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 signals from the MDSC experiment. All other MDSC signals are calculated from these two measured signals.

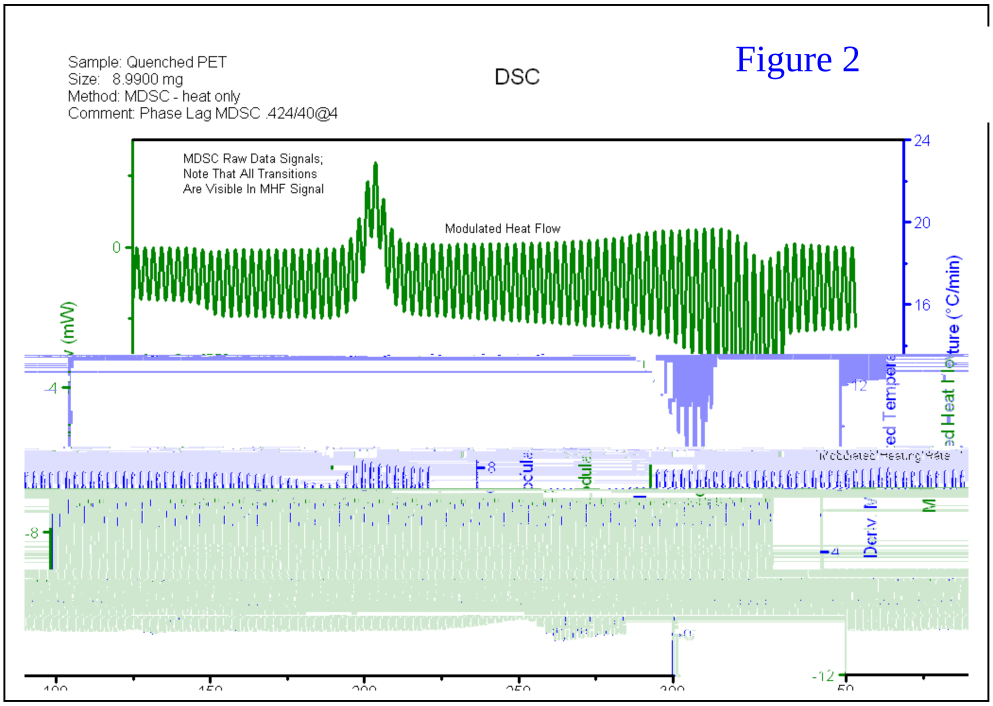


Figure 2

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:

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

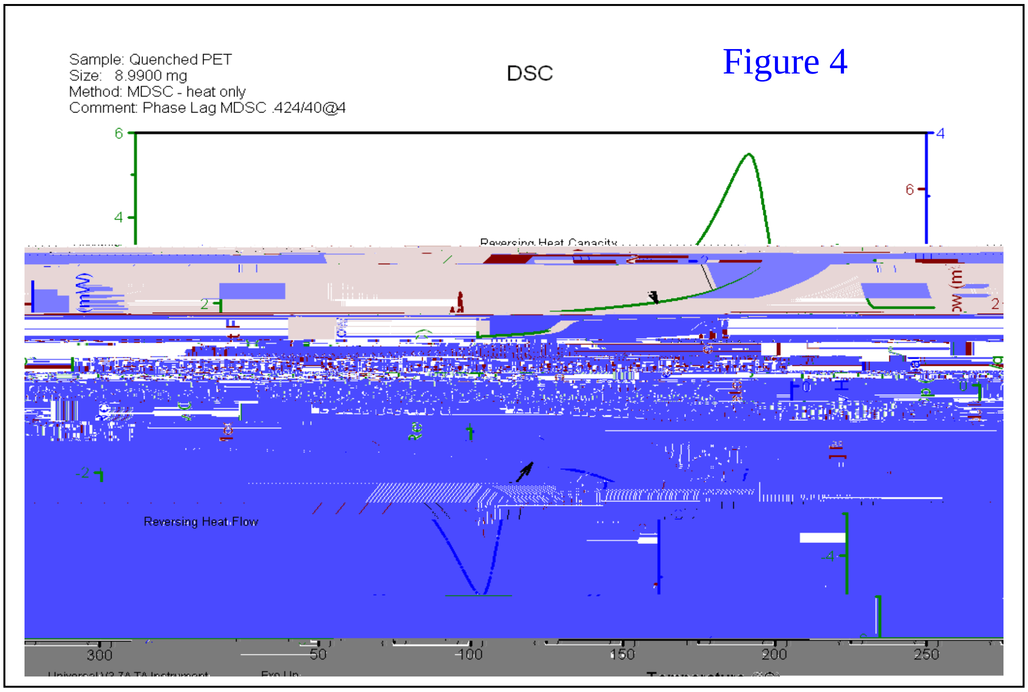
dH/dT = Total Heat Flow Rate (mW, which is = mJ/s)

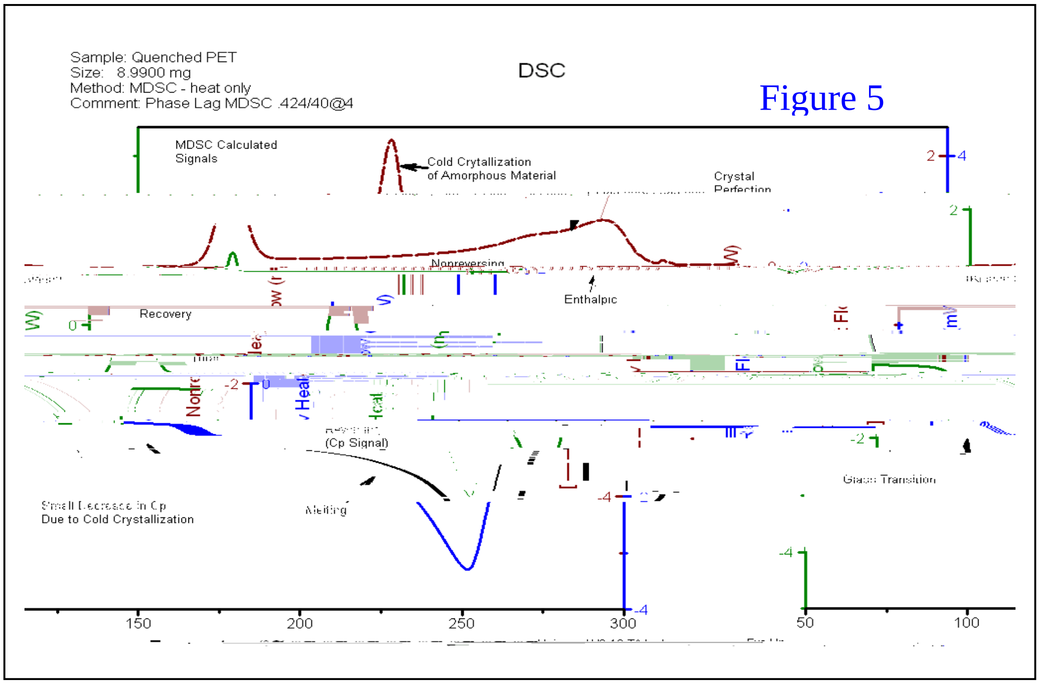
Cp = Sample Heat Capacity; Specific Cp x Sample Mass (J/ºC)

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.


Sample: Quenched PET
Size: 8.9900 mg
Method: MDSC - heat only
Comment: Phase Lag MDSC .424/40@4
DSC
Figure 4
Reversing Heat Flow


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
Enthalpic
Recovery
(Cp Signal)
Glass Transition
Due to Cold Crystallization

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:

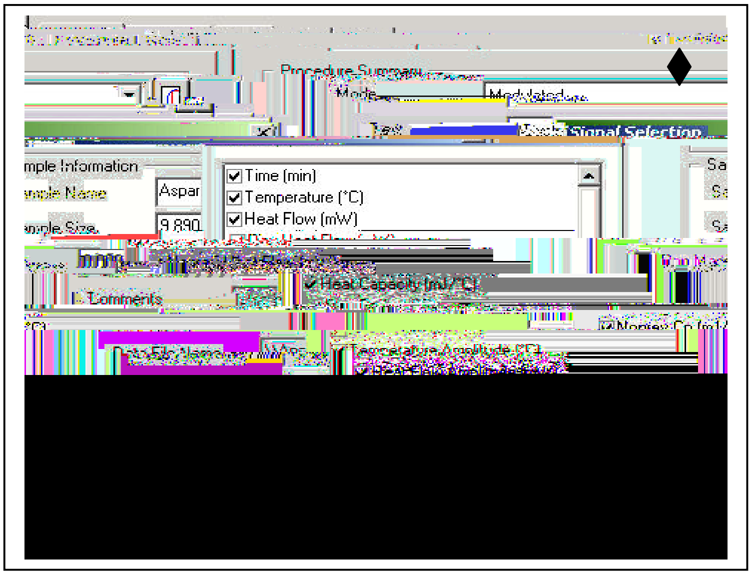
- *Total Heat Capacity = Total Heat Flow/Average Heating Rate* x KCp Total
- *Reversing Heat Capacity = Heat Flow Amp./Heating Rate Amp.* x KCp Rev
- *Nonreversing Heat Capacity = Total Heat Capacity - Reversing Heat Capacity*

where: KCp is a calibration constant for that specific signal

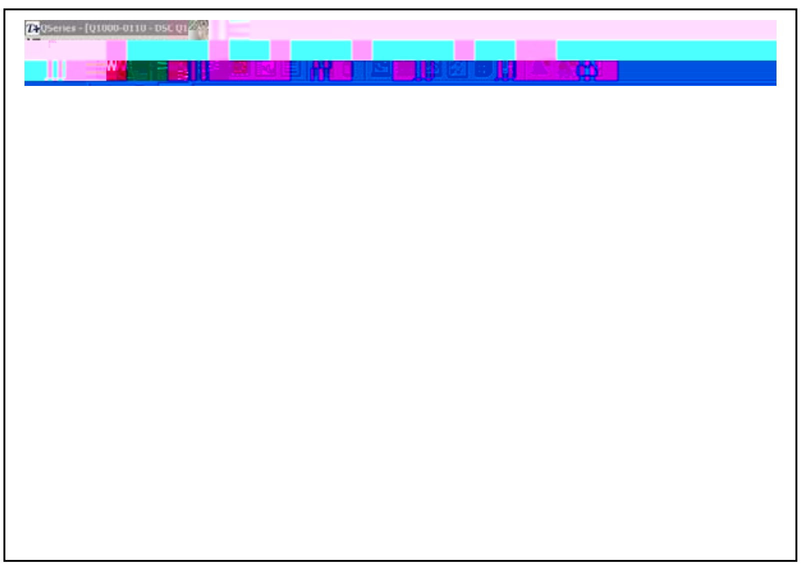
There are several circumstances when it is desirable to use heat capacity signals instead of heat flow signals. These include the ability to:

- 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

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.



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 э 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

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