Temperature Modulated DSC- What is really measured?

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The heat flow Φ into the sample is usually described as the sum of two components, sensible and latent heat flow:

$$\Phi(T,t) = m\,c_p\,\beta + m\,\Delta h_\mathrm{r}\,\frac{\mathrm{d}\alpha}{\mathrm{d}t} \tag{1}$$

where m is the sample mass, c_p the specific heat capacity, β the heating rate of the sample, Δh_r the specific enthalpy of a thermal event (e.g. enthalpy of reaction) and α is the extent of reaction (or more in general extent of structural change). Based on the discussion of Eq. (1) for the case of linear and time invariant conditions a generalized theory of a temperature modulated DSC is developed. Based on this theory, different temperature modulated DSC (TMDSC) techniques are discussed. These techniques use different kinds of temperature modulation functions and evaluation procedures (Fig. 1):

(i) Stepwise temperature changes with isothermal segments: These types of temperature programs are especially useful for the separation of the heat flow regarding Eq. (1). However, the time required for such experiments is relatively long because the sample should always relax to the equilibrium state during the isothermal segments.

(ii) Single frequency modulations: The modulation function can be sinusoidal or more complex, for example a saw-tooth modulation. Usually the first harmonic is used for evaluation procedures. The single-frequency modulation is used for the measurement of the frequency dependence of the heat capacity or for separating the reversing and non-reversing heat flow components. As discussed below, the disadvantage of this separation method is that the reversing and non-reversing heat flow generally do not match directly with the components in Eq. (1).

(iii) Multi-frequency periodic modulations generated by superposition of multiple sinusoidal functions or the use of non-sinusoidal modulation functions evaluated by use of the Fourier transformation to get the spectral information: These methods are used for calibration purposes of the heat capacity or to measure the thermal relaxation of the sample.

(iv) A new advanced technique of temperature-modulated DSC combines the separation of sensible and latent heat flow and the measurement of the frequency-dependent heat capacity over a wide frequency range. This technique is based on stochastic temperature modulation and yields the quasi-static heat capacity $c_{p,0}$ and the frequency-dependent complex heat capacity $c_p^*(\omega)$ without the need for additional calibration procedures. $c_\mathrm{p}^*(\omega)$ can be determined over a wide frequency range. A second result of the analysis is the non-reversing heat flow Φ_non. This is the non-correlated heat flow component. The reversing heat flow is calculated from the quasi-static heat capacity. All these quantities and their frequency dependency can be determined in one single measurement. The concept of stochastic temperature-modulated DSC has been recently realized in TOPEM® by METTLER TOLEDO.

Independent on the experimental conditions, all TMDSC techniques deliver the non-reversing and the reversing heat flow contribution. Both heat flow components depend on the experimental parameters frequency, amplitude and underling heating rate. The reasons of this could be

- the use of experimental parameters which valuate the prediction of the TMDSC techniques (linearity and stationary) or
- the irreversible, time dependent behavior of the sample.

For different practical examples the selection of optimal experimental parameters are discussed to fulfill the limits of linearity and time invariance. Only from such measurement thermodynamic relevant data can be received.

Furthermore the relation between the measured reversing and non-reversing heat flow to thermodynamic properties are shown.

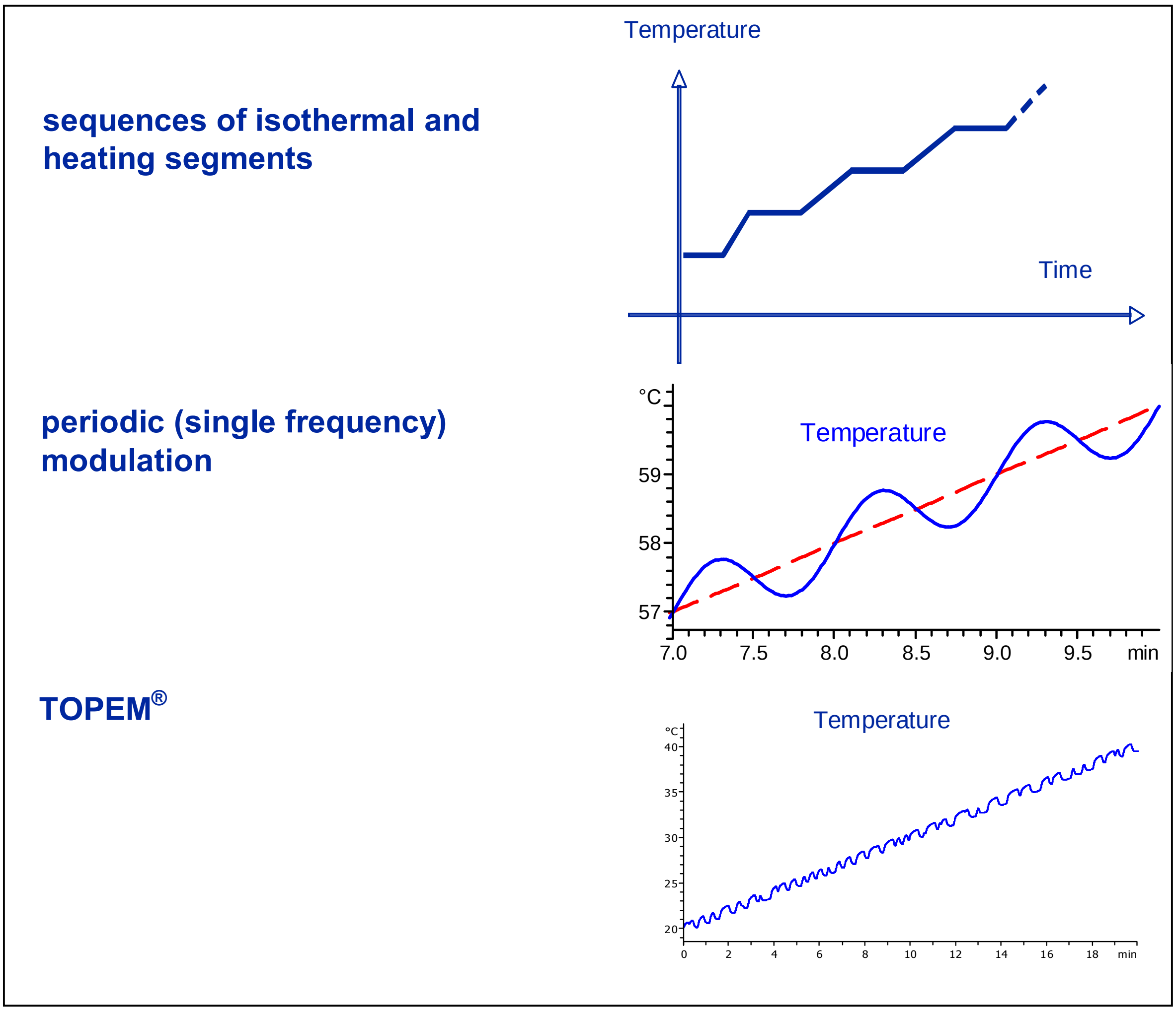

Fig. 1: Typical temperature profile of different TMDSC techniques.