**Chemistry Education Title:**

**Measurement of Enthalpy of Formation using Differential Scanning Calorimetry**

**Overview: The 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 () of the sample with respect to the reference pan.

The DSC can be used to measure the heat capacity of material systems, as well as the change of enthalpy () 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.

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. **Switch on:**
   1. Controller, Measuring unit, Computer system, Thermostat approximately 60 min. before starting the measurement. Purge gases must be connected to the system.
2. **Start a Baseline Measurement**
   1. **Place** two empty crucibles (with lid) into the sample carrier. The crucible material may be chosen based on the temperature range to be measured.
   2. **Move** the furnace to measuring position.
   3. **Adjust** the measuring conditions (gas, vacuum).
   4. **Start** the measurement program.
      1. **Proceed** to create a baseline measurement using Sample Mass = 0
      2. Open Temperature Recalibration, Open Sensitivity programs
      3. Set Temperature Program, initial temperature, heating rate.
      4. **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).
      5. **Start** the measurement.
      6. 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.
3. **Measure a Standard sample 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.
      1. **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.
   4. **Insert** standard sample carefully in the sample crucible using tweezers.
   5. **Move** the furnace to measuring position.
   6. **Adjust** the measuring conditions (gas, vacuum).
   7. **Proceed** as follows to combine the standard measurement with the correction measurement:
      1. **Use** sample mass = x mg (mass of standard sample).
      2. **Open** Temperature Recalibration**, Open** sensitivity
      3. **Use** thesame Temperature program (temperature program remains the same as the baseline temperature program)
      4. **Start** the measurement.
   8. **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.
   9. Measurement conditions (e.g. heating rate, gases, type of crucible) for the baseline and the subsequent standard measurement must be the same.
   10. Using the same sensitivity and temperature calibration files, the start program to measure the standard sample.
4. **Sample Preparation**
   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.
5. **Open** the measuring unit after the furnace has cooled down.
   1. **Remove** the standard sample from the crucible.
   2. **Clean** the crucible using alcohol. **Insert** the sample to be measured in the crucible replacing the standard.
   3. **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.
   4. Follow step 3 to complete the measurement.
6. **Analyse DSC Data**
   1. **Principle**: The change in enthalpy per degree, at constant pressure is equivalent to the heat capacity of a material at constant pressure given by: . The enthalpy change is obtained by estimating the area under the curve between two temperature limits given by:
   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.

**Representative Result: ZnO formation via decomposition of ZnCO3**

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*. [[[1]](#endnote-1)] following the release of H2O and CO2 according to the equation:



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.

Figure 1 below shows the DSC plot in red and the thermogravimetry (TG) plot in black. The second y-axis corresponding to the DSC plot depicts heat flow *vs*. temperature. The TG technique monitors changes in the mass of the sample on heating as it decomposes at elevated temperatures. This is a data published by Liu *et al*. and the DSC plot is of interest in this study. The peak represents exothermic behavior relating to the decomposition of ZnO. Heat is released when ∆Hf <0 (exothermic reaction like crystallization), or absorbed when ∆Hf > 0 (endothermic reaction like melting). More information about the plot may be found in the reference given below.



Fig 1: DSC plot of decomposition of Zn5(CO3)2(OH)6 [Ref: 1]

The result of our experiment of heat of formation of a metal oxide (e.g. ZnO or MgO) from a metal carbonate (ZnCO3 or MgCO3) will be demonstrated on the day of filming. X-ray diffraction may be performed on the remaining solid after decomposition of the metal carbonate to identify the oxide phase formed.

**Representative Result: Application in medicine**

A major application area of DSC is the glass transition (Tg) 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* [[[2]](#endnote-2)] Nanostructured lipid carriers (NLC) have potential applications in medicine and have been considered as drug delivery carriers.



Figure 2: DSC curves of NLCs prepared by different methods [Ref. 2]

Figure 2 exhibits the DSC curves of NLCs reported by Gill et al [2], where the different DSC curves indicate NLCs prepared by different techniques. Our expertise is in inorganic materials. The readers are encouraged to consult the reference given below, for detailed information.

**Applications**

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 bio-chemistry 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.

1. S. Liu, C. Li, J. Yu and Q. Xiang, *CrystEngComm*, **13**, p 2533 (2011) [↑](#endnote-ref-1)
2. P. Gill, T. Tohidu Moghadam and B. Ranjbar, J. Bimolecular Techniques, **21**, p 167-193 (2010) [↑](#endnote-ref-2)