# Modulated DSC® Paper #2
# Modulated DSC® Basics; Calculation and Calibration of MDSC® Signals

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**ABSTRACT**

This monograph reviews the principles of Modulated DSC and provides an understanding of the calculation and calibration of the various signals used in MDSC.

**INTRODUCTION**

As discussed in the initial overview of this series on MDSC (1), Modulated DSC differs from standard DSC in that it applies two simultaneous heating rates to the sample. The linear or average heating rate provides the same information (*Total* heat flow rate) as standard DSC, while the sinusoidal (modulated) heating rate is used to determine the fraction of the Total heat flow rate that responds to a changing heating rate. In general, this heat flow rate is caused by heat capacity (Cp), changes in heat capacity, and by most melting. This fraction of the Total heat flow is called the *Reversing* heat flow or the heat capacity component of the Total heat flow. Heat flow that does not respond to the changing heating rate is determined by subtracting the Reversing signal from the Total signal. This difference signal is called the *Nonreversing* heat flow or the kinetic (time-dependent) component. Although DSC instruments measure the rate of heat flow, for the purpose of simplicity "Heat Flow" will be used in place of "Heat Flow Rate" in the remainder of this paper.

As mentioned in initial paper (1), there are three general misunderstandings associated with technique of MDSC. They are repeated and summarized here so that the reader can fully understand the basis for the technique and therefore can better interpret the data that it provides. These misunderstandings include:

**MDSC Measures the Reversibility and Non-Reversibility of Transitions**

This is not true. For example, the change in heat capacity due to a glass transition is generally considered to be a reversible process (molecular motion) and is seen in the Reversing signal. However, the Reversing signal shows a step decrease in heat capacity during the cure of an epoxy resin. Even though this process is completely non-reversible, the step appears in the Reversing signal. When water or solvent evaporates, there is a step in the Reversing signal and this is clearly not a reversible process. The Reversing signal is the "Heat Capacity Component" of the Total heat flow and all of the above processes undergo a change in heat capacity. All Cp changes appear in the Reversing signal and MDSC makes no attempt to determine if the process is reversible or non-reversible.

**MDSC is Only a Heating-Cooling Technique**

This is also not true, although experimental conditions can be selected, as described in the next paper in the Modulated® DSC series (2), that provide heating and cooling during the temperature modulation. MDSC works on the basis of providing a periodic change in heating rate. The rate can be heat-only or heat-cool as required by the analysis.

**MDSC is a Different Instrument than DSC**

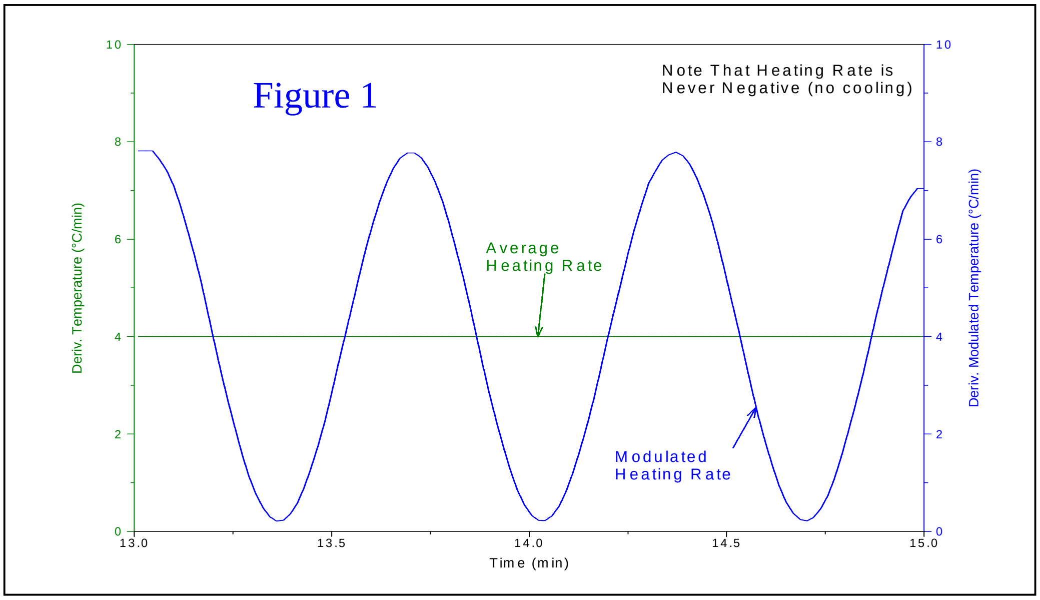
This is not true. The same instrument is used to run DSC experiments, which use linear changes in temperature, and MDSC experiments that use both a linear and sinusoidal change in temperature. In fact, an experiment on a single sample can have both DSC and MDSC segments as part of the same experimental method.

## CALCULATION OF MDSC SIGNALS

In order to perform an MDSC experiment, the operator must specify both the average and modulated rates of temperature change. This is done by selecting:

- an average heating rate, typically in the range from 1 to 10 °C/min
- a temperature modulation period, typically between 30 and 100 seconds
- a temperature modulation amplitude, typically in the range of ± 0.1 to 2.0 °C

The process or rational for selecting optimum modulation conditions is detailed in a forthcoming paper (2). MDSC signals that are used to analyze transitions in materials are calculated from three measured signals; time, temperature and heat flow. Temperature changes sinusoidally, rather than linearly, and the heating rate changes similarly as seen in Figure 1.




As a result of the sinusoidal change in temperature, the heat flow also changes sinusoidally as seen in Figure 2. It is important to realize that the two signals in Figure 2, _Modulated Heat Flow (MHF)_ and _Modulated Heating Rate (MHR)_ are the measured signals from the MDSC experiment. All other MDSC signals are calculated from these two measured signals.

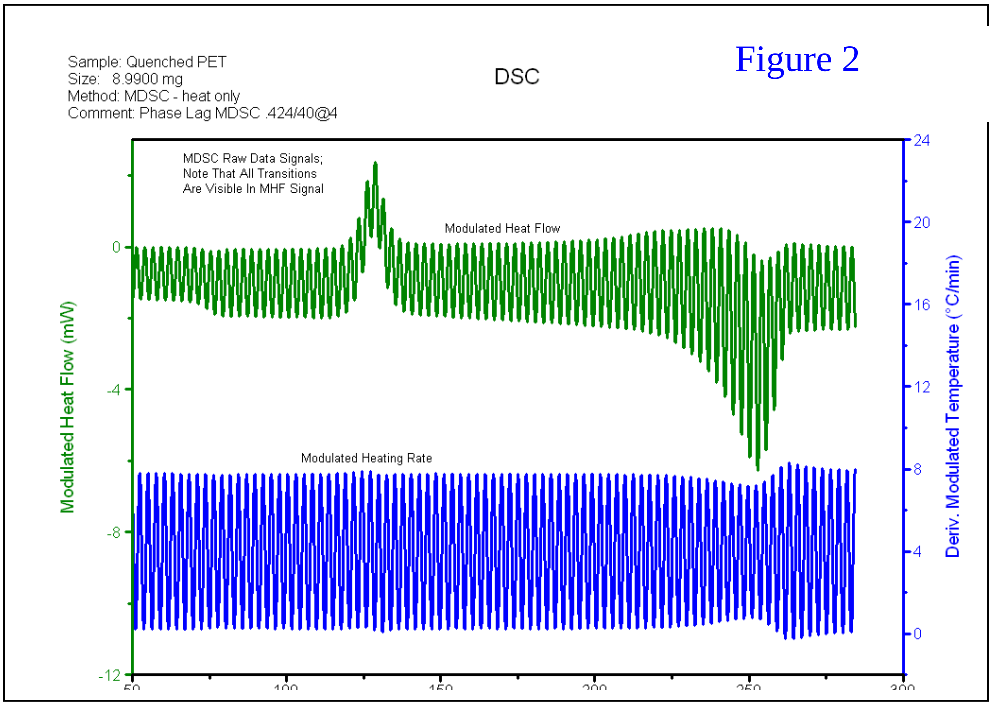


Figure 2

Before discussing how MDSC signals are calculated, it is necessary to briefly discuss the theoretical basis for the signals and their relationship to each other. This basis can be described in the following simple equation.

Where:

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

dH/dT = Total Heat Flow Rate (mW, which is = mJ/s)

Cp = Sample Heat Capacity; Specific Cp x Sample Mass (J/ºC)

dT/dt = Heating Rate (ºC/min)

*f*(T,t) = Heat Flow That is Function of Temperature and Time (mW)

Analysis of this equation shows that the ***Total*** heat flow has two components, one that is a function of the applied heating rate (dT/dt), and another that is a function of time at an absolute temperature. A natural limitation of standard DSC is that it measures only the sum of these two components. The ***Total*** heat flow is the sum of all heat flow occurring at any point in time and temperature. When two or more transitions occur at the same time, it may be impossible to interpret the DSC results. MDSC solves this problem by calculating not only the ***Total*** heat flow but also the two individual components. This permits analysis and data interpretation even when two transitions occur at the same time.

Signal Names

*Total Heat Flow* = dH/dt, the sum of all heat flow
*Reversing Heat Flow* = Cp x dT/dt (also called Heat Capacity component)
*Nonreversing Heat Flow* = *f*(T, t) (also called Kinetic component)

**Calculation of MDSC Signals**

- The *Total Heat Flow* signal is calculated from the average value of the measured *Modulated Heat Flow* signal as seen in Figure 3. The process of determining the average involves use of Fourier Transform (FT) analysis on the sine wave. The average is continuously calculated (every 0.1 seconds) rather than using the simple average that would significantly limit resolution.

- The *Reversing Heat Flow* signal is calculated from the *Reversing Heat Capacity* signal as described below and as shown in Figure 4. As with *Total Heat Flow*, the amplitudes of the heat flow and heating rate signals are calculated using Fourier Transform analysis.

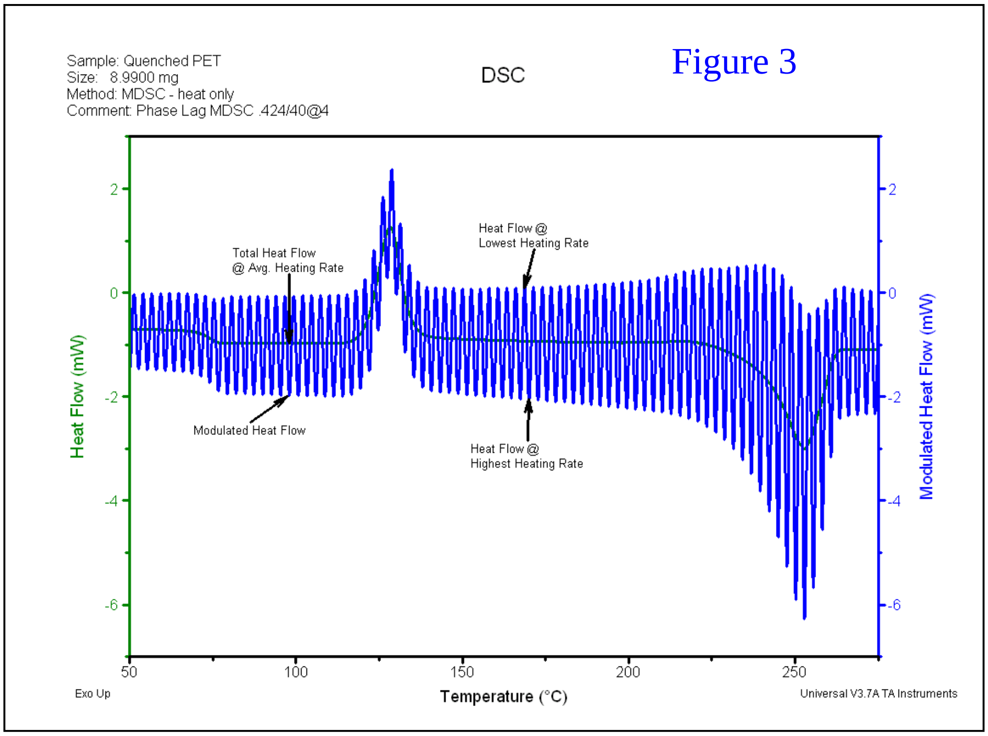
$$\text{Rev Cp} = \frac{\text{Heat Flow Amplitude}}{\text{Heating Rate Amplitude}} \text{ x KCp Rev}$$

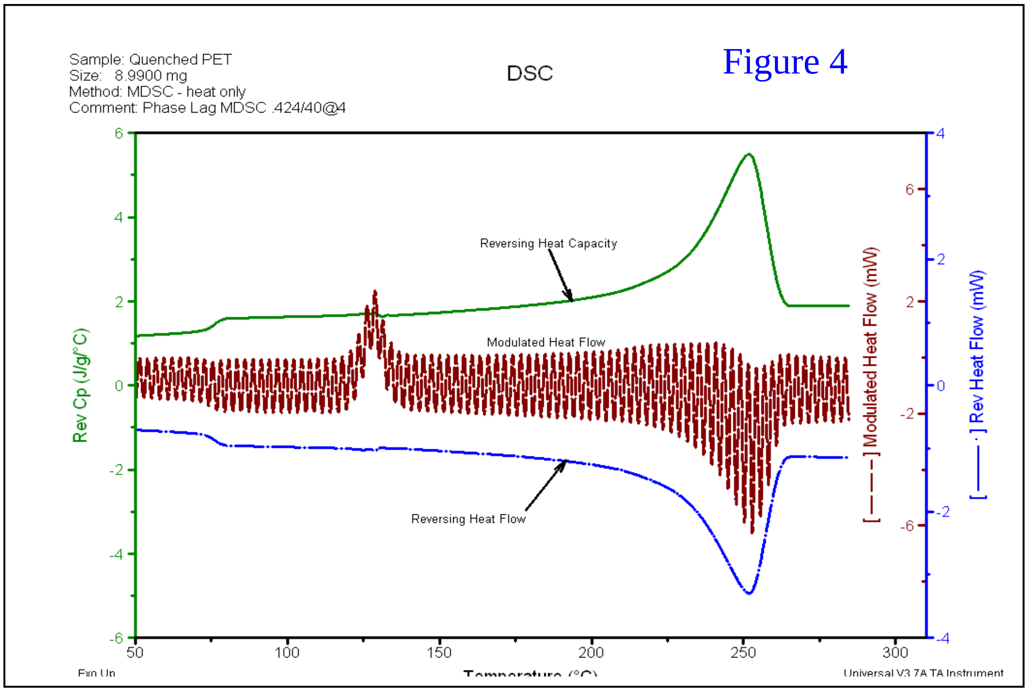
where:

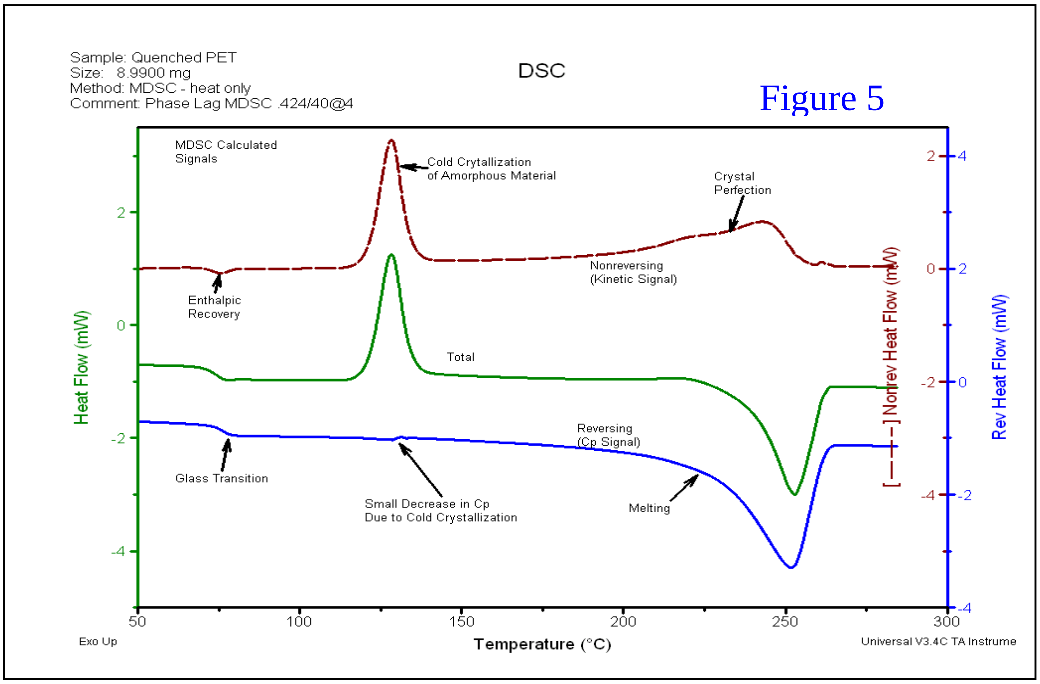
KCp Rev = Calibration Constant for Reversing Cp

Rev Heat Flow = Rev Cp x Average Heating Rate

- The *Nonreversing Heat Flow* signal is calculated by subtracting the *Reversing Heat Flow* signal from the *Total Heat Flow* signal. All three signals are shown in Figure 5 on a sample of quench-cooled Polyethylene Terephthalate (PET).




Sample: Quenched PET
Size: 8.9900 mg
Method: MDSC - heat only
Comment: Phase Lag MDSC .424/40@4
DSC
Figure 4
Reversing Heat Capacity
Modulated Heat Flow
Reversing Heat Flow
Rev Cp (J/g/°C)
[ — — ] Modulated Heat Flow (mW)
[ —— · ] Rev Heat Flow (mW)
Exo Up
Universal V3.7A TA Instrument


Sample: Quenched PET
Size: 8.9900 mg
Method: MDSC - heat only
Comment: Phase Lag MDSC .424/40@4
DSC
Figure 5
MDSC Calculated Signals
Cold Crytallization of Amorphous Material
Crystal Perfection
Nonreversing (Kinetic Signal)
Enthalpic Recovery
Total
Reversing (Cp Signal)
Glass Transition
Small Decrease in Cp Due to Cold Crystallization
Melting
Heat Flow (mW)
[ — — ] Nonrev Heat Flow (mW)
Rev Heat Flow (mW)
Temperature (°C)
Exo Up
Universal V3.4C TA Instrume

In the examples above, the emphasis was on heat flow signals. However, all of the same information is available in Heat Capacity signals, which are calculated as follows:

- *Total Heat Capacity = Total Heat Flow/Average Heating Rate* x KCp Total
- *Reversing Heat Capacity = Heat Flow Amp./Heating Rate Amp.* x KCp Rev
- *Nonreversing Heat Capacity = Total Heat Capacity - Reversing Heat Capacity*

where: KCp is a calibration constant for that specific signal

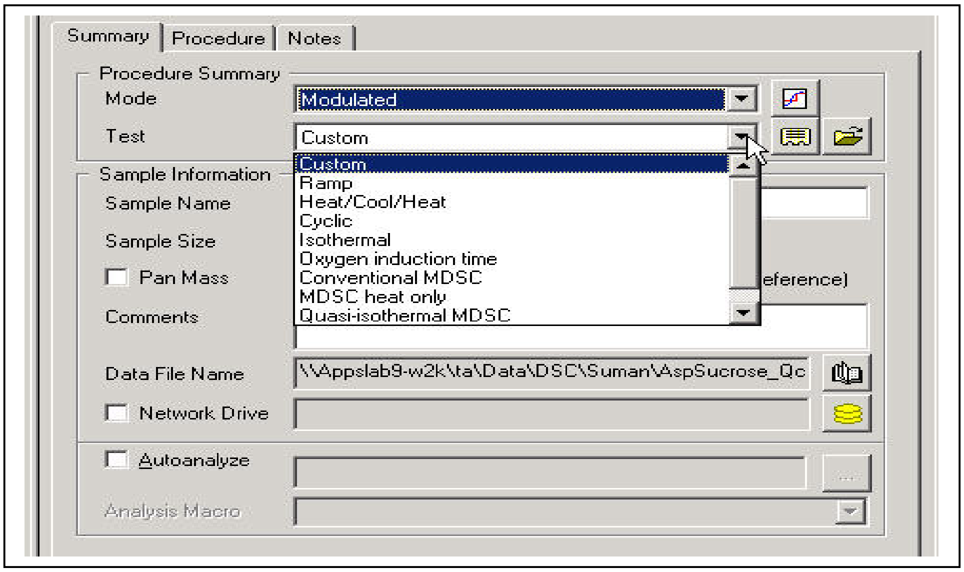
There are several circumstances when it is desirable to use heat capacity signals instead of heat flow signals. These include the ability to:

- Overlay experiments that are done at different heating rates in order to better understand kinetic processes
- Overlay heating and cooling experiments to verify the presence of a weak glass transition
- Follow the change in heat capacity (Reversing Cp signal) during an isothermal reaction in order to better understand changes in structure

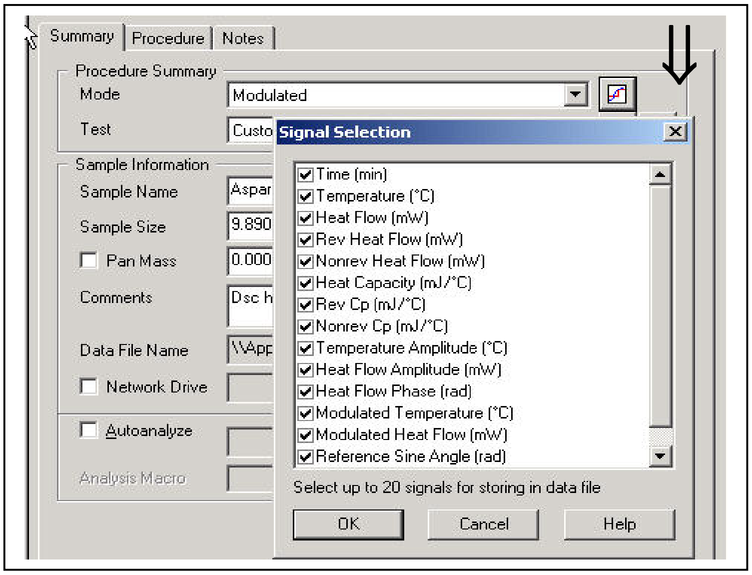
A more complete discussion on the subjects of heat flow phase and phase lag correction of MDSC signals are provided in the fourth paper of this series (3).

**CALIBRATION OF MDSC SIGNALS**

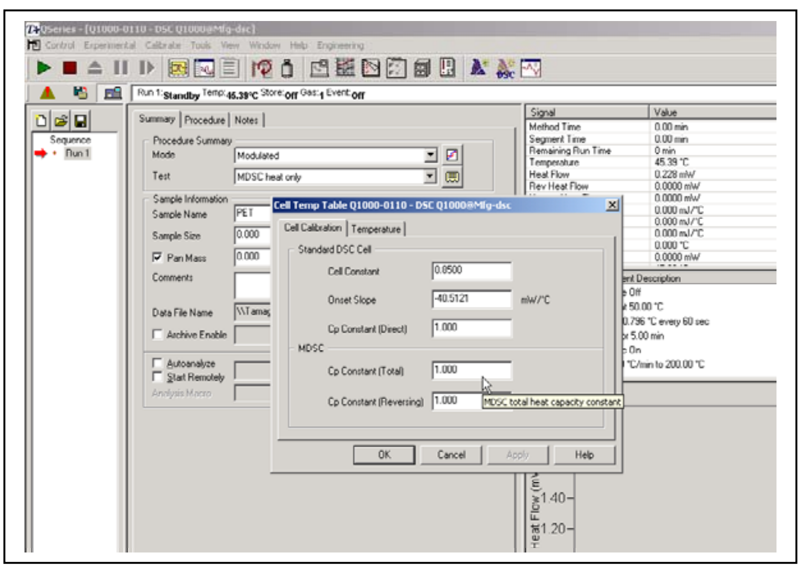
As previously stated, the same instrument is used to run both DSC and MDSC experiments. Therefore, it is necessary to calibrate the DSC for heat flow, temperature and baseline (sensor capacitance and resistance for Tzero™ technology) using standard calibration techniques. Once the DSC mode is calibrated, it is also possible to calibrate the heat capacity signals in the MDSC mode (see below). Note that there is no calibration mode for MDSC signals.



After selecting the mode of operation, the operator should verify that desired MDSC signals are selected from the signal icon on the *Summary* page as shown below.




Before calibrating the MDSC heat capacity signals, it is necessary to set any existing calibration constants to 1.0. This is done with the instrument control software by selecting "***Calibrate***" followed by "***Cell/Temperature Table...***" which provides the screen below. Place values of 1.0 in the windows provided for the MDSC Total and Reversing Cp calibration constants.




Once the calibration constants are set to 1.0, the sapphire standard provided in the DSC accessory kit should be run under the desired conditions. Recommended conditions for optimization of MDSC results provided in the next paper in this series (2).

At a temperature in the middle of the range of interest, the measured Cp values for the Total and Reversing signals should be compared to the theoretical values for sapphire at that temperature and new calibration constants determined as follows:

**Calibration Constant = Theoretical ÷ Measured Values**

These new values should then be inserted in the "*Cell/Temperature Table..."* in place of the values of 1.0 previously entered. As a guideline, and as long as modulation periods of 60 seconds or longer are used, heat capacity calibration constants should be between 1.0 and 1.2. Values significantly different from these are probably in error. In general, the MDSC Total heat capacity signal is not very accurate because of the low average heating rates used in MDSC experiments. Therefore, it is recommended that the calibration constant for the MDSC Total Cp signal be left at 1.0 for all experiments.

## SUMMARY

The technique of MDSC is more than ten (10) years old and has been well established in providing significant advantages over the traditional DSC. Conversion of measured heat flow signals to calculated MDSC signals are straightforward, easy to perform and is well supported by theory. In order to obtain the most accurate heat capacity measurements, it is recommended that the Reversing Cp signal be calibrated with sapphire prior to running actual samples.

## REFERENCES

1. Modulated DSC Paper #1, Why Modulated DSC?; An Overview and Summary of Advantages and Disadvantages Relative to Traditional DSC; TA Instruments Technical Paper TP 006.
2. Modulated DSC Paper #3, Optimization of MDSC Experimental Conditions; TA Instruments Technical Paper TP 008.
3. Modulated DSC Paper #4; Advanced Tzero™ MDSC; Calculation of MDSC Signals Including Phase Lag; TA Instruments Technical Paper TP 009.

**KEY WORDS**
modulated differential scanning calorimetry, mdsc, heat capacity, reversing, non reversing, calculation, calibration



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