

The Study of Solid-Liquid Phase Equilibria With Phase Technology Analyzers

Summary

The determination of freezing and melting temperatures using a light scattering method developed by Phase Technology is described. The method's requirements as well as its merits over differential scanning calorimetry and time-temperature cooling curve methods are discussed.

Introduction

Since 1989, Phase Technology has installed several thousand analyzers in laboratories to measure freezing and melting temperatures of various materials that are in liquid phase under room conditions. Most of these materials are petroleum distillates such as jet fuel and diesel. Some of them are engine coolants (ethylene and propylene glycols) in various dilutions with water. The methods employed by these instruments have been approved by international standards organizations.

A number of these analyzers are also used by chemical producers to characterize the solid-liquid phase behavior of organic and inorganic chemicals.

Accuracy and precision are of prime importance to the users as the information is critical to maximal functional use and optimized quality. It also impacts product handling and quality. In all cases, the demand on precision, sensitivity and speed by the industrial users exceeds those obtainable from differential scanning calorimeter (DSC) and classical time-temperature cooling curves.

Measurement approach

The freezing point of a pure substance is the same as the melting point. To avoid supercooling, which obscures true freezing point measurement, Phase Technology prefers the determination of melting point. Careful considerations are given to test conditions to ensure the sample is warmed slowly to approach solid-liquid equilibrium. The sample quantity is small (in the 150 micro-liters range); therefore, diffusion and heat transfer are efficient and responsive to temperature change. The cooling and warming rates can be faster than those used for larger samples, yet without affecting the quality of results. With this advantage, the test elapse time is reasonably short. For many organic liquids, the test time is 10-15 minutes. The test procedure and result analysis are automated. Operator intervention and interpretation are not required.

For a multi-component system of defined composition (with the exception of eutectic composition and colligative system), solids are first formed at the Initial Freezing Temperature (IFT). More solids appear as temperature decreases. Again, supercooling is a prime concern. Phase Technology adopts the approach of cooling the mixture to partial solidification, followed by controlled warming

until the last crystals disappear. The temperature at which the last crystals disappear is recorded as the Final Melting Temperature (FMT) of the system. It is the same as the Initial Freezing Temperature, which is often referred to, by the industries, as "Freezing point" of the material.

Figure 1. Phase Plot of a Typical Jet Fuel

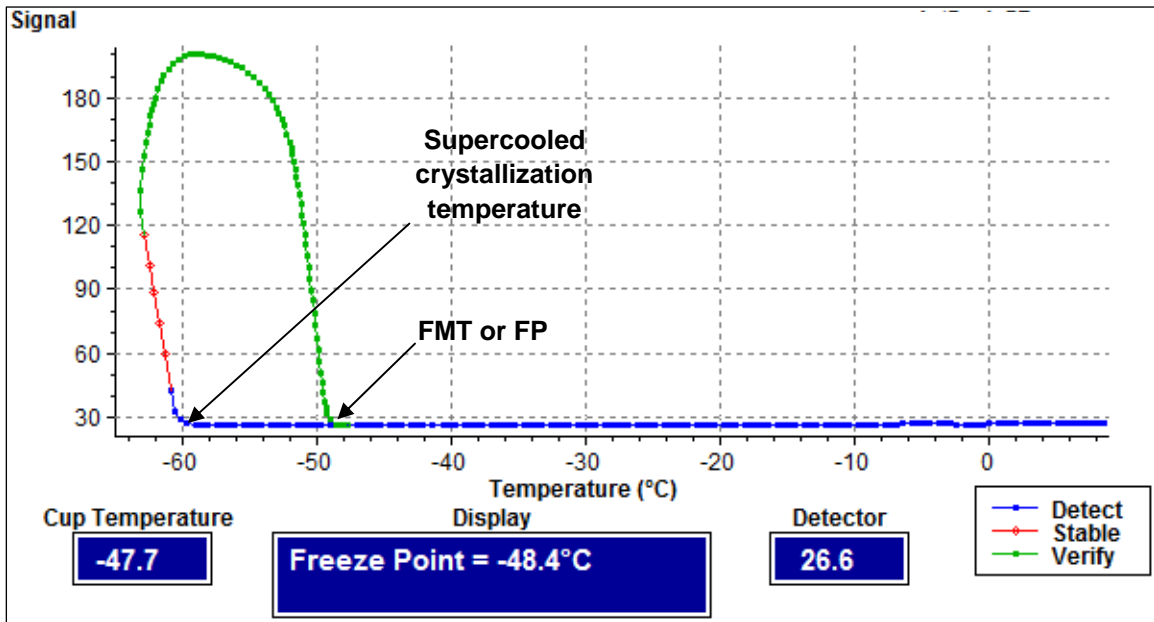
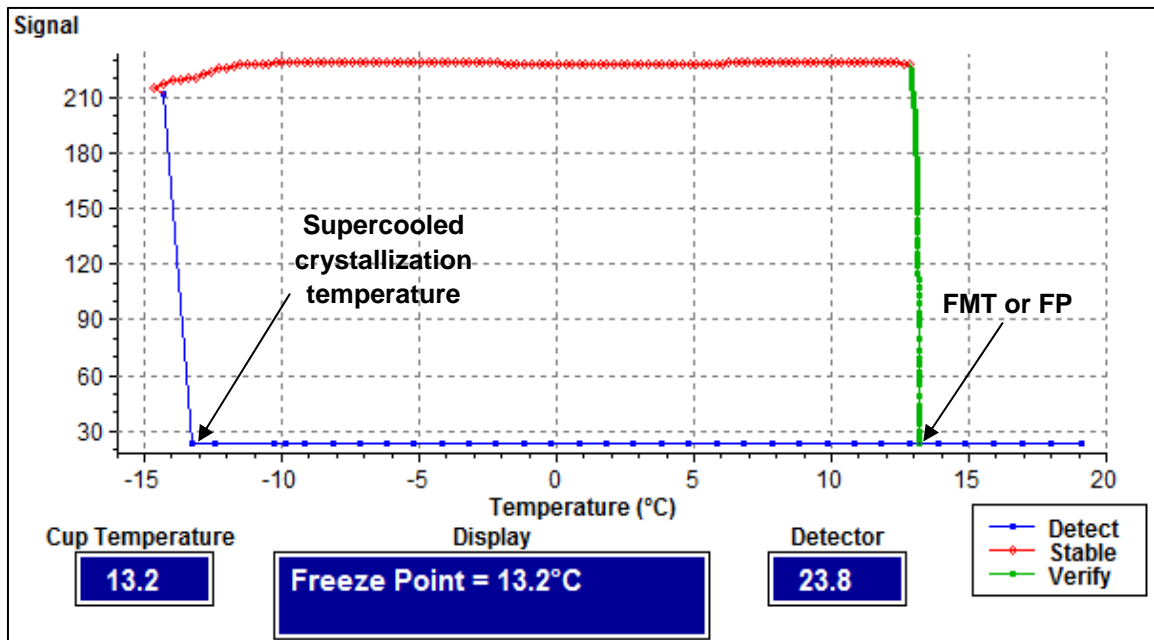


Figure 2. Phase Plot of a Pure Chemical



Apparatus design and measurement principle

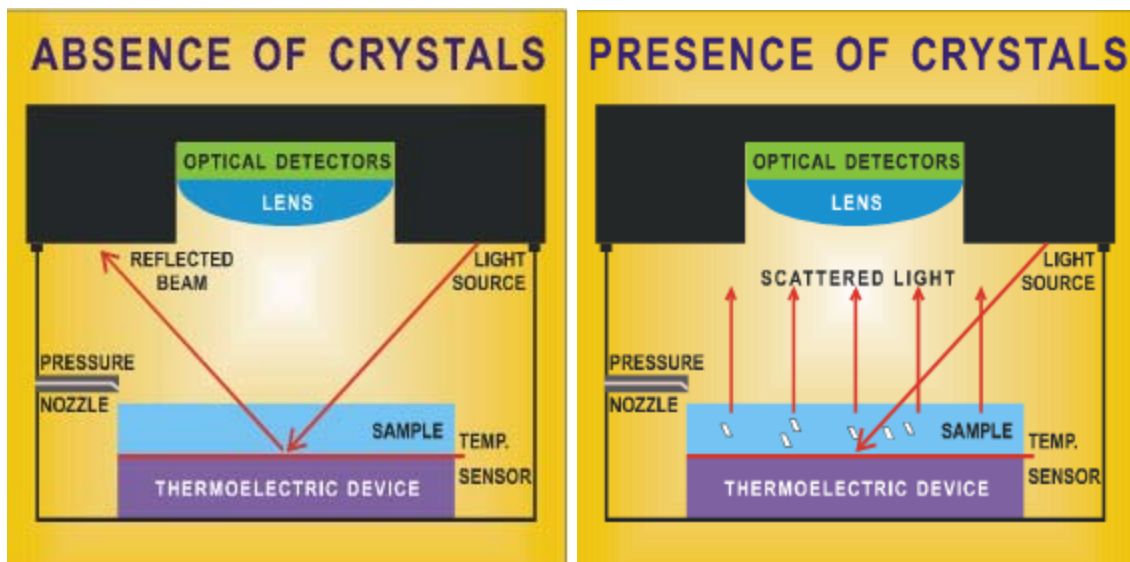
A small sample (150 micro-liters) is pipetted into the sample cup of a test chamber that is constructed of non-reflective black materials. The chamber is optically and pneumatically sealed once the lid is closed. Depending on the needs of the test, the air trapped inside the chamber can be dried by an internal mechanism to ensure measurements down to -90°C without interference of moisture condensation onto the sample.

The sample temperature is controlled by a solid state cooler with an operating range of -90 to $+70^{\circ}\text{C}$. The cooling and warming rates can be varied from 0.1 to $30^{\circ}\text{C}/\text{min}$. Sample temperature is monitored by a platinum resistance thermometer embedded in the sample cup. There is full flexibility in multiple-steps temperature programming through specification of target temperature, cooling/warming rate and soak time.

During measurement, a light beam is directed onto the sample at a fixed angle. With the sample being a transparent liquid (a pre-requisite of the test), the beam passes through the sample and reflected off the chromium mirror surface of the sample cup bottom. The reflected beam is absorbed by the black chamber wall.

In the presence of crystals in the sample, light is scattered by the crystals. The scattered light is collected by a lens assembly and focused onto an optical detector with over 100,000 light sensors. The light signal is plotted in real-time on the analyzer display. An increase of light signal from a baseline (formed by a single liquid phase) indicates the presence of a second phase. This optical system has been proven to be capable of detecting very small quantities of crystals in a liquid-solid system.

Figure 3. Principle of Operation



Requirements

This design has a number of requirements; some of them are listed below:

1. The test must begin with a liquid sample that can be pipetted into the sample cup. If necessary, there is provision to pipette in a heated sample.
2. The sample must not have a high vapor pressure as there is an air space above the sample. Even though the test chamber is sealed and the air space is small, it is undesirable to lose a significant quantity of the sample through evaporation in the course of the test. On the other hand, since most of the tests involve sub-ambient temperatures, the concern with evaporative loss is small, especially with low temperature tests. This design has been found to work satisfactorily with materials as volatile as naphtha and p-Xylene.
3. The sample must be chemically compatible with the materials used in constructing the sample cup. Detailed information on these materials is available from Phase Technology.
4. The liquid sample must be transparent to visible light in a thin layer (up to 2 mm in thickness).

Comparison with DSC and Time-temperature cooling curves

The Phase Technology method monitors the light (dependent variable) scattered by the sample at different temperatures (independent & controlling variable). In liquid phase, the level of scatter is low. The level rises with an increasing amount of solid.

Light scatter is an intrinsic property of the solid-liquid phase boundary. As long as a solid phase exists, the scatter is present. One can control (i.e. change or maintain) the temperature with great flexibility in order to measure the scattered light without other constraints.

Also, the arrangement of the optical components in the apparatus is such that the light sensors receive practically no light when the sample is in full liquid phase. The occurrence of a small amount of solid causes a large increase in the light received by the sensors.

DSC and time-temperature curves depend on the latent heat of fusion to cause a disturbance in heat flux for detecting phase transition. Latent heat is only released during phase transition. It is a transitory effect. Once the phase change is complete, latent heat exchange ceases. There is no more signal to be measured; for example, a stable solid phase in a liquid medium does not give off any latent heat.

Due to the transitory nature of the signal, it is always tempting to increase the cooling or warming rate to make the signal more pronounced. However, the faster the rate, the farther is the system away from equilibrium and the larger lag in temperature measurement.

A related issue is the convoluted thermal nature of the methods. Although DSC monitors the heat flux (dependent variable) as a function of temperature (independent variable), the significant release or absorption of latent heat itself could raise or lower the temperature of the system, rendering the attempt to control the temperature itself not truly independent. Subsequently, the determination of the phase-transition temperature can be interfered. This type of feedback interference is not present with an optical measurement technique, whereby the release or

absorption of heat would not affect the optical properties of the samples being tested, so long as the temperature is being controlled accurately.

DSC and time-temperature curve methods are more straightforward in dealing with pure or nearly pure materials, where there is an abundant amount of latent heat exchange at phase transition. When it comes to multi-component systems, these techniques are challenged, particularly in systems where a minor component is responsible for the IFT (common in petroleum liquids). Being a minor component, the amount of latent heat available is small at IFT; consequently, the heat flux is small for DSC measurement.

For a time-temperature cooling apparatus, the latent heat may cause a temporary increase in temperature, or a change in slope in the cooling curve. However, the liquid phase composition changes with increasing solid formation, the freezing temperature changes with it. Unlike a pure material, a thermal arrest is not expected in a multi-component system (except for eutectic composition and colligative system); as such, a horizontal section on the time-temperature curve is not available to confirm the freezing temperature. Instead, a downward slant line is the expected outcome. The maximum temperature point before the downward slant is usually taken as the IFT. However, one cannot be sure if there is sufficient latent heat released to compensate for the supercooling effect plus the heat outflow to the external cooling medium. It is possible that the maximum temperature point is not as high as the IFT; therefore, the adoption of the maximum temperature point as IFT is controversial and can at best be used as an estimate only.

Figure 4. Time-Temperature Cooling Curve of a Pure Material

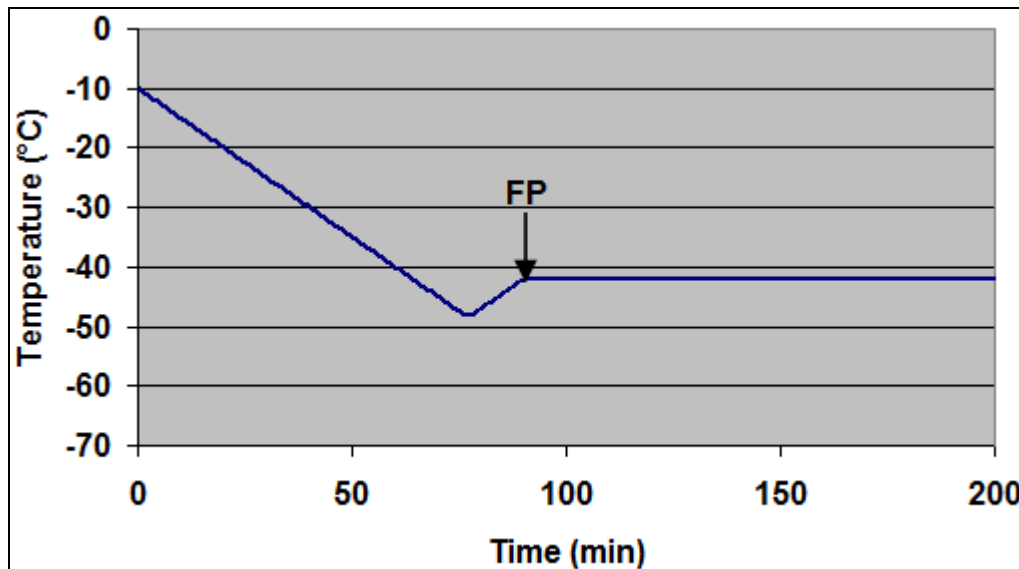
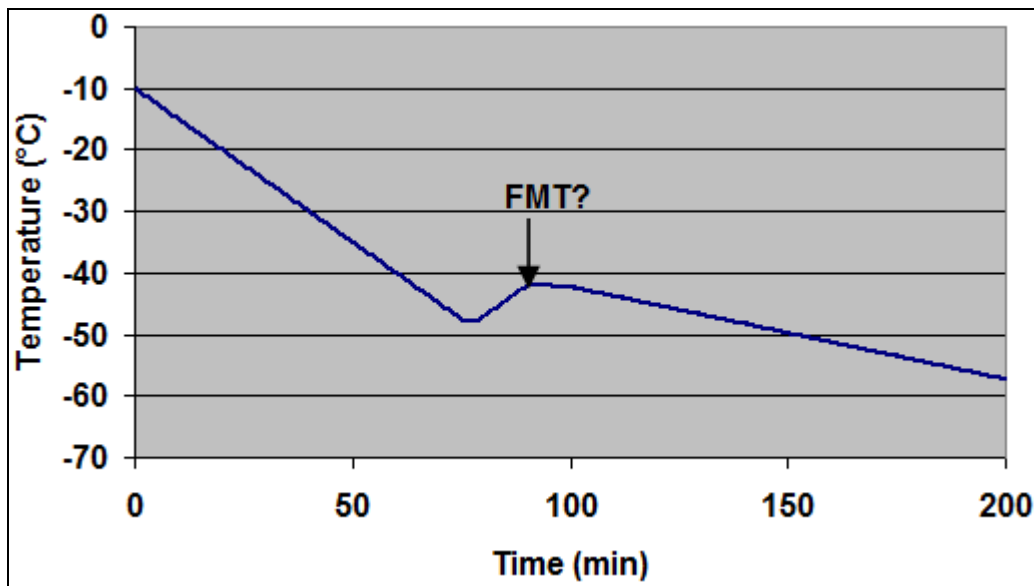


Figure 5. Time-Temperature Cooling Curve of a Multi-component System



The time-temperature curve technique is subject to further inaccuracies caused by poor mass and heat transfer if the sample is not well-stirred during test. Mixing is important to minimize, and better still, eliminate temperature gradients. Without mixing, solid is first formed in the coldest part of the sample, which is often on the sample tube wall. The thermometer, which is located at the center of the tube, may record a warmer temperature in a cooling test.

In some situations, operators of time-temperature cooling curve method prefer to shorten the test by setting a large temperature differential between the sample and the cooling medium. They may also use single-wall sample tube. In both cases, the test elapse time is shortened and the slope change on the cooling curve may become more distinct. However, the measurements are farther away from equilibrium and the temperature lag of the thermometer is more severe, which means unreliable freezing and melting temperatures.

Key advantages of Phase Technology's light scattering method over DSC and time-temperature cooling curve

1. Closer approach to equilibrium conditions
2. More reliable for impure and multi-component systems
3. Full automation
4. Short analysis time
5. Small sample size