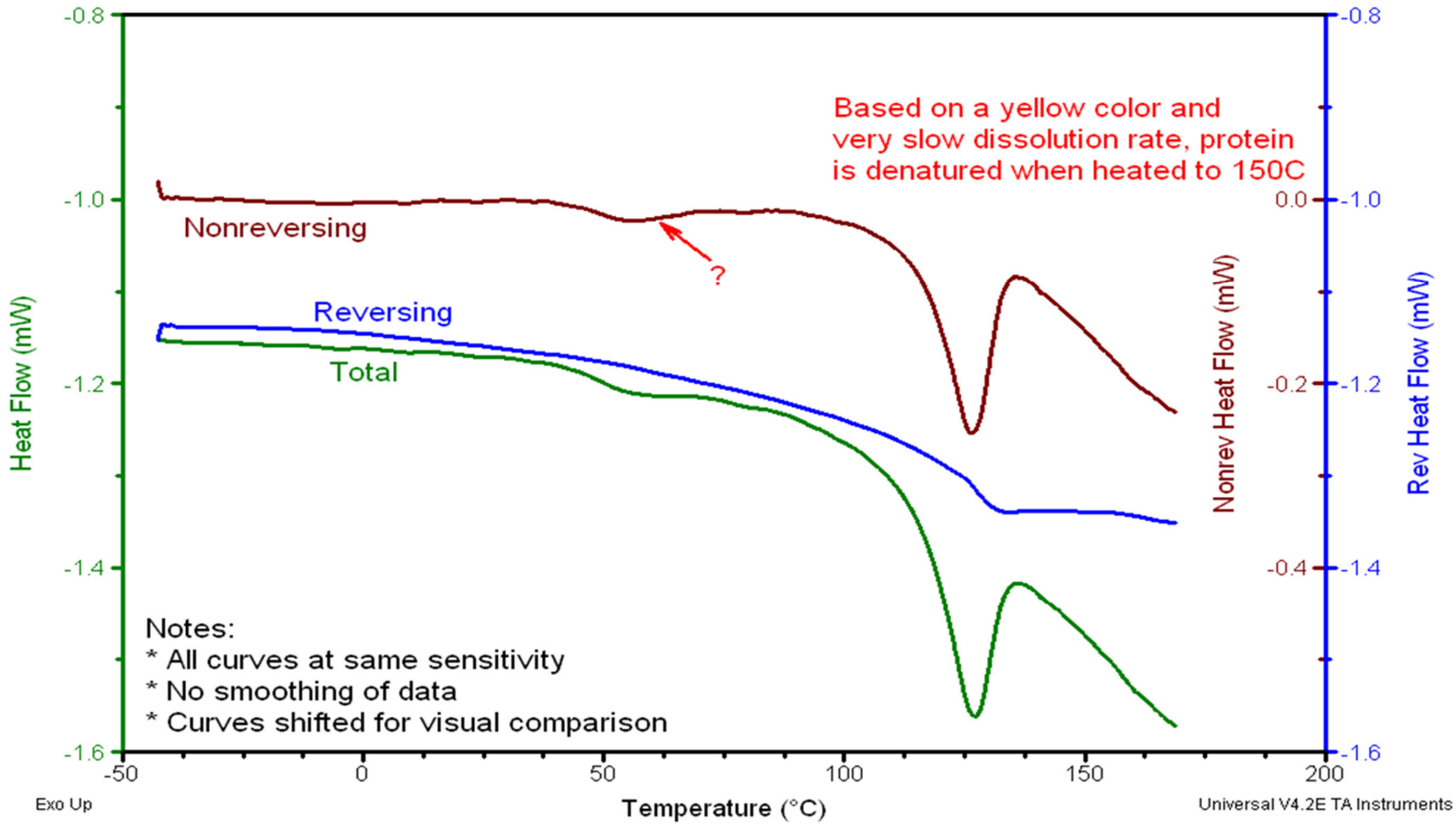
MDSC for Drug Microspheres



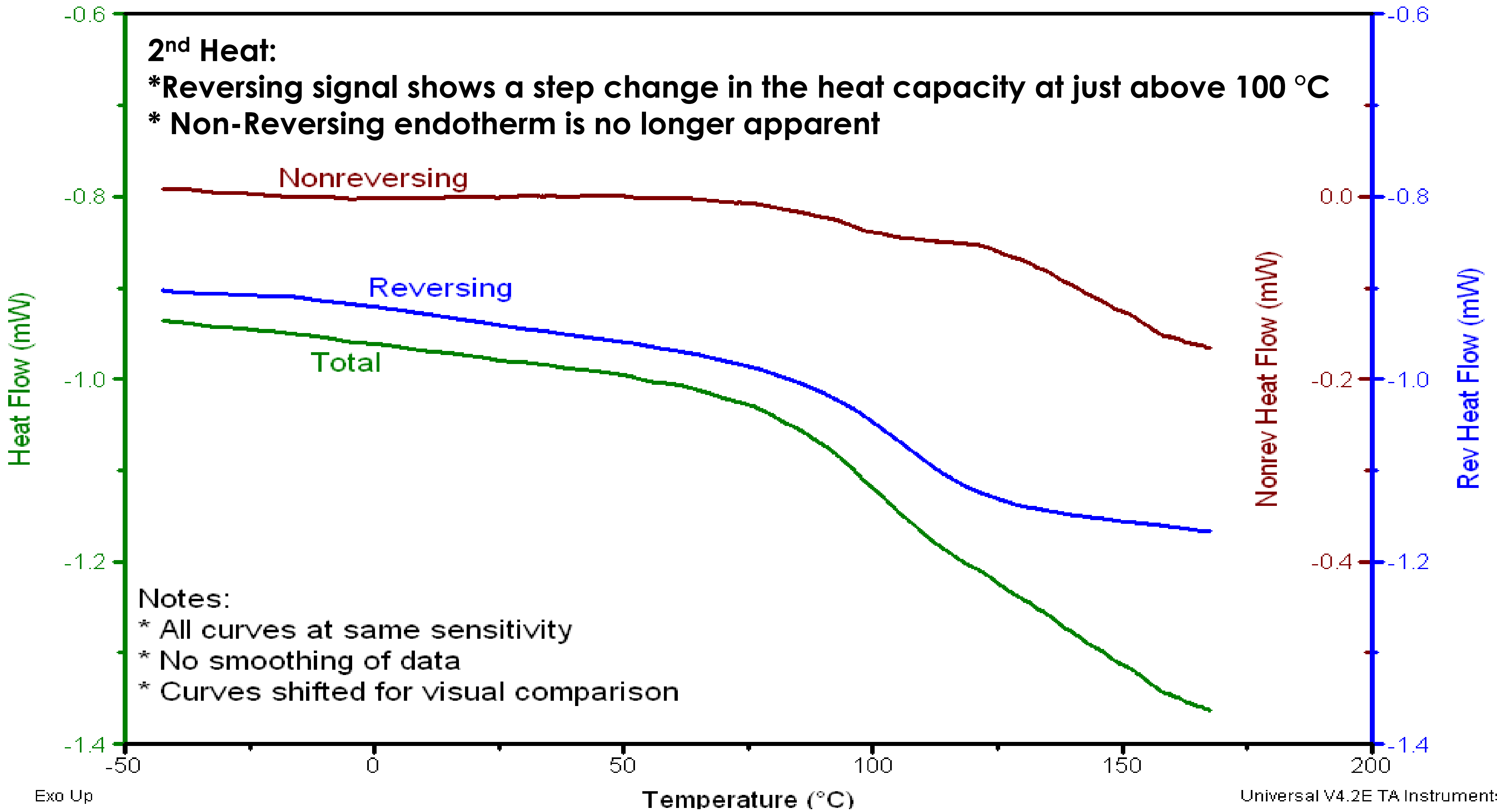
Optimized MDSC Results for Casein Protein



MDSC of Egg Albumin – 1st Heat



MDSC of Egg Albumin – 2nd Heat



Specific Heat Capacity

What is Heat Capacity?

- Heat capacity is the amount of heat required to raise or lower the temperature of a material by 1°C.
- Specific heat capacity refers to a specific mass and temperature change for the material (J/g°C)

Why is Heat Capacity Important?

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

Measuring Heat Capacity

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

$$dH/dt = Cp\ dT/dt$$

$$Cp = \left[\frac{dH/dt}{dT/dt} \right] \times K$$

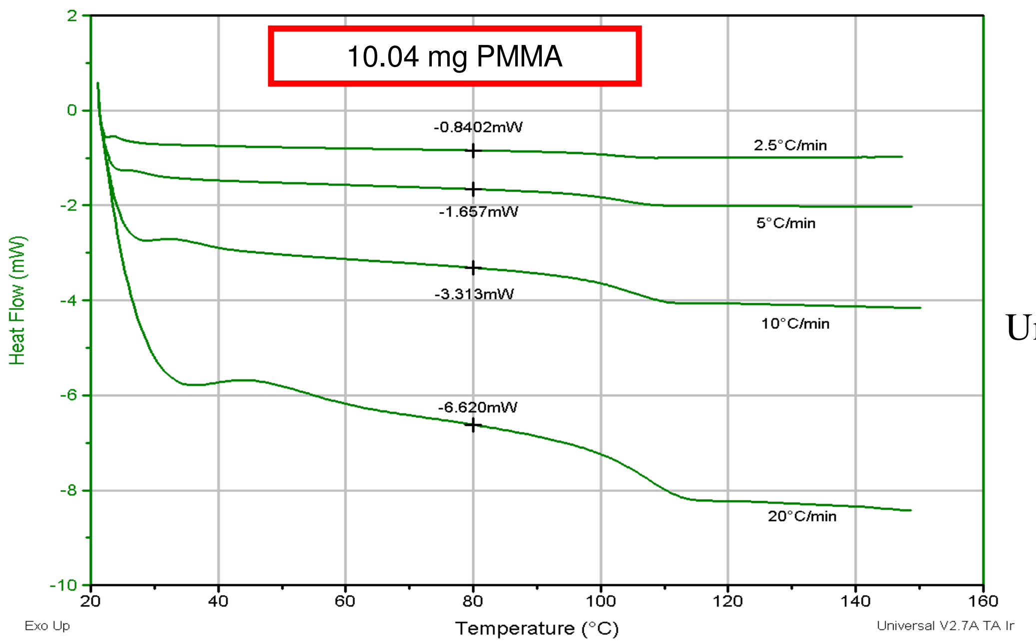
Sample Heat Capacity

Heat Flow

Heating Rate

Calibration constant

Calculating heat capacity from heat flow data



$$\text{Uncal. Cp}\left(\frac{\text{J}}{\text{g.°C}}\right) = \frac{\text{Heat flow}\left(\frac{\text{mJ}}{\text{sec}}\right)}{\text{Heat Rate}\left(\frac{\text{°C}}{\text{min}}\right) \text{ x wt (mg)}} \text{ x } 60\left(\frac{\text{sec}}{\text{min}}\right)$$

Heating rate (℃/min)	Heat flow (mW)	Uncalibrated Cp (J/g℃)
2.5	0.8402	2.008
5	1.657	1.980
10	3.313	1.980
20	6.620	1.978

Actual Cp = Apparent Cp x K (the heat capacity calibration constant)

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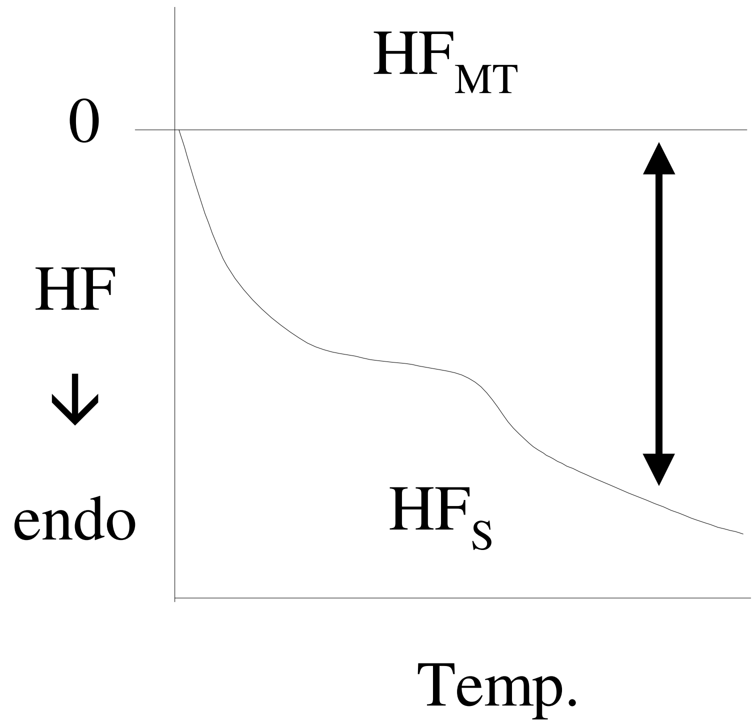
Conventional DSC Cp Measurement

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



Where:

K = Calibration constant

HF_S = Differential heat flow with sample

HF_{MT} = Differential heat flow with empty pans

wt = weight of sample

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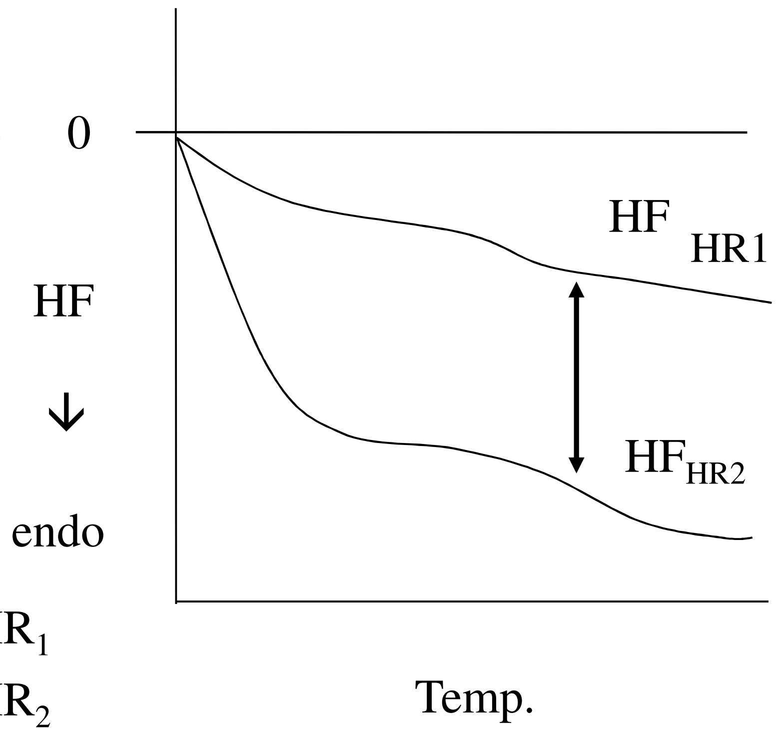
Alternative DSC Cp Measurement

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



Where:

K = Calibration constant

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

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

HR_2 = Heating rate 2

HR_1 = Heating rate 1

wt = weight of sample

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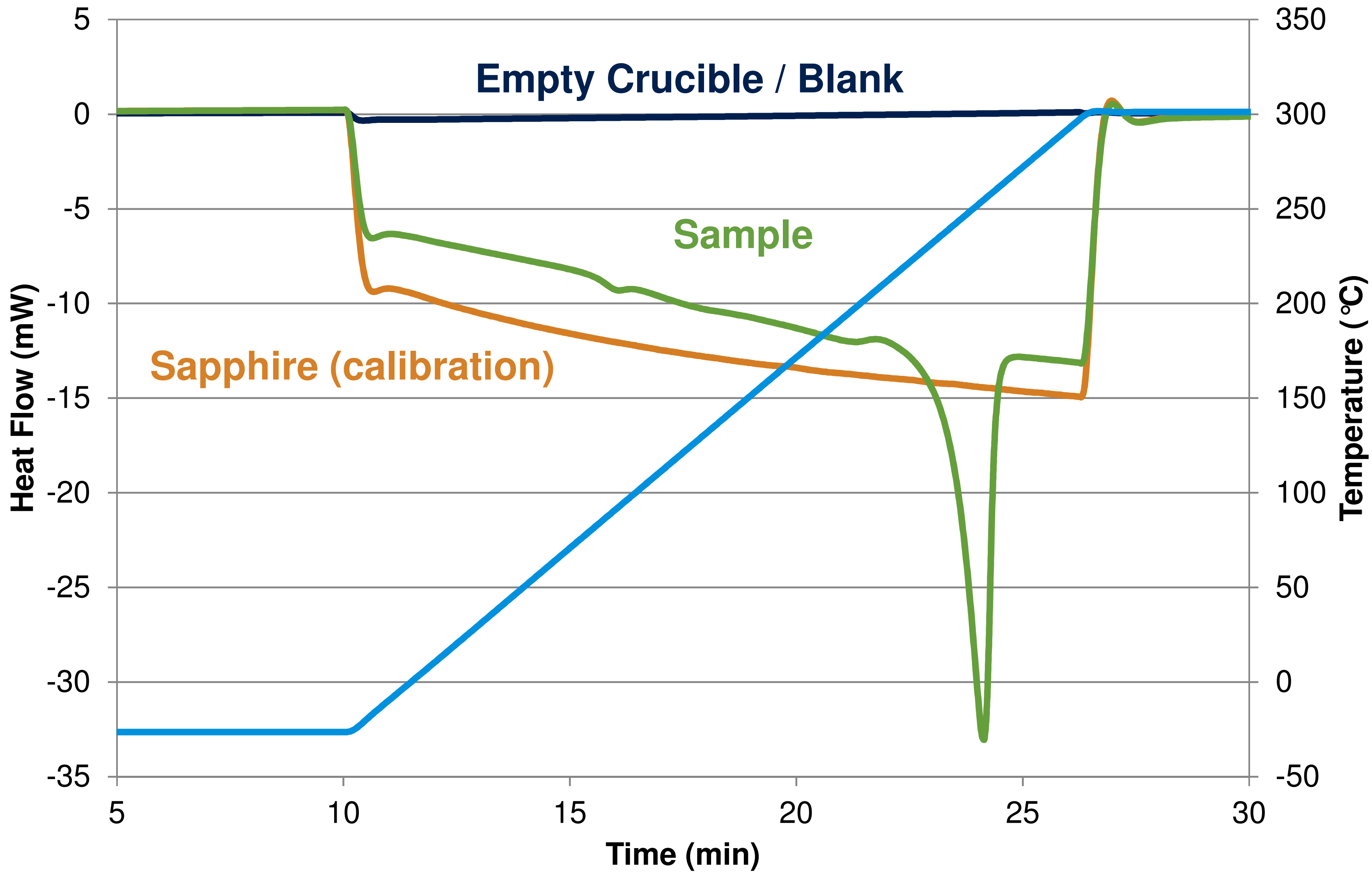
ASTM E1269 “3-Run” Method for Determining Cp



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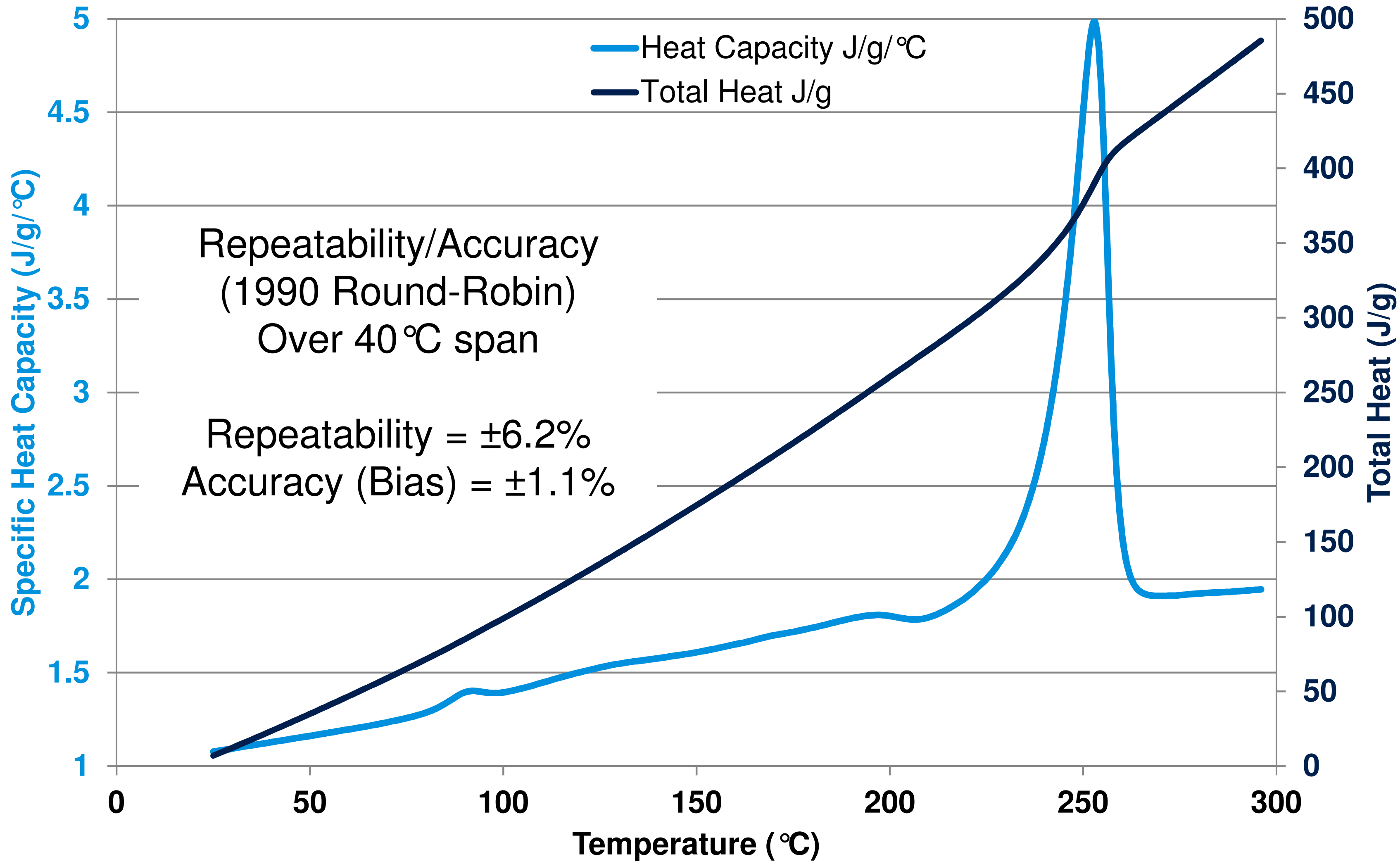
Specific Heat Capacity (ASTM Method)



Reversing Cp Signal

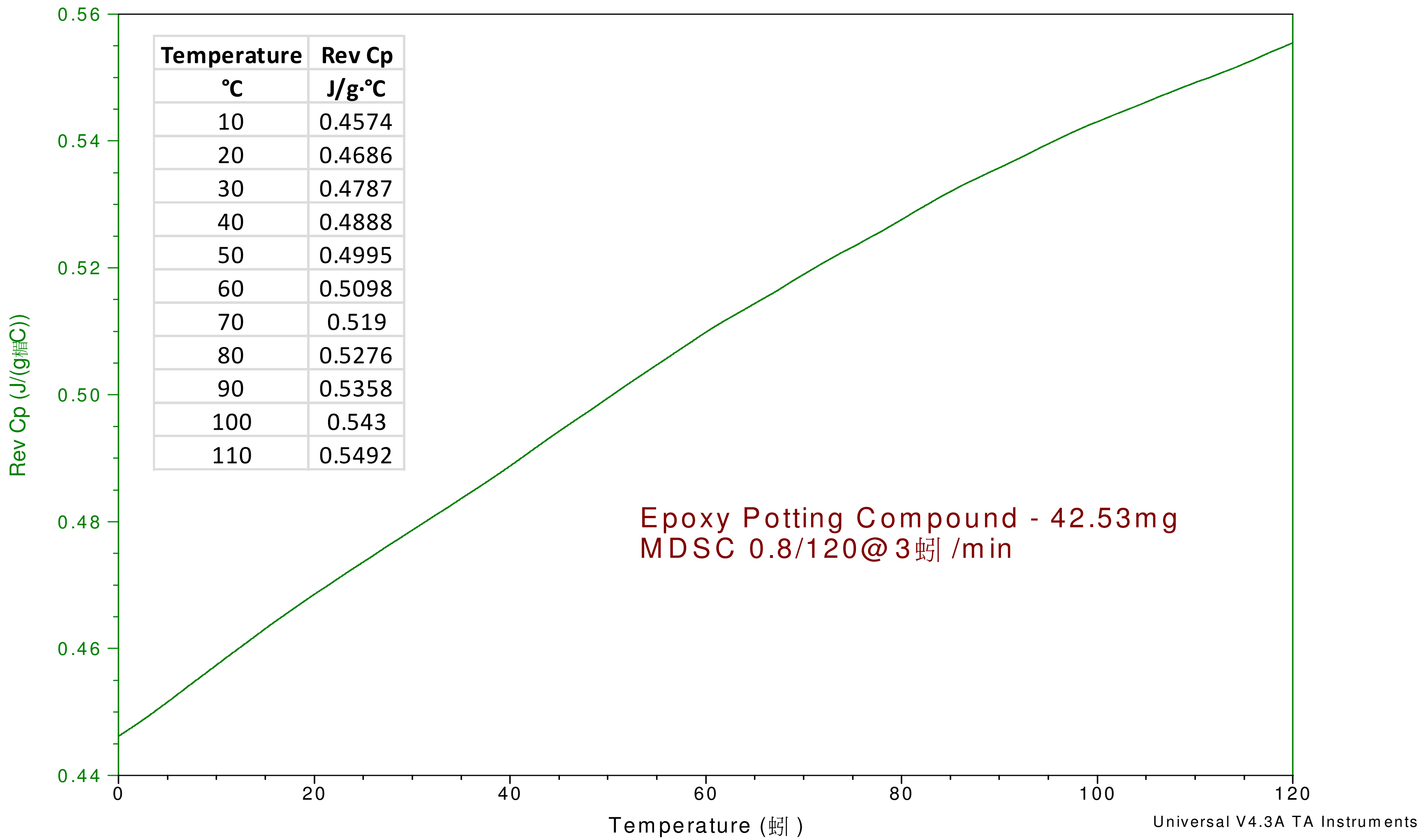
Reversing Heat Flow

- Calculated from Reversing Heat Capacity signal

$$\text{Rev Cp} = \frac{\text{Heat Flow Amp}}{\text{Heating Rate Amp}} \text{ x KCp Rev}$$

$$\text{Rev Heat Flow} = \text{Rev Cp x Avg Heat Rate}$$

Heat Capacity by MDSC



Temperature	Rev Cp
°C	J/g·°C
10	0.4574
20	0.4686
30	0.4787
40	0.4888
50	0.4995
60	0.5098
70	0.519
80	0.5276
90	0.5358
100	0.543
110	0.5492

Direct Cp Measurement on Q2000 & Discovery

- Unlike any other DSC, the heat flow signal of the Q2000/1000 and the Discovery is an absolute signal:
  - Baseline is flat
  - Absolute zero heat flow value established as part of method
- By knowing absolute values of the heat flow and heating rate, heat capacity is calculated in real time and stored in data file

$$\mathrm{Cp} = \frac{\text{Heat flow (mW)}}{\text{Heat Rate } (°C/\text{min}) \text{ x wt (mg)}} \text{ x 60 x K}$$

- Accuracy and precision is generally ± 2% with just single run measurements

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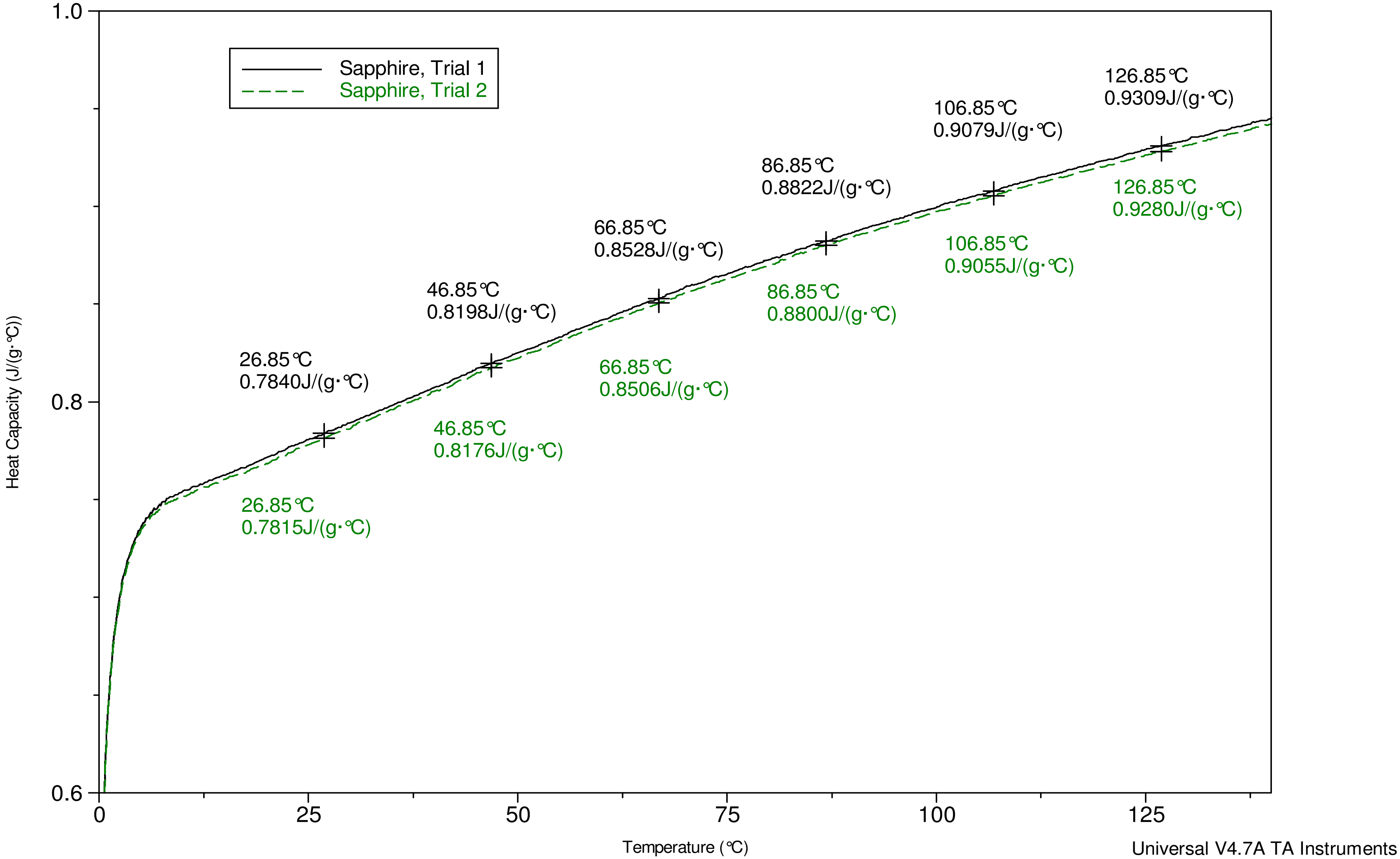
Verifying Heat Capacity with Sapphire Standard An Overlay of Trials 1 and 2



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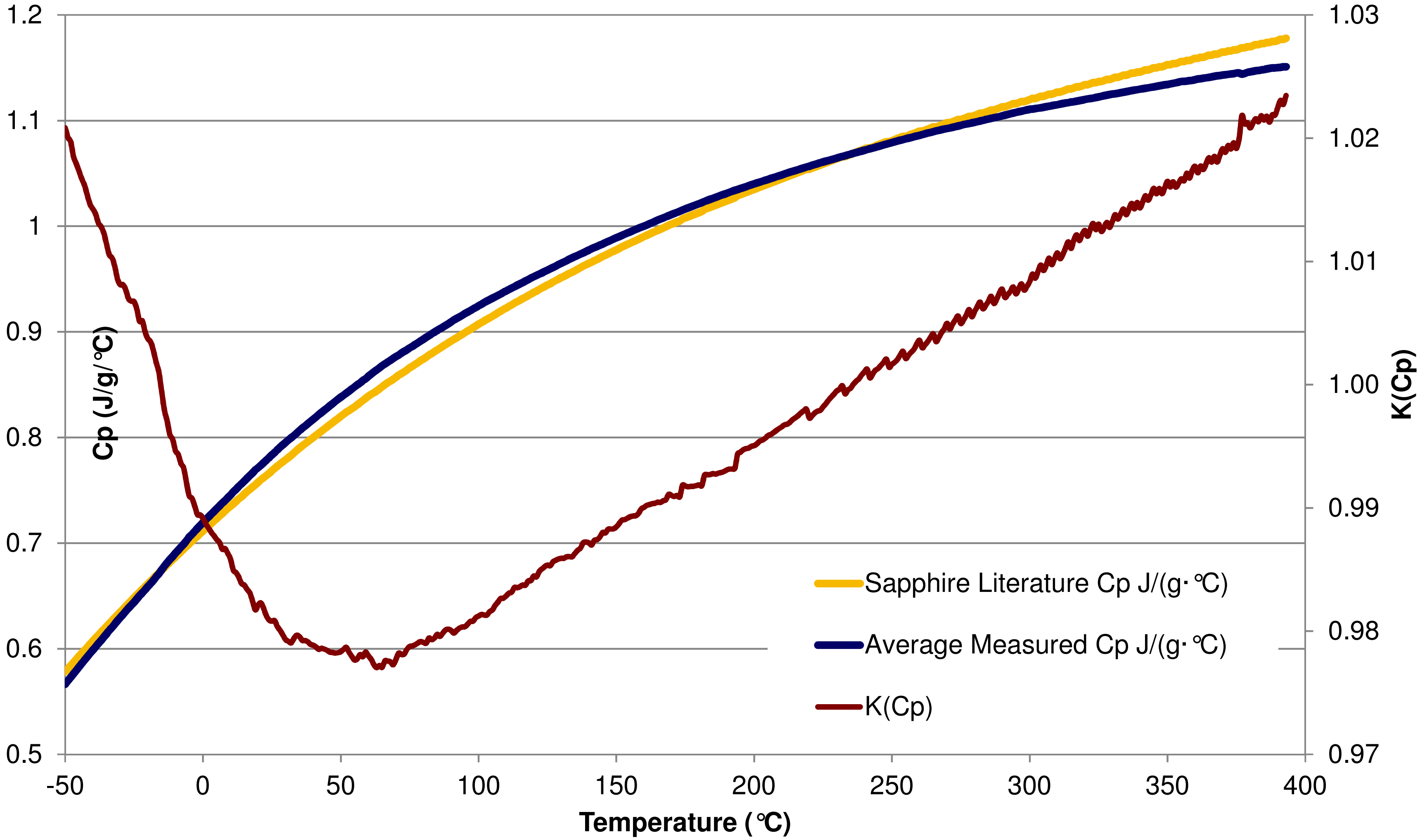
Verifying Heat Capacity with Sapphire Standard

Temperature (°C)	Lit. Cp (J/g. °C)	Measured Cp (J/g. °C) Trial 1 (and % error)	Measured Cp (J/g. °C) Trial 2 (and % error)	% Variation (between runs)
26.85	0.7788	0.784 (0.7%)	0.7815 (0.3%)	0.31
46.85	0.8188	0.8198 (0.1%)	0.8176 (0.1%)	0.27
66.85	0.8548	0.8528 (0.2%)	0.8506 (0.5%)	0.26
86.85	0.8871	0.8822 (0.6%)	0.88 (0.8%)	0.25
106.85	0.9161	0.9079 (0.9%)	0.9055 (1.1%)	0.26
126.85	0.9423	0.9309 (1.2%)	0.928 (1.5%)	0.31

The experimental % error is well below a 5% error.

% variation defined as the difference of the two experimental values divided by the average of those two values. Sapphire was removed and replaced into the cell for each run.

Discovery Direct Cp Calibration - Sapphire



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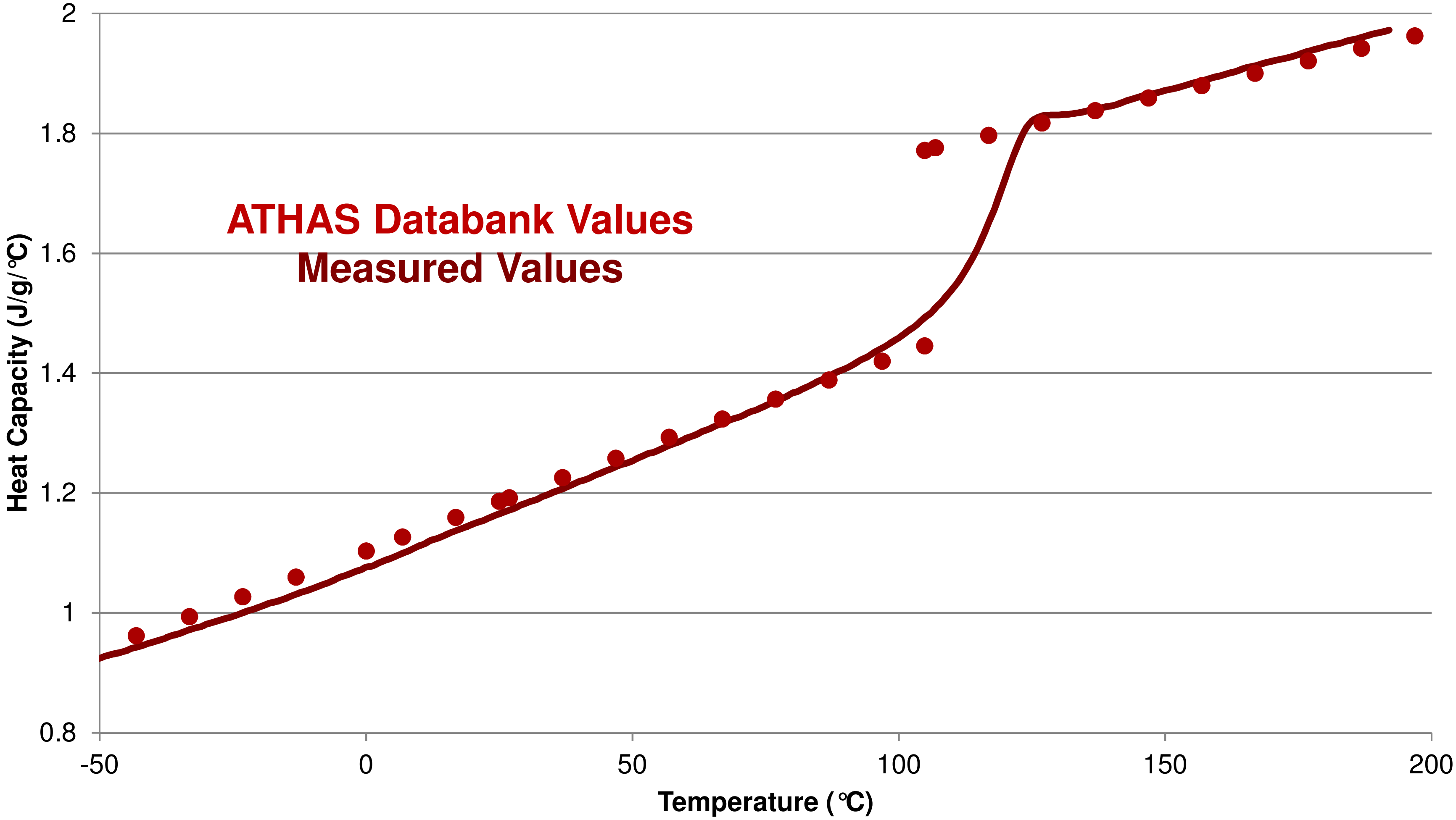
Discovery Calibrated Direct Cp of PMMA



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What Affects the Specific Heat Capacity?

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

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

Effect of Amorphous Content on Cp

- Amorphous Cp is greater than Crystalline Cp
- Amorphous Content increases Specific Heat Capacity

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

Heat Capacity Summary

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

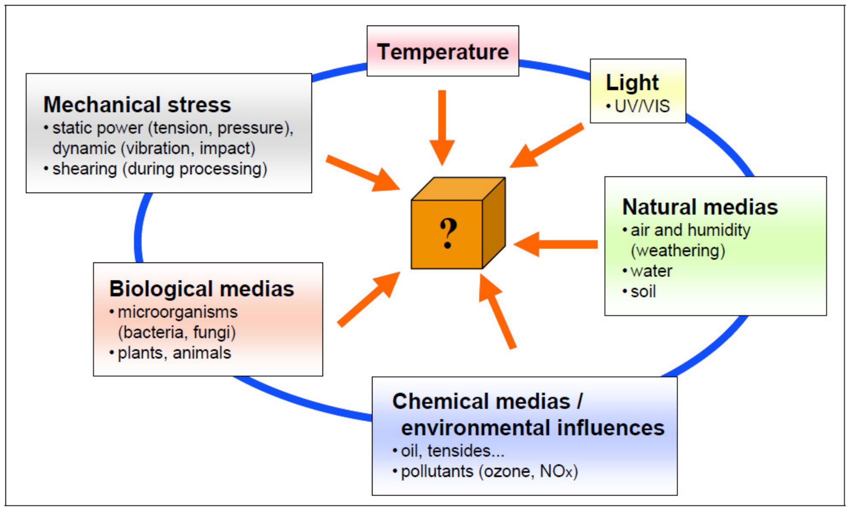
- Heat capacity can be determined through
  - ASTM E1269 (three run method on Q20, Q2000 and Discovery DSC)
  - MDSC (Q20, Q2000 and Discovery DSC)
  - Direct measurement/single run on the Q2000 and Discovery DSC

OIT & OOT Test

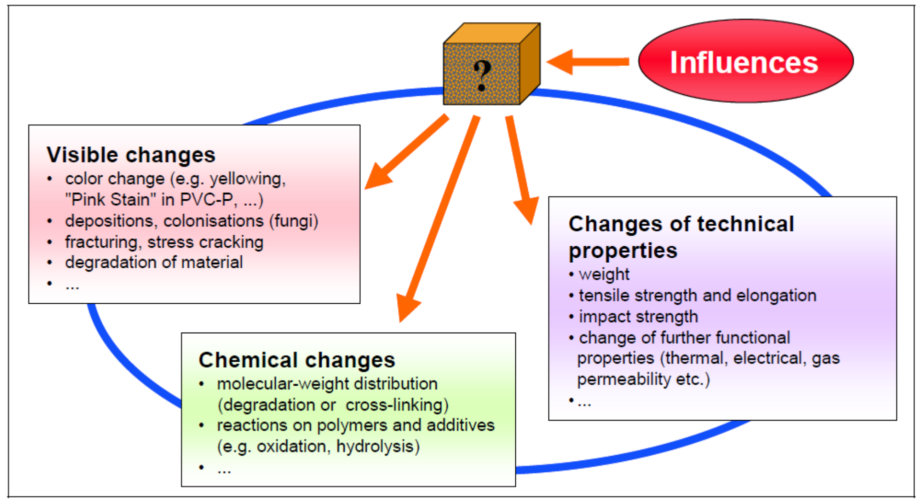
The Factors on Polymer Long-term applications

The most relevant stresses / stress combinations for long-term use of polymer material.

Stress influences on polymers



Effect of stress influences on polymers



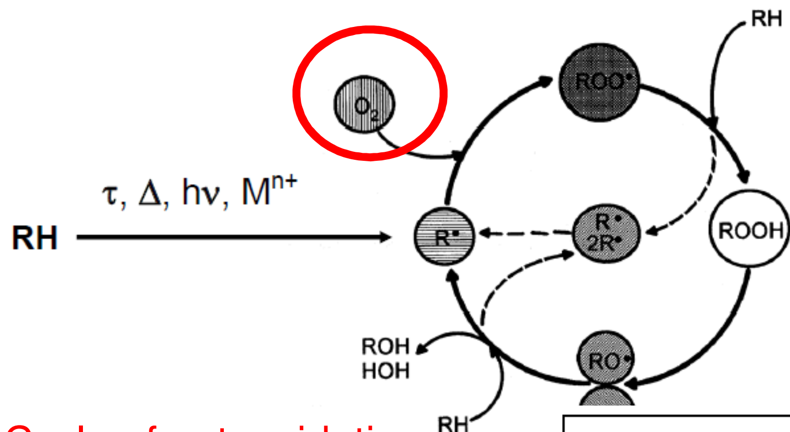
Autooxidation: thermooxidative (T, O2) and photooxidative ageing (hv, T, O2)

Resistance to chemical attacks and possibly to additional simultaneous mechanical stress (σ) (environmental stress cracking behaviour, ESC))

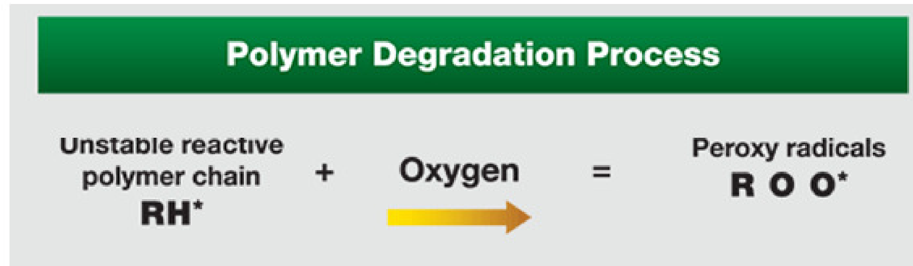
Biodegradation

伴隨熱與氧的老化狀態 – 熱氧劣化

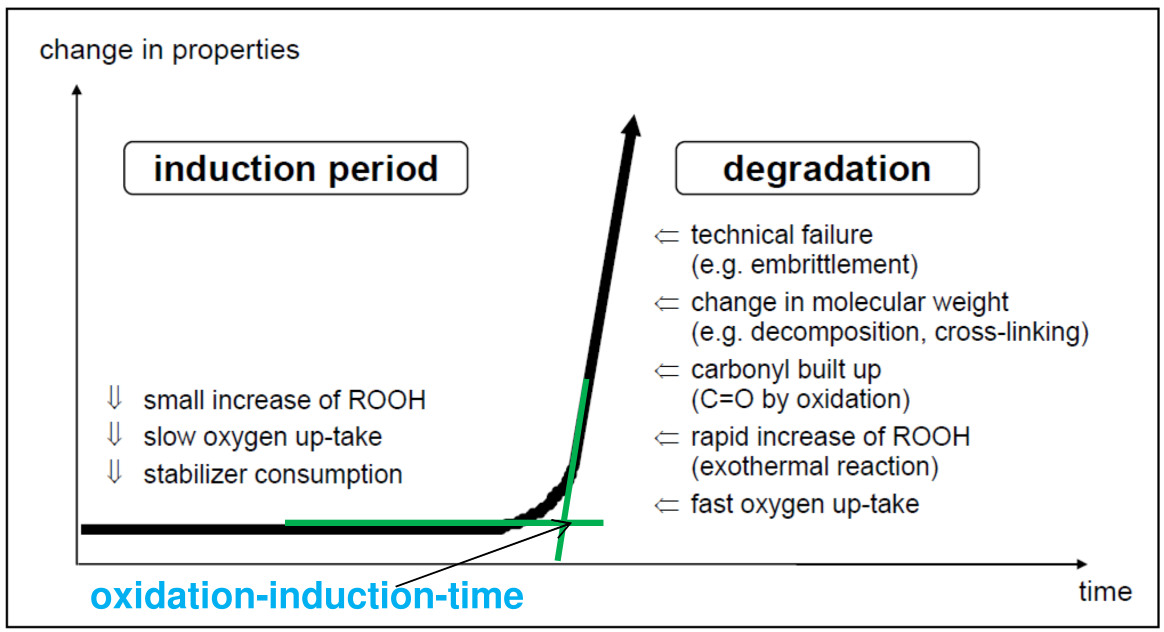
例子：壓延加工，室內或機箱內使用



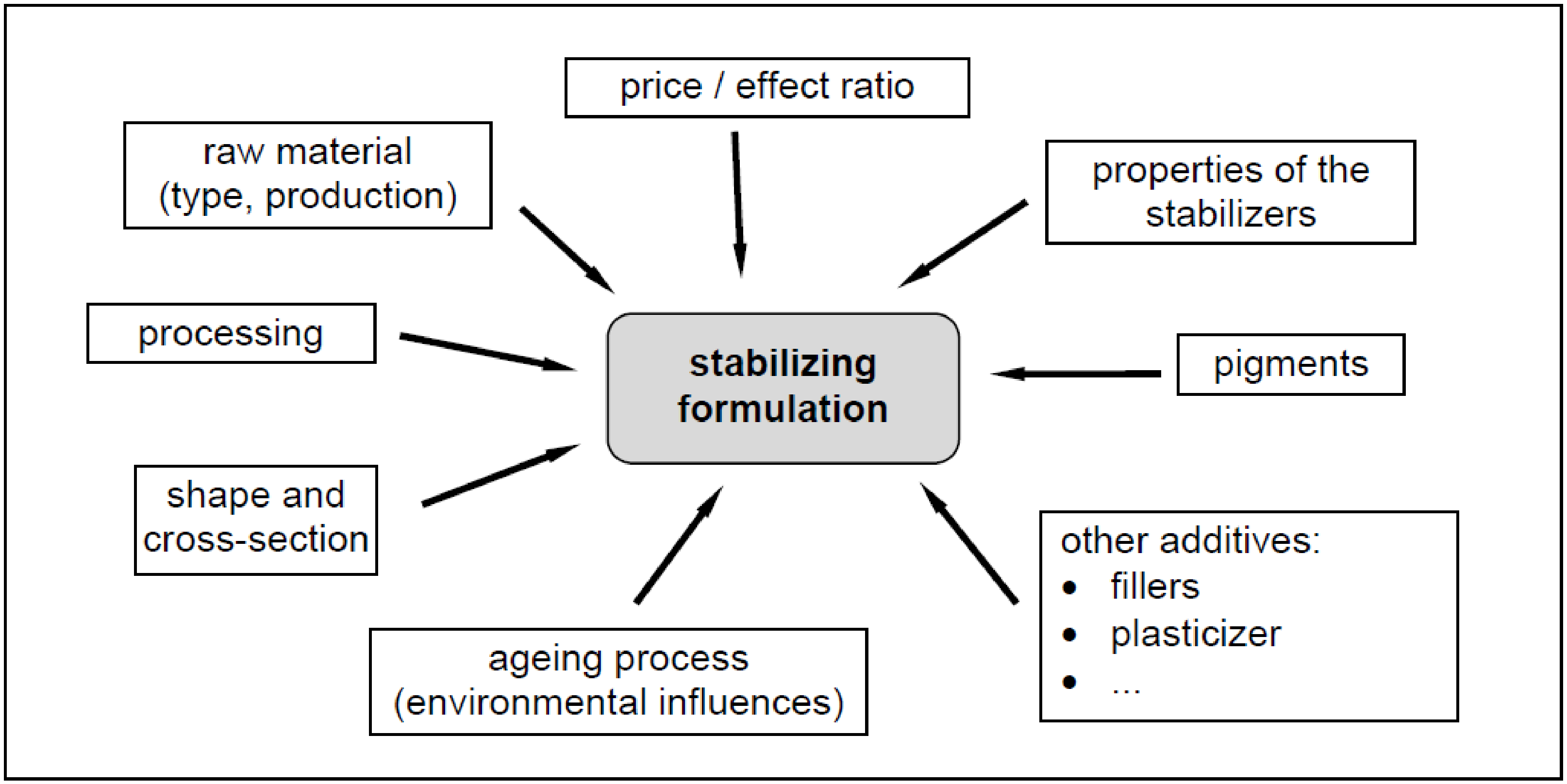
Cycle of autooxidation



Change of properties after the induction period.



Influencing factors on the stabilizing formulation



ASTM及ISO標準 -- 氧化誘導期OIT

- • 樣品厚度，650μm±100μm
- • 溫度校正，金屬銦與金屬錫2點校正
- • 實驗程序
- 首先在氮氣氣氛中以20℃/min的升溫速率從室溫到實驗溫度，然後恆溫3分鐘，切換為氧氣氣氛，開始恆溫實驗。出現明顯的拐點後至少要再繼續實驗2min才可以停止實驗。

測試的OIT時間以10min到60min之間為宜，小於10min或大於60min應考慮適當改變恆溫溫度。改變應該為10的倍數，如190度，220度等。

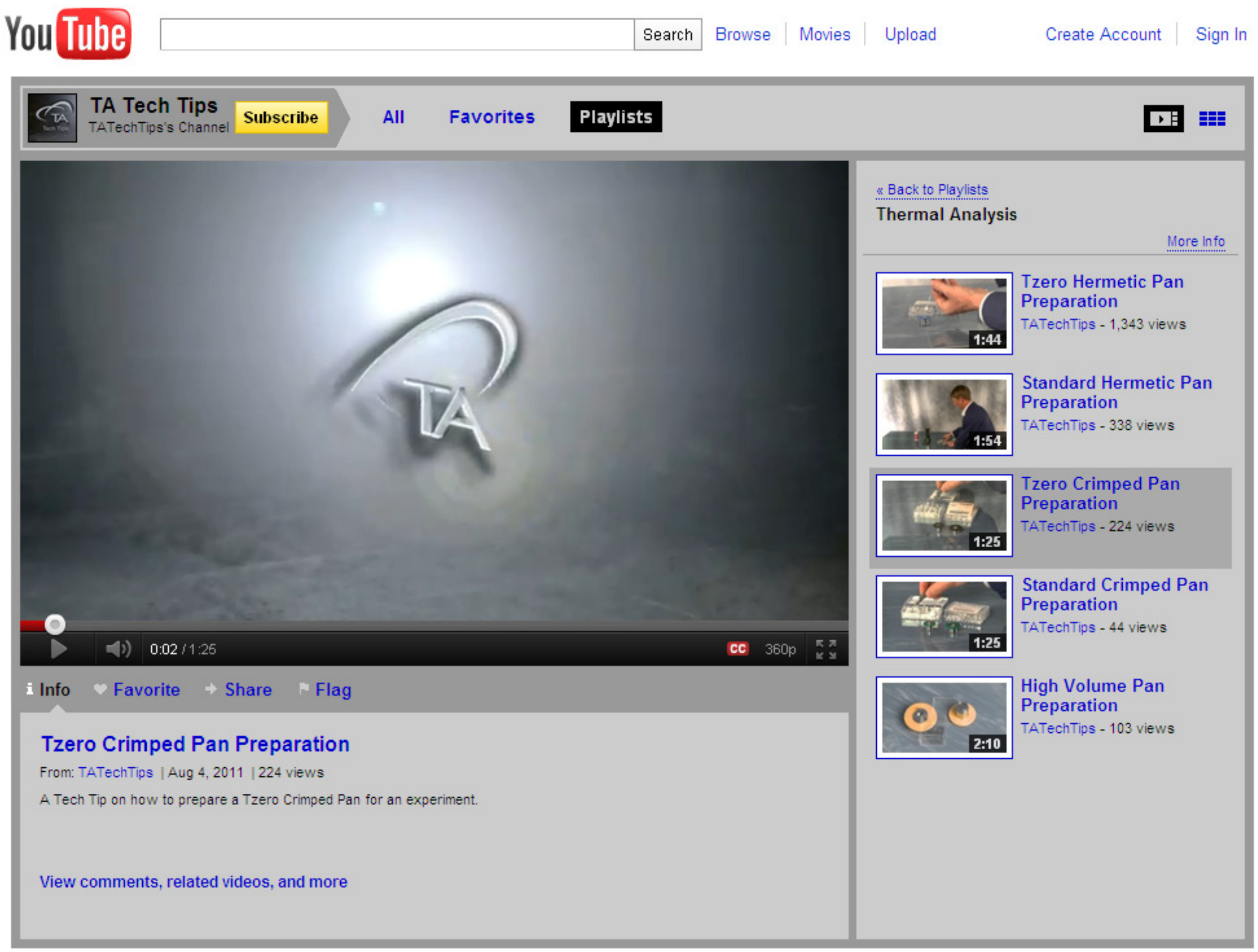
ASTM及ISO標準 -- 動態OIT的測試（OOT方法）

- • 樣品厚度，650μm±100μm
- • 溫度校正，金屬銦與金屬錫2點校正
- • 實驗程序
- • 開始實驗前，在室溫下用氧氣或空氣吹掃樣品5分鐘，在氧氣或空氣的氣氛中以10℃/min或20℃/min的升溫速率進行加熱，直到出現明顯拐點後至少30℃才可以停止實驗。

What if I need help?

- TA Tech Tips
  - http://www.youtube.com/tatechtips
- On-site training & e-Training courses - see Website
- Call the TA Instruments Thermal Applications Hotline
  - 302-427-4163   M-F   8-4:30 Eastern Time
  - mailto:thermalsupport@tainstruments.com
- Main Line for service, applications (thermal, rheology, microcalorimetry, thermophysical properties)
  - 302-427-4070
- Check out our Website
  - http://www.tainstruments.com/

TA Tech Tips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