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.

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:

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

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

\(C_p\) = Sample Heat Capacity; Specific \(C_p\) x Sample Mass (J/°C)

\(dT/dt\) = Heating Rate (°C/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* = \( \frac{dH}{dt} \), the sum of all heat flow

*Reversing Heat Flow* = \( C_p \times \frac{dT}{dt} \) (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.

\[
Rev\ Cp = \frac{\text{Heat Flow Amplitude}}{\text{Heating Rate Amplitude}} \times KCp_{Rev}
\]

where:

\[
KCp_{Rev} = \text{Calibration Constant for Reversing } C_p
\]

\[
Rev\ Heat\ Flow = Rev\ Cp \times \text{Average Heating Rate}
\]

- 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).
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.

![Screen showing signal selection]

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.

![Screen showing calibration settings]

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**

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

© COPYRIGHT 2005 TA INSTRUMENTS

**TA INSTRUMENTS**

United States, 109 Lukens Drive, New Castle, DE 19720 • Phone: 1-302-427-4000 • Fax: 1-302-427-4001
E-mail: info@tainstruments.com

Spain • Phone: 34-93-600-9300 • Fax: 34-93-325-9896 • E-mail: spain@tainstruments.com

United Kingdom • Phone: 44-1-293-658900 • Fax: 44-1-293-658901 • E-mail: uk@tainstruments.com
Belgium/Luxembourg • Phone: 32-2-706-0080 • Fax: 32-2-706-0081
E-mail: belgium@tainstruments.com

Netherlands • Phone: 31-76-508-7270 • Fax: 31-76-508-7280
E-mail: netherlands@tainstruments.com

Germany • Phone: 49-6023-9647-0 • Fax: 49-6023-96477-7 • E-mail: germany@tainstruments.com

France • Phone: 33-1-304-89460 • Fax: 33-1-304-89451 • E-mail: france@tainstruments.com

Italy • Phone: 39-02-27421-283 • Fax: 39-02-2501-827 • E-mail: italia@tainstruments.com

Sweden/Norway • Phone: 46-8-594-69-200 • Fax: 46-8-594-69-209
E-mail: sweden@tainstruments.com

Japan • Phone: 813 5479 8418 • Fax: 813 5479 7488 • E-mail: nurayama@taij.po-jp.com

Australia • Phone: 613 9553 0813 • Fax: 61 3 9553 0813 • E-mail: steve_shamis@waters.com

To contact your local TA Instruments representative visit our website at www.tainst.com