



Interpretation of the Crystallization Peak of Supercooled Liquids Using Tzero[®] DSC

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INTRODUCTION

One of the benefits of the Tzero approach to measuring heat flow is the improvement in peak resolution. The fourth term of the Tzero heat flow equation (Equation 1) accounts for the heating rate difference between the sample and reference, which minimizes thermal lag and reduces the measurement time constant (1).

$$q = -\frac{\Delta T}{R_r} + \Delta T_0 \left(\frac{1}{R_s} - \frac{1}{R_r} \right) + (C_r - C_s) \frac{dT_s}{d\tau} - C_r \frac{d\Delta T}{d\tau}$$

Equation 1

This translates to improved resolution compared to the traditional heat flux signal (T1 heat flow). Advanced Tzero (T4P heat flow) further improves resolution by incorporating the contact resistance between the sample pan and sensor. As such, the T4P measured temperature is the pan temperature (as opposed to sensor temperature), and the measurement time constant is further reduced. The improvement in resolution between T1, T4 and T4P is illustrated when comparing the heat flow signals for the melting of indium (Figure 1).

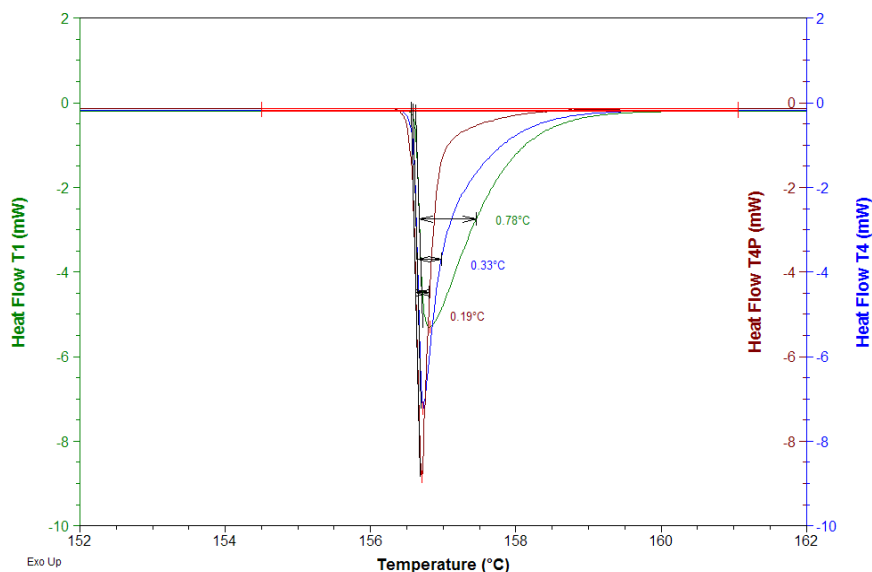


Figure 1: Comparison of the T1, T4 and T4P Peak Shapes of the Indium Melt Peak

The progressively shorter time constant allows the heat flow signal to return to baseline much faster in T4P, resulting in improved signal resolution. This improvement

can easily be quantified by comparing the individual peak widths. The peak width of 0.78 °C for the T1 signal results from a significantly longer measurement time constant compared to the width of 0.19 °C in the T4P signal.

Theoretically, the time constant of a measurement should be 0 seconds if no lags are present. This would result in an instantaneous return to baseline after the melting process is complete, and a corresponding negligible peak-width. As such, the measurement with the lowest time constant and sharpest melting peak approaches the theoretical response, and is the most fundamentally accurate (i).

DISCUSSION

Applying Tzero[®] DSC to Cyclohexane Crystallization

When analyzing crystallization peaks by DSC, it is important to understand the kinetics of the crystallization process. Crystallization from the melt is a two-step process; nucleation (the rate-limiting step) must first occur then rapid growth proceeds. In addition, most materials will exhibit some supercooling behavior. A supercooled liquid is a compound, which exists in the liquid state below its melting temperature resulting in an inherently unstable phase. Crystallization of a supercooled liquid is a rapid and energetic process, which can result in “self-heating” of the sample.

Tzero DSC optimizes crystallization peaks in exactly the same manner as melting peaks. The reduction of the time constant in the T4P signal results in a faster return to steady state when the crystallization process is complete. This improvement in response is illustrated when comparing the T1, T4 and T4P heat flows associated with the crystallization of 3 mg of cyclohexane, a compound which exhibits minimal supercooling prior to crystallization (Figure 2). The data are plotted as a function of time, and the peak widths at half height are recorded.

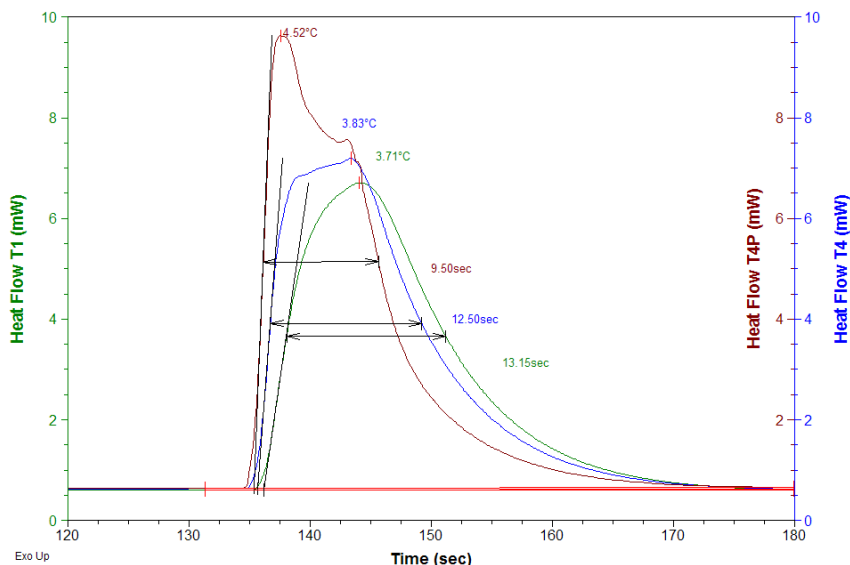


Figure 2: Comparison of the T1, T4 and T4P Peak Shapes of the Cyclohexane Crystallization Peak versus Time

Note that the T4P signal results in the sharpest crystallization peak and fastest return to baseline, due to the short time constant. The unusual shape of the T4P crystallization peak has been previously explained in the literature (2).

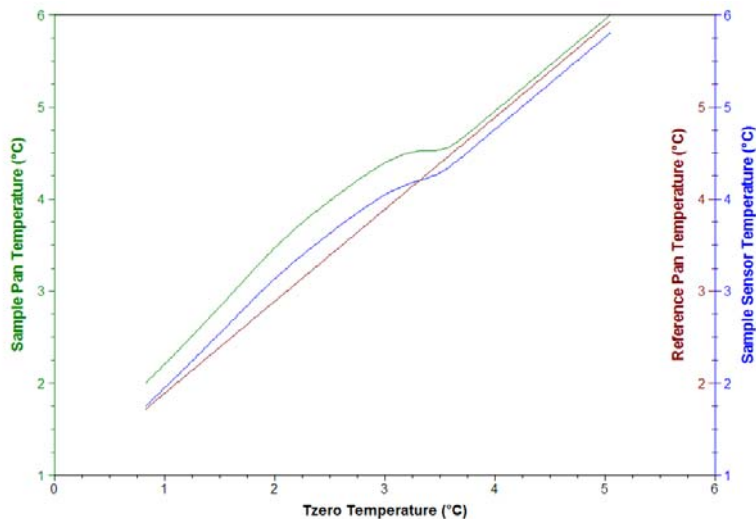


Figure 3: Comparison of Sample Pan, Sample Sensor, and Reference Pan Temperatures During the Crystallization of 3 mg of Cyclohexane

The crystallization of cyclohexane is a relatively low-energy process, as the enthalpy of melting is rather small. As such, temperature hysteresis during the crystallization would not be expected, as minimal self-heating would occur. Figure 3 compares the sample pan temperature, sensor temperature, and reference pan temperature versus Tzero temperature during the cyclohexane crystallization. The data in Figure 3 indicate that the temperature of the sample is only minimally disturbed during the crystallization process, as expected. Figure 4 contains a comparison of the T1, T4 and T4P heat flow signals for the cyclohexane crystallization, plotted versus temperature.

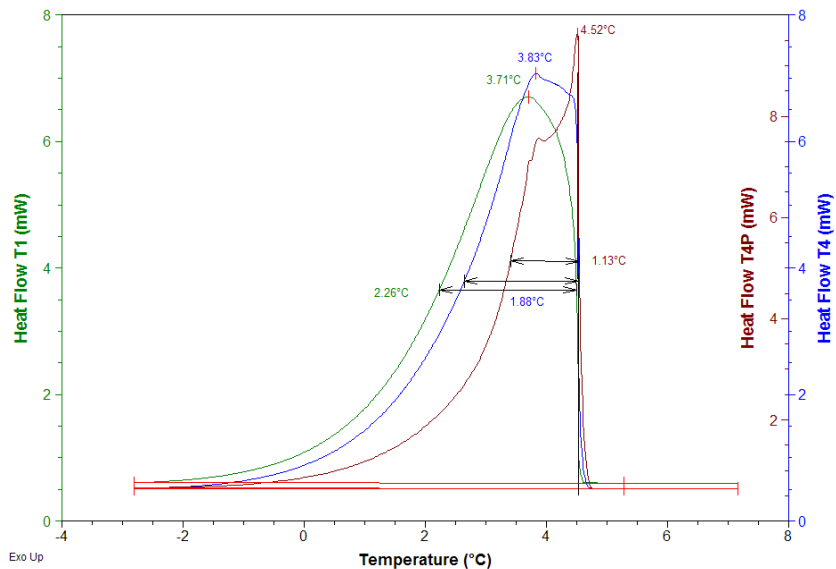


Figure 4: Comparison of the T1, T4 and T4P Peak Shapes of the Cyclohexane Crystallization Peak versus Temperature

This direct comparison further illustrates the shorter time constant of the T4P signal, evidenced by the narrow peak width compared to the T1 and T4 signals. The data from each signal is easily interpreted and quantified.

Applying Tzero[®] DSC to Supercooled Water Crystallization

The analysis of the crystallization of water is not as straightforward, as it is complicated by supercooling and the resultant energetic fusion. The data in Figure 5 contain a comparison of the three heat flow signals for the crystallization of 1 mg of water, plotted versus time with a superimposed temperature scale.

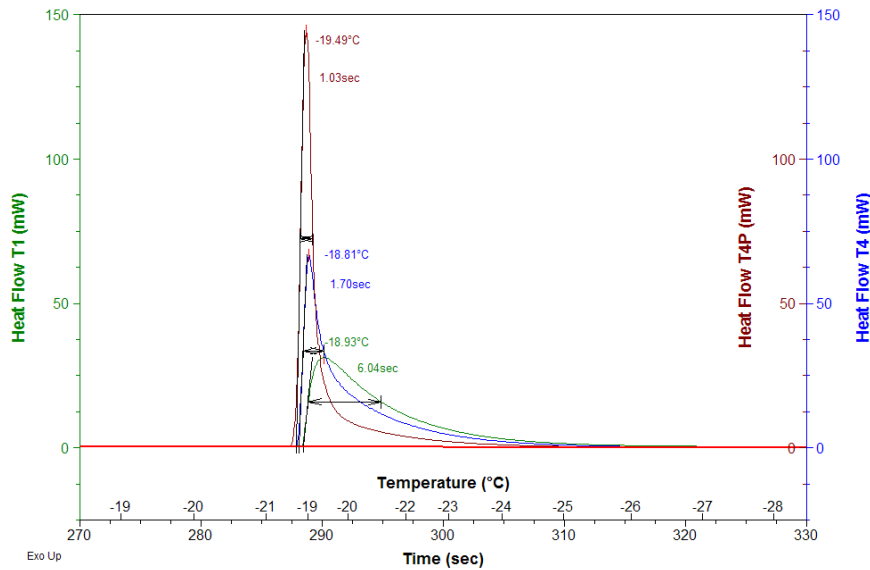


Figure 5: Comparison of the T1, T4 and T4P Peak Shapes of the Water Crystallization Peak versus Time

This water sample supercooled about 21°C, and the subsequent crystallization process is much more energetic than the cyclohexane example, resulting in peak heat flow rates about 15X larger. The reduced time constant of the T4P signal is clearly apparent, as the peak width of the T4P signal is about 6X narrower than the T1 signal. The heat flow is also returning to steady state much faster when measured in the T4P mode, as evidenced by the more rapid decay of the heat flow signal toward baseline. A simple comparison of the observed peak onset to the measured peak maximum temperature indicates that the sample is self-heating during the crystallization process, which is not unexpected given the highly energetic process. This is further illustrated in Figure 6, in which the sample pan temperature, sample sensor temperature, and reference pan temperature are compared versus Tzero temperature.

The data in Figure 6 indicate that the sample temperature rises about 2.9 °C during the crystallization process. The sample sensor is less sensitive to this self-heating (as it is decoupled from the actual sample), and measures only a 1.7 °C rise.

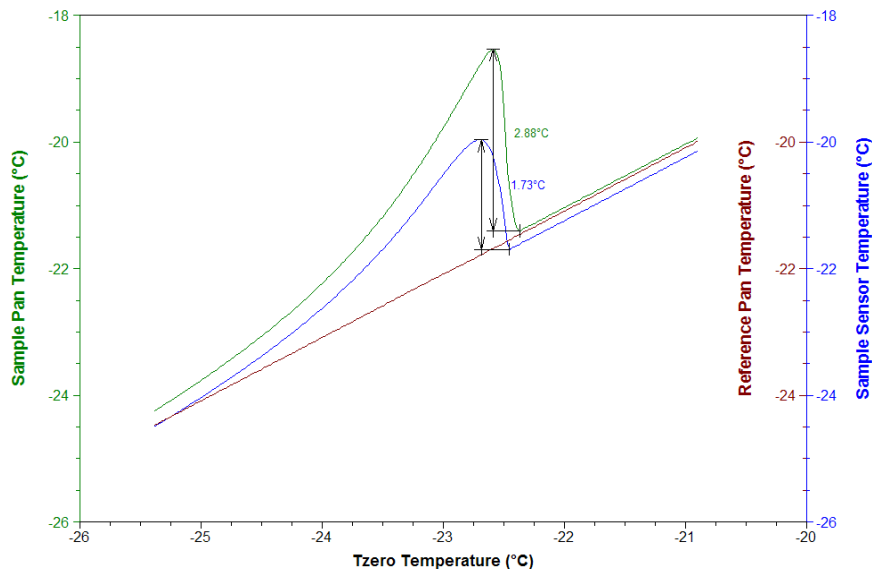


Figure 6: Comparison of Sample Pan, Sample Sensor, and Reference Pan Temperatures During the Crystallization of 1 mg of Water

When plotting the Tzero[®] heat flow signals, each respective temperature measurement is used as the X-axis. As such, the T4P heat flow is plotted versus sample-pan temperature, and the T1 and T4 heat flows are plotted versus sample-sensor temperature. As a result, the shapes of the crystallization peaks are indicative of the time constant of the measurement, as well as the accuracy of the measured temperature. Figure 7 contains a comparison of the three types of heat flow plotted versus temperature, for the crystallization of supercooled water.

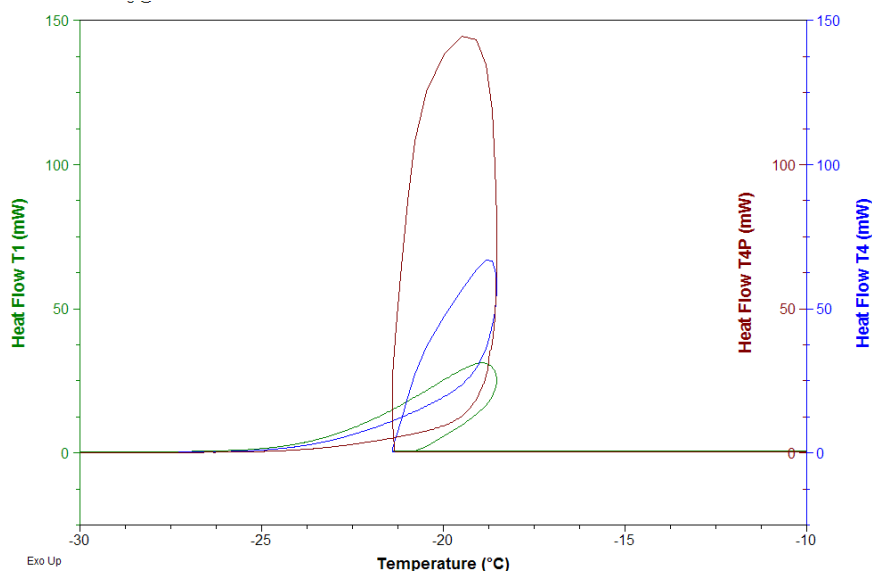


Figure 7: Comparison of the T1, T4 and T4P Peak Shapes of the Water Crystallization Peak versus Temperature

While the shapes of these crystallization peaks are unusual compared to the cyclohexane example, they are easily explained. When measured in T1 mode, the water crystallization is manifest as a leaning peak. The T1 heat flow has the largest time

constant, which means the signal will take the longest to return to baseline after peaking (Figure 5). In addition, the T1 temperature measurement is made at the sample sensor, making it less sensitive to self-heating of the sample (Figure 6). The slope of the leading edge of the peak is due to self-heating during crystallization. Just prior to the conclusion of crystallization, the self-heating subsides, the sensor temperature begins to re-establish equilibrium with the cell temperature, and the slope of the heat flow reacts. As the crystallization concludes, the sample returns to temperature equilibrium, resulting in a slow decay of heat flow as the sensor temperature returns to cooling.

In the T4 signal, the measured temperature is also the sensor temperature, but the heat flow measurement time constant is about 2X faster than T1. As such, the enthalpy of crystallization is fully detected as the sample is self-heating (i.e. the time scale of the crystallization is slightly faster than that of the self-heating). As the crystallization concludes, the heat flow rapidly returns to baseline, even before the sample temperature is able to re-establish equilibrium with the measuring cell. The result is a hysteresis loop in temperature. Note however, that as the sample sensor re-establishes temperature equilibrium, the T4 signal approaches the same response as T1. This is not unexpected, as the measured temperature is identical for both modes.

The T4P signal contains the shortest time constant (fastest response to heat flow), and the most accurate temperature measurement (pan temperature). As such, the enthalpy of crystallization is almost completely detected prior to the onset of self-heating. The rapid return to baseline occurs during the self-heating phase, and the heat flow has nearly returned to equilibrium as the temperature signal recovers steady state. The result is the largest temperature hysteresis response, and the most pronounced heat flow loop.

CONCLUSION

A major benefit of the Tzero[®] approach to measuring heat flow lies in the fundamental accuracy of both the temperature and the heat flow measurement. By reducing the time constant, the heat flow signal approaches the theoretical response. By incorporating the pan contact resistance, the T4P signal contains a fundamentally more accurate temperature measurement. Elimination of artifacts inherent in previous generation or alternate instrumentation results in an unusual, but easily understandable, peak shape for the crystallization of supercooled fluids. By considering the relative time scales of the heat flow and temperature axes, these “unusual” results are found to be the more accurate representation of the true crystallization process.

REFERENCES

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KEY WORDS

Tzero DSC, Supercooling, Crystallization

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