Drop calorimetry

Introduction

Drop calorimetry is not the most well known calorimetric method. However most of the high-temperature heat capacity data found in the literature are coming from the use of this technique. Different types of drop calorimeters are existing, but in this technical note is only presented the technique corresponding to the drop of a sample outside of the calorimeter into a vessel located in the furnace at a known temperature.

The technical will explain the principle of the technique, the different modes of operation and the different types of applications.

Principle and operation modes

In the drop calorimetry technique, a small sample heated to a known temperature (most of the time closed to room temperature) outside the calorimeter is rapidly dropped into the experimental vessel located into the calorimeter block, surrounded by the heating furnace, controlled at a known temperature.

Two types of operation are available:

- the direct drop calorimetry (figure 1)
  By dropping the sample at T₁ in the calorimetric vessel at T₂, the total heat to elevate the temperature of the sample from T₁ to T₂ is measured.
  Different types of applications are investigated according to this technique:

  - Determination of heat capacity
    If there is not a transition or reaction occurring within the sample on the temperature range, the following heat relation is obtained:
    \[
    \Delta H = \int_{T_1}^{T_2} C_p \, dT
    \]
    It is needed to repeat sample drops at different temperatures in order to determine the variation of heat versus sample temperature. From the derivation of this curve according to temperature the variation of the sample heat capacity is obtained on the measured temperature range.
    It is also possible to calculate a mean \( C_p \) value between two closed temperatures.
    The \( C_p \) determination will be explain more in details in a further paragraph.

Figure 1: Direct drop calorimetry
Determining enthalpy of transition

On the temperature range under investigation, the sample can undergo a structure change (melting, crystallisation, phase transition ...). The measured heat will contain the heat capacity contribution before and after the transformation and the corresponding heat of transition

\[ \Delta H_{\text{total}} = \int_{T_1}^{T_2} C_p \, dT + \Delta H_{\text{transition}} \]

To obtain the heat of transition, the \( C_p \) variation has to be calculated before and after the transition. The difference between the two curves provides the heat value.

Determining reaction by ignition (direct synthesis)

The synthesis of specific alloys may require elevated temperatures and very high heating rates to reach this temperature. This is especially the case for the thermite reaction (aluminium + ferrite). The fastest way to heat the corresponding mixture is to drop the pellet containing the two components in the calorimetric vessel at the desired reaction temperature.

\[ \Delta H_{\text{total}} = \int_{T_1}^{T_2} (xCp_A + yCp_B) \, dT + (\Delta H_A + \Delta H(AxBy)_{\text{formation}}) \]

To determine the heat of formation, it is needed to drop the pure A and B components. The term \( \Delta H_A \) corresponds to the heat of melting of A that is needed to produce the reaction.

The solution drop calorimetry (figure 2)

With the drop solution calorimetry, the sample at \( T_1 \) is dropped in a high temperature solvent (metallic or oxide) contained in the calorimetric vessel at \( T_2 \). In such a situation, the total heat corresponds to the heat to elevate the temperature of the sample from \( T_1 \) to \( T_2 \) added with the corresponding heat of dissolution. Different types of applications are investigated according to this technique:

\[ \Delta H_{\text{total}} = \int_{T_1}^{T_2} C_p \, dT + (\Delta H_{\text{transition}}) + \Delta H_{\text{solution}} \]

The first term of the equation corresponds to the heat content from \( T_1 \) to \( T_2 \), and the last term corresponds to the heat of dissolution of the sample into the solvent. According to the sample, a transition or transformation can occur on the temperature range. In that case it is also needed to consider the corresponding heat of transition (term under bracket). Successive additions of sample are run in order to get an average value. For a correct determination it is needed to have an infinite dilution of the sample in the solvent.
**Determinations of heat of formation**

The measurement of heat of dissolution is an indirect method for the determination of the enthalpy of formation of an alloy (metal or oxide). For measuring the formation of an alloy of AxBy type, the corresponding dissolution have to be performed in a given solvent:

- Dissolution of pure A
- Dissolution of pure B
- Dissolution of AxBy alloy

From the different tests, the following heat relation is obtained:

\[
\Delta H(AxBy)_{\text{formation}} = x\Delta H(A)_{\text{solution}} + y\Delta H(B)_{\text{solution}} - \Delta H(AxBy)_{\text{solution}}
\]

This technique can successfully be used for the determination of the enthalpy of formation of binary or ternary systems.

**The drop calorimetric detector**

The drop calorimeter requires a large-volume sample, and the calorimeter detector is designed to accommodate two crucibles, arranged vertically. The calorimetric detector offers a large working volume (5.3 cm\(^3\)) for investigating samples up to 1300 or 1500°C, depending on the type of thermocouple used. The arrangement of thermocouple weldings on the surface of the experimental chamber at varying heights provides good integration of the heat exchanges and produces a calorimetric sensitivity practically independent of the amount of material in the crucible.

The large volume of the crucible enables a significant number of samples drops and to guarantee an infinite dissolution in the case of solution calorimetry.

The calibration of the drop calorimetric detector is obtained by dropping pieces of materials with known specific heat capacity such as sapphire (α-Al\(_2\)O\(_3\), platinum).

**Applications**

**Cp determination**

The principle of the Cp determination has been explained in a previous paragraph. However, contrarily to the traditional methods (continuous and step heating), the drop method does not directly measure the Cp of a material as it is an enthalpy value that is obtained.

Two situations can be differentiated:

- the determination of one Cp value at a given temperature
- the Cp variation on a temperature range

**Cp determination at a given temperature**

For such a determination, it is needed to work at two different temperatures T\(_1\) and T\(_2\). The difference between T\(_1\) and T\(_2\) has to be not too large in order to extract a mean Cp value according to the following relations:

\[
\left[H\right]_{T_0}^{T_1} = \int_{T_0}^{T_1} Cp.dT
\]

\[
\left[H\right]_{T_0}^{T_2} = \int_{T_0}^{T_2} Cp.dT
\]
For a given temperature, several drops of sample are performed in order to get an average value. Before and after each sample drop, is intercalated a calibrant (sapphire or platinum) drop for the determination of the different heat values (Figure 4). Such a calibration allows to take into account the influence of the vessel filling. Figure 4 gives an example of such successive drops.

![Figure 4: Example of successive drops of sample and calibrant at 550°C](image)

From the average heat value measured at $T_1$ and $T_2$, it is possible to calculate the mean $C_p$ value for a temperature on the $(T_1, T_2)$ interval according to the following relation:

$$C_p = \frac{[H]_{T_2}^T - [H]_{T_1}^T}{(T_2 - T_1)} \quad T = \frac{T_1 + T_2}{2}$$

- $C_p$ variation on a temperature range
As seen previously, the drop method does not provide a direct measurement of the specific heat of a material. For a determination of $C_p$ on a given range of temperature, it is needed to measure the corresponding heat variation on this curve. The derivation of this curve will give the expected $C_p$ variation.

If the enthalpy variation is represented by the following relation:

$$[H]_{T_1}^T = A_0 + A_1T + A_2T^2 + A_3T^3 + A_4T^{-1}$$

the corresponding standard $C_p$ variation is obtained:

$$C_p = A_1 + (2A_2)T + (3A_3)T^2 - \frac{A_4}{T^2}$$
An example is given for alumina with the corresponding enthalpy curve from room temperature to 1400°C and the calculated Cp variation (Figure 5). Sapphire is used as a standard in the experiment.

- Heat of transition

The determination of heat of transition is illustrated with the example of a composite ceramic-salt (SiO$_2$/Na$_2$SO$_4$) packed bed configuration, being developed for high-temperature thermal storage. The thermophysical properties of the more particular hybrid system SiO$_2$/Na$_2$SO$_4$ have been investigated in the range from room temperature above the melting point of the salt, 884°C. The Na$_2$SO$_4$ fraction in the composite materials vary between 20 and 50%.

Figure 6a: Specific enthalpy of a 50/50 sample in comparison with the pure materials
Figure 6b: Specific enthalpy of 20/80, 40/60 and 50/50 samples

Samples (cylinder of 5 mm in diameter and 5 mm long) are dropped from room temperature to temperature below and above the melting point of the salt. Figure 6a shows measured total enthalpy values of Na$_2$SO$_4$, cristobalite and the quartz phase of SiO$_2$ and of a 50/50-sample (quartz and cristobalite are SiO$_2$ polymorphs). The measured values above and below the melting point are linearly interpolated. The enthalpy of melting is obtained by difference between the two lines.

An examination of the calorimetric measurements shows that a simple weight fraction mixture rule can be applied, which is reasonable since chemical reactions between SiO$_2$ and Na$_2$SO$_4$ are not expected. Assuming the cristobalite fraction to be 80% of the ceramic matrix material, calculated enthalpy values fit the measurements of 20/80, 40/60 and 50/50 samples shown on Figure 6b.

**- Heat of reaction**

The thermite reaction (a type of aluminothermic reaction) is selected to show the use of drop calorimetry for measuring heat of reaction. In such a reaction, aluminium metal is oxidized by an oxide of another metal, most commonly iron oxide.

$$Fe_2O_3 + 2Al \rightarrow Al_2O_3 + 2Fe$$

Although the reactants are stable at room temperature, when they are exposed to sufficient heat to ignite, they burn with an extremely intense exothermic reaction. Thermitite contains its own supply of oxygen, and does not require any external source (such as air). To reach ignition, the mixture in a form of a pellet (about 50 mg) is dropped from room temperature to 1550°C. Sapphire is used as a calibrant.

![Figure 7. Drops of (Fe$_2$O$_3 + 2$ Al) pellets at 1550°C](image)

According to Figure 7, the average value between the two pellets is $-2076.2 \text{ J/g}$ or $-444.3 \text{ kJ/mol}$ of (Fe$_2$O$_3 + 2$ Al).

Such a test has to be run in an alumina crucible with an inner sleeve made of boron nitride in order to resist to the high exothermic effect of the reaction.
Heat of dissolution

The solution drop calorimetry allows the determination of heat solution as described in a previous paragraph. This calorimetric mode is illustrated by the dissolution of iron in aluminium. In such a test, a molten aluminium bath is used as a solvent at 1200°C (Figure 8). A first piece of aluminium is dropped in the aluminium bath providing the calorimetric calibration. The endothermic effect that is measured is only due to the heat capacity of the metal. When dropping a piece of iron, a first endothermic effect is detected followed by a strong exothermic effect. The first peak partly characterizes the heating of the sample before the exothermic dissolution of iron in aluminium.

The full endothermic contribution of the sample heating is obtained from literature data knowing the Cp variation of iron or by dropping a sample of iron at 1200°C without the aluminium bath.

The heat of dissolution is obtained by subtracting this value from the total measured heat.

A molten oxide bath can also be used for the determination of heat solution in the field of inorganic materials. As an example, silicate melts are complex inorganic molten salts showing various temperature dependent speciation and structural changes. The determination of their thermodynamic properties is a very difficult experimental challenge. Drop oxide solution calorimetry provides an unique way of approaching these challenging measurements, especially for nuclear waste disposal investigations.

This is illustrated by the dissolution of La₂O₃ in potassium silicate solvents (K₂O·3SiO₂) at 1760 K (Figure 9). Pellets of La₂O₃ with and without P₂O₅ are dropped in the calorimeter containing the molten silicate bath, in order to measure the effect of P₂O₅ on the heat of solution.
Heat of formation

As seen in a previous paragraph, the enthalpy of formation of the investigated phase is obtained from the difference of heat effects accompanying the dissolution in the selected bath of the studied phase and its components.

An example is given with the determination of heat formation of different aluminium nickel alloys (AlNi₃, AlNi and Al₃Ni₂).

Figure 9: Heat of solution of La₂O₃ in potassium silicate solvents at 1760 K (from M.C. Wilding and A. Navrotsky, J. Non-Crystalline Solids 265 (2000), 238-251).

Figure 10: Formation enthalpy of Al₃Ni₂, AlNi, AlNi₃ compounds as a function of temperature (from K. Rzyman, Z. Moser / Progress in Materials Science 49 (2004) 581–606)
Aluminium bath is used as a solvent. The drop of pieces of Al allows to calibrate the calorimetric detector at the different temperatures of experimentation.

For each selected temperature of experiment, drops of pure Al and Ni, of high purity prepared AlNi$_2$, AlNi and Al$_3$Ni$_2$ materials are performed. From the different measured heats of dissolution, it is possible to calculate the corresponding heat of formation for a given AlNi intermetallic compound according to the following relation:

$$\Delta H(Al_xNi_y)_{\text{formation}} = x\Delta H(Al)_{\text{solution}} + y\Delta H(Ni)_{\text{solution}} - \Delta H(Al_xNi_y)_{\text{solution}}$$

The corresponding enthalpy of formation of Al$_3$Ni$_2$, AlNi, AlNi$_3$ compounds as a function of temperature is shown on figure 10.

The same type of determination can also be applied with an oxide bath if heat of formation of inorganic compounds has to be measured.

**- Special adaptation (work in glove box)**

The investigation of radioactive materials using drop calorimetry requires a dedicated adaptation of the instrument. For alpha type radioactivity, the calorimeter is introduced in a alpha-tight glove box. In such a situation, the electronic parts remain outside the glove box (Figure 11).

![Figure 11. A drop calorimeter installed in an alpha-tight glove box](source: JRC – ITU website)

For stronger level of radioactivity (beta and gamma types) it is possible to adapt the calorimeter to be inserted in a hot zone (lead chamber).