Phase Transitions and Differential Scanning Calorimetry

Overview

Differential scanning calorimetry (DSC) is an inexpensive and rapid method to measure heat capacities of condensed phases. From these measurements, enthalpy changes for phase transitions can easily be determined. DSC has been applied to a wide variety of problems, from coal combustion to protein denaturation.

In this experiment, we will begin with a standard reference substance, indium, and then examine several types of materials: an inorganic salt (NH₄Cl), the polymer polyethylene, and two liquid crystals: p-azoxyanisole, and cholesterylmyristate. Ammonium chloride has been studied for several years and is now considered to provide an excellent example of solid structural phase transitions. It has two such transitions, at 242 K and 457 K. The enthalpy change of the transition at 457 K can be measured to within a few percent. However, so far, we have only an estimate for \( \Delta H \) for the transition at 242 K; we will study only the higher temperature one of the two phase transitions.

The next part of this experiment consists of determining the percent crystallinity in a sample of the polymer polyethylene. Our polyethylene sample melts at about 386 K. By computing the enthalpy change of melting of a completely crystalline sample, we can compute the percent crystallinity.

The liquid crystal p-azoxyanisole exhibits two transitions (the normal solid to the so-called nematic liquid-crystal phase and the nematic to the normal or isotropic liquid) within an accessible temperature range. Similarly, cholesterylmyristate exhibits several transitions of its own.

Introduction

DSC provides a convenient and moderately accurate method of measuring heat capacities and enthalpy changes. Commercial instruments provide a recorder output of the constant-pressure heat capacity,

\[
C_P = \left( \frac{dq}{dT} \right)_P = \left( \frac{\partial H}{\partial T} \right)_P
\]

as a function of temperature. The area under such a curve between any two temperature limits yields an enthalpy change:

\[
\Delta H = \int_{T_1}^{T_2} \left( \frac{\partial H}{\partial T} \right)_P dT = \int_{T_1}^{T_2} C_P dT
\]

The differential scanning calorimeter operates on the “null balance” principle. Within the assembly there are two small sample holders: one for the sample and the other to hold a reference material. Energy (as electrical work) is supplied to each sample holder independently, and the
temperatures of each are monitored. Energy (as an associated heat) which is absorbed or evolved by the sample is compensated by increasing or decreasing the electrical energy delivered to the sample-holder heater. The temperatures are monitored by comparing the respective signals from platinum resistance thermometers in each of the sample holders. This adjustment of electrical input to the heating unit provides a varying electrical signal which is opposite but equivalent to the varying thermal behavior of the sample. For example, when a phase transition point is reached from lower temperatures, the sample will absorb additional energy. Then additional electrical power must be supplied to the heater of this sample so that the reference and sample holders will be at the same temperature. When the transition is completed, the temperature of the sample will rise, and additional heat need no longer be supplied. The varying electrical signal thus provides a record of the thermal behavior of the sample.

In this experiment several different types of phase transitions in one-component systems will be observed. Under ideal conditions common phase changes (e.g., solid-to-liquid, liquid-to-gas, etc.) occur, under a given constant pressure, entirely at a single temperature, at which the apparent heat capacity is infinite. The sharp spike in $C_p$ at the transition temperature is an example of a so-called *delta function*, defined to be zero except at one value of its independent variable where it becomes infinite, but with a definite finite area beneath it (in our case, the enthalpy change for the transition). The sharp spike to infinity in $C_p$ at the transition temperature cannot be observed in practice. Often the system may contain impurities or may be slightly non-uniform in structure; furthermore, the rate of transfer of heat through the system is not zero, so that different parts of the system cannot all have exactly the same temperature; and finally, all phase transitions occur at less than infinite rates. For these reasons, the experimental $C_p-T$ curve displays a broader peak, and the enthalpy change $\Delta H$ for the transition is taken as the area under the peak (see Figure 1). The nominal transition temperature is often taken as the point at which the curve first rises from the base line; alternatively, if the peak is very sharp, the temperature at the maximum can be used.
Melting Transitions

In the first run, the melting of indium metal at 429 K will be observed and used as a calibration for the instrument, since its enthalpy of fusion per gram is well known ($\Delta H = 28.45 \text{ J g}^{-1}$). Thus the area under a $C_p$ vs. $T$ curve for an unknown sample can be converted into energy units by comparison to the In data.

A second melting transition to study is that in a sample of polyethylene:

$$(\text{CH}_2)_n(s) \rightarrow (\text{CH}_2)_n(l)$$

Under ideal conditions a completely crystalline sample of the polymer would be used, and it would presumably have a more or less sharp melting point, like any other crystal. However, real polymers cannot be obtained in 100% crystalline form, because of their long-chain structure. Amorphous regions of entangled chains inevitably are produced when the material is cooled down from the melt, and the typical “crystallites” may be only 20 or 30 nm in dimension. When the polymer is heated, melting takes place over a broader range of temperatures, as in Figure 1, and the area under the curve can be used as a measure of the degree of crystallinity in the sample, provided we can somehow get a value of the specific enthalpy of fusion per gram of crystal. Fortunately, the Clapeyron equation (Engel and Reid, eq. 8.13) comes to our aid! The melting temperature as a function of pressure can be determined, its slope can be measured and used to determine $dP/dT$; the value of $\Delta V$ can be obtained from a combination of the measured density of the melt (the liquid phase) and the crystal unit-cell dimensions as observed by X-ray diffraction. From these data, a value of $286 \text{ J g}^{-1}$ has been found for the specific enthalpy of fusion of crystalline polyethylene. The melting temperature of an ideal crystal of the polymer has been estimated to lie at about 418 K, but for various reasons the observable melting range usually lies well below this value.

Structural Transitions in Ammonium Chloride

Solid ammonium chloride is an ionic substance that can exist in several different crystal structures. Phase I, which is stable above 457.6 K, is a cubic crystal which resembles common NaCl: each chloride ion is surrounded by six nearest neighbor ammonium ions, and in turn each $\text{NH}_4^+$ ion is surrounded by six chlorides. Below the transition temperatures quoted above the stable Phase II is again cubic, but it now resembles CsCl: each $\text{NH}_4^+$ has eight $\text{Cl}^-$ nearest neighbors, and vice versa.

Transitions between such different crystal structures are quite common, and are generally also of the sharp type called “first order”. However, they may take a longer time to occur, and so there is some danger of superheating or supercooling. You should be able to get fairly good values of the transition temperature and of $\Delta H$ for the change in state

$$\text{NH}_4\text{Cl}(s, \text{II}) \rightarrow \text{NH}_4\text{Cl}(s, \text{I}) \quad T = 457.6 \text{ K}, \ P = 1 \text{ atm}$$
Transitions in Liquid Crystals

When most solids melt the atoms or molecules become much freer to move around the space occupied by the material, and also (where applicable) gain the freedom to orient themselves in many different ways. Thus, molecules lose both positional and orientational order in the transition from solid to liquid, and the entropy of the system increases. In liquid crystals there are one or more states which lie between the solid and the liquid, associated with varying degrees of orientational and translational order. For example, in p-azoxyanisole (PAA) (shown below) there is a solid-to-liquid crystal phase change at 391 K, and then the transition to the normal liquid follows at 408 K.

\[
\text{PAA}
\]

By determining the enthalpy change associated with each of the transitions you should be able to deduce whether the liquid crystal phase resembles more closely that of the solid or the liquid.

Several kinds of liquid crystal phases are possible, depending on the system. For rod-like molecules, such as those studied here, these are labeled by characterizing the direction of prefered orientation and also by the tendancy to form layers. A good system in which to study transitions between liquid crystal phases is cholesterylmyristate:

\[
\text{C}_{13}\text{H}_{27}
\]

This material exhibits a solid-to-smectic-A transition at 344 K, a smectic-A-to-chiral-nematic transition at 352 K and then the transition to the normal liquid at 358 K, all easily accessible to us.

Liquid crystals are classified into three structural types based on broad classes of order:

(1) nematic: translationally disordered but orientationally ordered

(2) smectic: translationally ordered in one dimension (yielding a system of layers of two dimensional liquids with a well-defined layer spacing) and orientationally ordered in the layers (at least)

(3) cholesteric: orientationally ordered like a nematic, but with a helical twist to the direction of orientation. (This phase is also called twisted or chiral nematic.)

The name nematic is derived from the Greek word for thread. This is less a statement about the shape of the molecules in a nematic liquid than a description of the long, thread-like
patterns often formed by liquid crystalline packing defects. But the molecules of nematic liquid crystals (and of all types of liquid crystals to some extent) are themselves commonly “rod-shaped” if not truly “thread-like.” Our first liquid crystal, p-azoxyanisole, forms a nematic phase.
Experimental

As the calorimetric analysis is carried out on a sample, a plot of heat capacity as a function of temperature will be produced. Since the area under the curve determines the enthalpy change, it will be desirable to maximize this area in order to minimize the error in its measurement. The area can be maximized by adjusting several controls on the DSC. The scan rate refers to the speed at which the temperature is being increased. As the scan rate is decreased a taller and sharper peak results. The range specifies the sensitivity range; as the range is decreased small changes in the heat capacity become amplified. The operating instructions for the DSC are given below; you must take care to record all your settings for each run that you do. After the section on Operating Instructions there is a description of the calibration measurements you must make and then a summary of the additional transitions to study. Following that there are some questions which should be addressed in your writeup.

DSC12E Operating Instructions

1. Overview

The DSC control panel is shown below:

**temperature display** - The current temperature of the measuring cell.

**Status and Parameter display** - Shows the status of the instrument and current measurement parameters.

In the upper **status line**, messages such as Heating or Cooling and error messages are displayed.

In the lower **parameter line**, the measurement parameters are displayed:

T start, the temperature at which the measurement starts.

T end, the temperature at the end of the measurement.

rate, the heating rate in K/min from 0.1 to 20 K/min.
time, time in minutes for an isothermal measurement.

range, the sensitivity range of the DSC12E; 20, 50, 100, 200 or 500 μV.

up indicator - Lights when the instrument is heating under program control.

down indicator - Lights when the instrument is cooling under program control.

furnace control indicator - This indicator is green when the furnace temperature matches the set temperature of the program. If the indicator is red the actual heating or cooling rate is different from the programmed rate. This could affect the accuracy of the data, and therefore the run should be repeated.

set key - Pressing this key aborts the run and returns the furnace to T start.

run/hold key - Pressing this key starts a measurement. Pressing it again causes the measurement to be interrupted and the sample held isothermally for five minutes. Then the furnace is returned to T start.

The Measuring Cell

- Never touch the furnace lid with your fingers. Use the tweezers supplied in the sample preparation kit.

- Remove the measuring cell lid with tweezers and place it on the stainless steel plate.

- Remove the furnace lid with tweezers and place it on the stainless steel plate.
The sample and reference crucibles are centered on the raised circles of the sensor, sample on the left and reference on the right. An empty crucible with a perforated lid will be used as the reference.

2. Sample Preparation

In preparation of the sample the goal is to establish good thermal contact with the crucible in order to minimize the thermal resistance between the sample and the sensor. The quality of the measurement depends greatly on the temperature gradients within the sample. Therefore, the weight of the sample and the heating rate should both be as low as practicable, and the thermal contact between the sample and the crucible as well as between the crucible and the sensor must be optimized.

Handling Different Types of Samples

Fine Powders - Distribute evenly over the bottom of the crucible.

Light Powders, Flakes, Fibers - Press into the bottom of the crucible with the teflon tipped rod supplied in the sample preparation kit.

Liquids - Add to the crucible with a syringe.

Sample Weight and Heating Rate

Both sample weight and heating rate influence the data obtained from the experiment. Increasing sample weight and/or heating rate correspondingly increases temperature gradients with a resulting decrease in signal quality and resolution. A reasonable starting point for obtaining good results is less than 10 mg of sample and a heating rate less than 10 °C/min.

Sealing the Crucible

- Using tweezers place the crucible containing the sample on the platform of the sealing press.

- Ensure that the sealing surface of the crucible is free from any sample particles or other debris.

- With the needle supplied in the sample preparation kit pierce a single hole in the center of the lid.

- Place the lid on the crucible.

- Insert the platform containing the crucible in the sealing press.

- Slowly rotate the lever counterclockwise one complete rotation.
-Using tweezers remove the crucible from the press.

3. Performing the Experiment

- Switch on the cooling bath and set the temperature to 20 °C.

- Set the Dry Gas flow to 35 mL/min (flowmeter reading of 60).

- Set the Purge Gas flow to 100 mL/min (flowmeter reading of 50)

- Switch on the printer and load a sheet of paper.

- Switch on the DSC12E. The display shows SELFTEST V*.**. When this test is completed the furnace temperature rises to the standby setting of 323 K. The status line shows: Scanning to T start. When the furnace has reached 323 K the status line shows: Ready. Wait 5 minutes until the status line shows: Standby.

- Load the sample and reference crucibles into the measuring cell.

- Enter the measurement parameters using the key pad.

- When all parameters are correct press the run/hold key.
Calibration Measurements

Temperature Calibration With Indium (Melting point 429.6 K)

- Flatten an approximately 6 mg piece of indium to insure good thermal contact with the base of the aluminum crucible.

- Weigh the sample into a tared crucible, and seal with a perforated lid.

- Place the sample crucible along with an empty reference crucible in the measuring cell.

- Heat from 423 to 433 K at a rate of 1 K/min on the 100 μV range.

- Determine the onset temperature, $T_{c\text{ onset}}$, of indium melting as shown on the curve.

Since the x-axis shows the furnace temperature $T_c$ and the true sample temperature $T_s$ lags behind this, $T_{onset}$ must be corrected using the following equation:

$$T_{onset} = T_{c\text{ onset}} - \tau_{lag} \beta$$

where $\tau_{lag}$ is the time the actual sample temperature lags behind the furnace temperature and is largely a function of the design of the DSC sensor. For our instrument, $\tau_{lag} = 0.2$ min. $\beta$ is the
heating rate when expressed in K/min units. $T_{\text{onset}}$ should be $429 \pm 0.7$ K. If it falls outside this range consult your TA.

Repeat the measurement starting at a temperature above the melting transition and cooling through it to a final temperature 5 to 10 K below it.

**Calorimetric Calibration**

The calorimetric (heat flow) calibration is based on the enthalpy of fusion of an exactly known quantity of indium. Using a known mass of indium you will be able to correlate a unit area (in turn associated with a particular mass) with an enthalpy (in joules).

- Select 200 $\mu$V range.
- Heat the same indium sample from the temperature calibration from 403 to 453 K at a rate of 10 K/min.
- Ask your instructor for directions on how to measure the area under the peak in your measurement in $\mu$V s units.
- Calculate the calibration constant $E = \frac{A}{m_I \Delta H_I}$.
  - $E$ is in units of $\mu$V/mW (microvolts/milliwatts; recall that 1 watt = 1 J/s)
  - $A$ is the area of the indium peak in $\mu$V s, determined as described above.
  - $m_I$ is the weight of the indium sample in mg.
  - $\Delta H_I$ is the specific enthalpy of fusion of indium, $–28.43$ mJ/g. (What is the value in J/mol?)

**Additional Transitions to Study**

(i) Ammonium Chloride @ 457 K.

(ii) Polyethylene M.P. 403 – 413 K; calculate percent crystallinity.

(iii) The liquid crystal cholesterylmyristate 338 – 373 K.

(iv) The liquid crystal p-azoxyanisole 383 – 423 K.
Summary of What to Report

1. For the In reference sample, report data for both increasing temperature and decreasing temperature runs, at the same instrument settings, and compare the areas and transition temperatures.

2. For each transition, report:
   - the mass of the sample,
   - the instrument settings used for each run,
   - the measured transition temperature (or range of temperatures) for each run,
   - the measured peak areas for each run, and
   - a printed graph (or a copy of your partner's) of the "best" curve you measured for each transition.

3. Calculate, with suitable error analysis (are there possible systematic errors in this lab? what is the largest source of error?), for each transition except the In reference, the following quantities:
   - $\Delta H$ for the entire sample
   - $\Delta H$ per gram of sample, and
   - $\Delta S = \Delta H/T$, the entropy change, per mole of sample (or per mole of $CH_2$ units for polyethylene).

4. For polyethylene, calculate the percent crystallinity of your sample.

5. Contrast the enthalpy changes associated with the two transitions in p-azoxyanisole and suggest reasons why one is larger than the other. In other words, is the liquid crystal phase more solid-like or more liquid-like?