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Using Differential Scanning Calorimetry to Measure Changes in Enthalpy

URL: <https://www.jove.com/science-education/5559>

Overview

Source: Laboratory of Dr. Terry Tritt — Clemson University

Differential Scanning Calorimetry (DSC) is a method of thermodynamic analysis based on heat-flux method, wherein a sample material (enclosed in a pan) and an empty reference pan are subjected to identical temperature conditions. The energy difference that is required to maintain both the pans at the same temperature, owing to the difference in the heat capacities of the sample and the reference pan, is recorded as a function of temperature. This energy released or absorbed is a measure of the enthalpy change (ΔH) of the sample with respect to the reference pan.

Principles

The DSC can be used to measure the heat capacity of material systems, as well as the change of enthalpy (ΔH) for dramatic phase transformation processes, chemical reactions, ionizations, dissolutions in solvents, vacancy formation, and so on. The standard enthalpy of formation is defined as the change in enthalpy, when one mole of a substance in the standard state are formed from elemental constituents in their stable states.¹

The DSC measurement setup consists of a furnace and an integrated sensor connected to thermocouples with designated positions for the sample and the reference pans. The temperature of the sample and the reference are controlled independently using separate but identical ovens. The DSC measurement is carried out in three steps: baseline measurement using empty pan and reference, standard reference measurement to test accuracy, and the sample measurement.

This video explains the sample preparation and the technique of measurement of enthalpy of formation of an oxide via decomposition of a carbonate.

Procedure

1. Baseline Measurement

1. Controller, Measuring unit, Computer system, Thermostat approximately 60 min. before starting the measurement. Purge gases must be connected to the system.
2. Place two empty crucibles (with lid) into the sample carrier. The crucible material may be chosen based on the temperature range to be measured.
3. Move the furnace to measuring position.
4. Adjust the measuring conditions (gas, vacuum).
5. Start the measurement program.
6. Proceed to create a baseline measurement using Sample Mass = 0.
7. Open Temperature Recalibration, Open Sensitivity programs.
8. Set Temperature Program, initial temperature, heating rate.
9. Set the initial conditions and the temperature threshold values. After purging the system with Argon/nitrogen gas a few times, allow the gas to continuously flow through the system, adjusting the flow rate to a steady rate (e.g. 50 mL/min).
10. Start the measurement.
11. The DSC measurements are started at room temperature after an initial stabilization at the starting temperature. The temperature stabilization is important step to avoid any offset due to a difference in the thermal capacities of the sample pan and the reference pan and contents. A steady heating rate of 20 °C /min, under Argon gas atmosphere is generally used. The range of temperature is determined according to the sample and the temperature range of interest.

2. Standard Sample Measurement to Ensure Accuracy of the System

1. Open the measuring unit after the furnace has cooled down.
2. Remove the empty crucible that is designated as the sample pan.
3. Choose the standard depending on the temperature range to be measured.
4. Weigh the standard. A finely polished synthetic sapphire (carborundum, aluminium oxide) disk is used as heat capacity and transformation enthalpy standard. Sapphire is stable over a wide range of temperature, and its heat capacity has been accurately determined over a wide range of temperature.
5. Insert standard sample carefully in the sample crucible using tweezers.
6. Move the furnace to measuring position.
7. Adjust the measuring conditions (gas, vacuum).
8. Proceed as follows to combine the standard measurement with the correction measurement:
9. Use sample mass = x mg (mass of standard sample).

10. Open Temperature Recalibration, Open sensitivity
11. Use the same Temperature program (temperature program remains the same as the baseline temperature program)
12. Start the measurement.
13. Set the initial conditions and the temperature threshold values. After purging the system a few times, allow the purging gas to continuously flow through the system, adjusting the flow rate.
14. Measurement conditions (e.g. heating rate, gases, type of crucible) for the baseline and the subsequent standard measurement must be the same.
15. Using the same sensitivity and temperature calibration files, the start program to measure the standard sample.

3. Sample Measurement

1. Polish the sample surfaces. Place the flattest sample surface facing the bottom of the pan. Use an optimal sample size that fits the pan, without touching the lid. The sample is finely polished to obtain good thermal contact with the sample pan, so the temperature can be accurately determined and the data is less noisy.
2. Measure the sample mass accurately.
3. Open the measuring unit after the furnace has cooled down.
4. Remove the standard sample from the crucible.
5. Clean the crucible using alcohol. Insert the sample to be measured in the crucible replacing the standard.
6. Follow step 3 to measure the sample. The measurement conditions (e.g. heating rate, gases, type of crucible) for the baseline measurement and the subsequent standard and sample measurement must be the same.
7. Follow step 3 to complete the measurement.

Results

ZnO formation via Decomposition of ZnCO₃

The change in enthalpy per degree, at constant pressure is equivalent to the heat capacity of a material at constant pressure given by **Equation 1**. The enthalpy change is obtained by estimating the area under the curve between two temperature limits given by **Equation 2**.

$$C_p = \left(\frac{\partial H}{\partial T} \right)_p \quad (\text{Equation 1})$$

$$\Delta H = \int_{T_1}^{T_2} \left(\frac{\partial H}{\partial T} \right)_p dT = \int_{T_1}^{T_2} C_p dT \quad (\text{Equation 2})$$

Using specific software, the area under the curve is obtained from any heat capacity measurement. The DSC provides a comparative accurate method of measuring heat capacities and enthalpy changes.

A representative result of the decomposition of zinc carbonate (ZnCO₃) forming ZnO is shown below. By the process of calcination, ZnCO₃ decomposes to ZnO releasing carbon dioxide. Using a starting composition of Zn₅(CO₃)₂(OH)₆ a broad exothermic peak around 281 °C was reported by Liu *et al.*² following the release of H₂O and CO₂ according to **Equation 3**.



The enthalpy of transformation of Zn₅(CO₃)₂(OH)₆ to ZnO may be estimated by calculating the area under the curve, at the point of decomposition given by the following exothermic peak. Using Hess's law of constant heat summation, the enthalpy of formation of ZnO may be estimated.

Applications and Summary

A major application area of DSC is the glass transition (*T_g*) in amorphous polymers, in which the material changes from a rigid glassy state to a viscous liquid state. Pharmaceutical research on nano-particles is also an emerging field, where the DSC has been used to quantify amorphous or crystalline phase in nano-solids. A review of DSC techniques on applications in biology and nano-science has been provided by Gill *et al.*³ Nanostructured lipid carriers (NLC) have potential applications in medicine and have been considered as drug delivery carriers.

Calorimetry is a method of analyzing thermal properties of materials to determine the enthalpy change associated with a physical or chemical reaction of interest. Calorimeters are frequently used for quantifying amorphous or crystalline phases. More recently, DSC measurements are used in the fields of nano-science and biochemistry to measure thermodynamic properties of nano-sized bio-molecules. The DSC can also be used to analyze the chemical changes in an oxidized sample. The enthalpy of formation of different metal oxides is useful for metallurgical and industrial calculations.

The estimation of heat of formation of oxides generally requires the combustion of the specific metal in oxygen inside a calorimeter, which may lead to damage of expensive sensors and thermocouples of the particular equipment. The estimation of heat of formation of an oxide, via calcination process through the decomposition of a carbonate producing non-toxic carbon-dioxide gas, gives a simpler method of estimation

of the heat of formation of the corresponding oxide. The estimation of the enthalpy of transformation of carbonates is not only applicable for modeling of geochemical process, but also useful for fundamental research, and industrial applications.

References

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3. Gill, P., Tohidu Moghadam, T., Ranjbar, B. Differential Scanning Calorimetry Techniques: Applications in Biology and Nanoscience. *Biomolecular Techniques*. **21**, 167-193 (2010).