Since its commercialization in 1992, Modulated DSC has been shown to provide significant advantages over traditional DSC and the list of benefits continues to grow as new applications are explored. These include:

- separation of complex transitions into more easily interpreted components
- ability to more accurately determine the crystallinity of semicrystalline polymers
- increased sensitivity for detection of weak transitions
- increased resolution without loss of sensitivity
- measurement of heat flow and heat capacity in a single experiment
- measurement of thermal conductivity

Because the technique provides such significant benefits, and because the transitions (phase changes, chemical reactions, etc.) observed in a sample as it is heated are often very complex, the technique of MDSC is often assumed to be more complex than it really is.

The benefits of MDSC, which include increased understanding of complex transitions, are the result of conducting two simultaneous, simple experiments and then making two simple calculations on the resulting heat flow signal. The purpose of this paper is to describe the measurements and calculations used in MDSC.

**Two Simultaneous Experiments**

Traditional DSC measures the difference in heat flow between a sample and inert reference as both are subjected to a linear change in temperature. It can also determine heat capacity by measuring the difference in heat flow between two experiments where two identical samples of the same mass are subjected to two different linear heating rates.

\[
\text{Heat Capacity} = KC_p \times \frac{\Delta \text{Heat Flow}}{\Delta \text{Heating Rate}}
\]

- \(KC_p\) = Calibration Constant
- \(\Delta \text{Heat Flow}\) = Heat Flow Difference (Exp₁ - Exp₂)
- \(\Delta \text{Heating Rate}\) = Heating Rate Difference (Exp₁ - Exp₂)
Modulated DSC™ measures both heat flow and heat capacity in a single experiment by superimposing a modulated heating rate (changing heating rate) on top of a linear heating rate. An example of the ability to do this is seen in Figure 1 where the average heating rate is 2°C/min. (linear) while the instantaneous heating rate is changing between a minimum of 0.3°C/min. and a maximum of 3.7°C/min.. The linear change in temperature permits the measurement of heat flow while the modulated change permits the calculation of heat capacity.

**Figure 1. MDSC™ TEMPERATURE CHANGE**

Two Simple Calculations

The heat flow that results from a linear change in temperature (traditional DSC) is seen in Figure 2, while Figure 3 shows the modulated heat flow signal that results from the modulated heating rate in MDSC. The benefits of MDSC are obtained from the following two measurements made on the modulated heat flow signal.

**Figure 2. QUENCH COOLED PET (STD DSC)**

**Figure 3. QUENCH COOLED PET (MDSC)**
(1) Heat Flow Average

The average value of the modulated heat flow signal is shown in Figure 4 as the solid line. An analysis of the three transition shows that the average value of the modulated heat flow signal is qualitatively and quantitatively equivalent to the heat flow signal from traditional DSC at the same average heating rate. The name given to this signal (average value) is Total Heat Flow because, like traditional DSC, it contains the heat flow associated with all thermal events in the sample.

(2) Heat Flow Amplitude

Figure 5 shows the modulated heat flow and modulated heating rate signals which are the raw signals created in an MDSC™ experiment. MDSC uses the amplitude of these two signals to calculate heat capacity in the same way that DSC could calculate heat capacity from two experiments at different heating rates.

\[
\text{Heat Capacity} = K C_p \times \frac{\text{Delta Heat Flow (Amplitude)}}{\text{Delta Heating Rate (Amplitude)}}
\]

Clearly MDSC has a significant advantage over DSC in calculating heat capacity because only one sample and one experiment are required once the instrument has been calibrated.

Obtaining the Benefits of MDSC

After the two simple measurements (average and amplitude) are made, the benefits of MDSC result from simple arithmetic treatment of the signals. This treatment results in two additional signals.

(1) Reversing Heat Flow  =  Heat Capacity  x  ( - Average Heating Rate)

(2) Nonreversing Heat Flow  =  Total Heat Flow  -  Reversing Heat Flow

Reversing Heat Flow is the heat capacity component of the total heat flow. The reason for multiplying the heat capacity by the average heating rate is to scale this signal to the same heating rate as the total heat flow signal. This permits subtraction of the two signals to create the Nonreversing Heat Flow signal which is the kinetic component of the total heat flow signal. The separation of the total heat flow into its reversing and nonreversing components is seen in Figure 6.
Summary

Modulated DSC™ is based on the time-proven technique of DSC. It provides significant benefits over DSC because it conducts two simultaneous experiments which permit the measurement of both heat flow and heat capacity. Simple calculations are used to separate the total heat flow into its heat capacity (reversing) and kinetic (nonreversing) components.