MHTC96 – DROP calorimetry

Drop calorimetry
Principles and applications

Introduction

Drop calorimetry is not the most well known calorimetric method. However most of the high-temperature heat capacity data found in the litterature 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 T_1 in the calorimetric vessel at T_2, the total heat to elevate the temperature of the sample from T_1 to T_2 is measured.

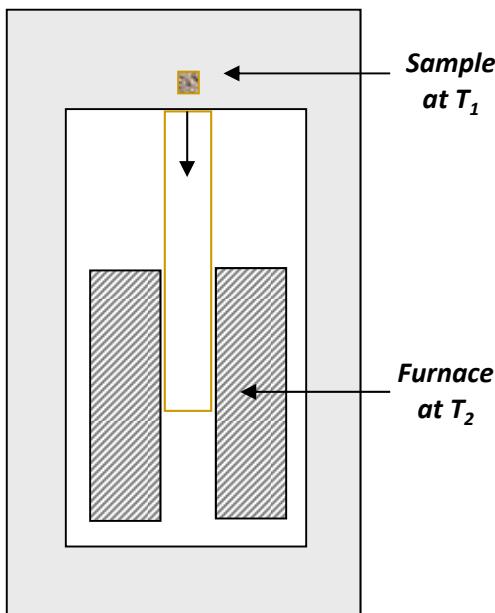Different types of applications are investigated according to this technique:

Sample at T_1

Furnace at T_2

Figure 1: Direct drop calorimetry

MHTC96 Drop
(RT to 1500°C)

-*Determination of heat capacity*

If there is not a transition or reaction occuring within the sample on the temperature range, the following heat relation is obtained:

$$\Delta H = \int_{T_1}^{T_2} Cp.dT$$

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 Cp value between two closed temperatures.

The Cp determination will be explain more in details in a further paragraph.

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-*Determination of 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

$$\Delta H_{total} = \int_{T_1}^{T_2} Cp.dT + \Delta H_{transition}$$

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

-*Determination of 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.

$$\Delta H_{total} = \int_{T_1}^{T_2} (xCp_A + yCp_B).dT + (\Delta H_A) + \Delta H(AxBy)_{formation}$$

To determine the heat of formation, It is needed to drop the pure A and B components. The term ΔH_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:

Sample at T_1

Solvent

Furnace at T_2

Figure 2: Solution drop calorimetry
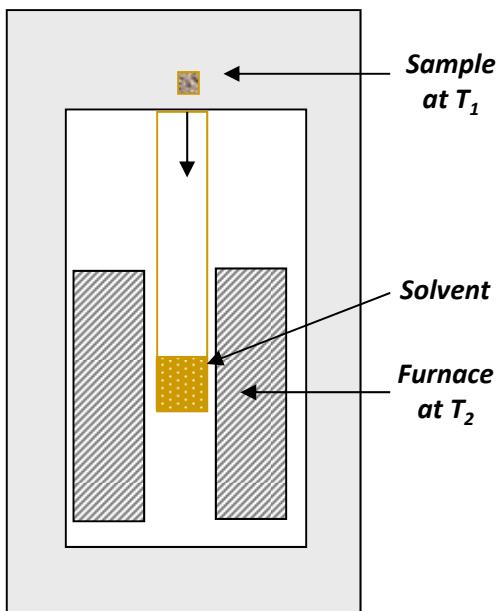
- *Determination of heat of dissolution*
One main application of the solution drop calorimetry is the determination of heat of dissolution of alloys in the metallic or oxides fields. To achieve such a measurement, the sample is dropped in the dedicated solvent. The following heat relation is obtained:

$$\Delta H_{total} = \int_{T_1}^{T_2} Cp.dT + (\Delta H_{transition}) + \Delta H_{solution}$$

The first term of the equation corresponds to the heat content from T1 to T2, 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.

- Determination 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:

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

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 cm3) 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)
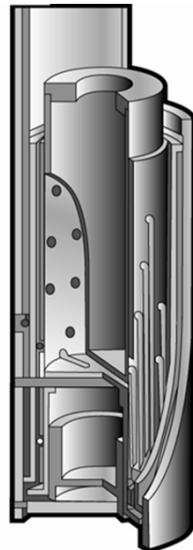

Figure 3: Drop calorimetry detector

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 *C*p 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 T1 and T2. The difference between T1 and T2 has to be not too large in order to extract a mean Cp value according to the following relations:

Drop from T_0 to T_1 Drop from T_0 to T_2

$$\left[H\right]_{T_0}^{T_1} = \int_{T_0}^{T_1} Cp.dT \qquad\qquad\qquad \left[H\right]_{T_0}^{T_2} = \int_{T_0}^{T_2} Cp.dT$$

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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.
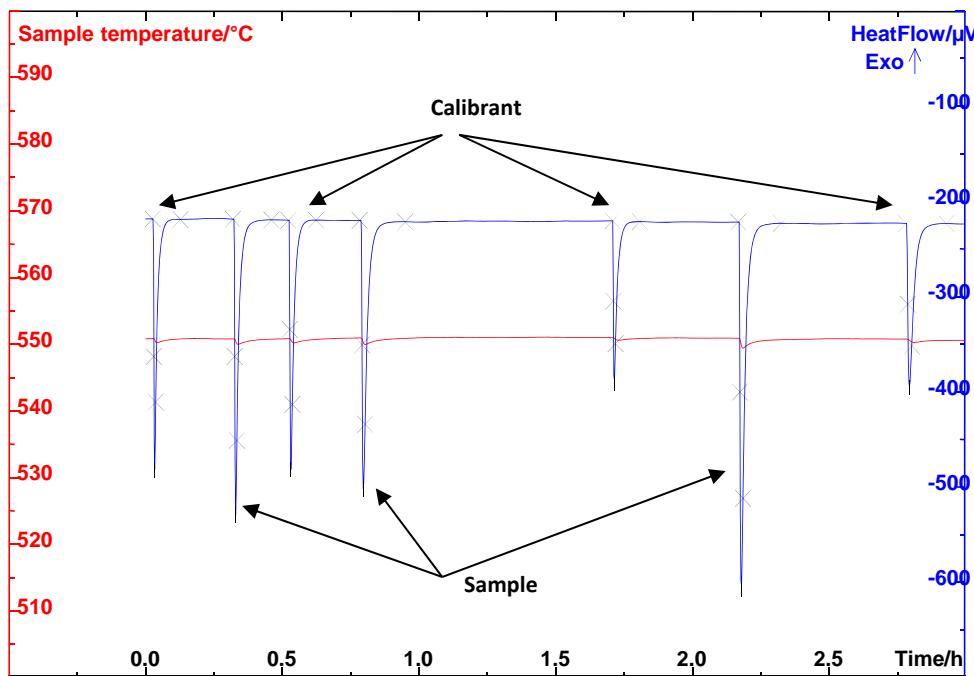

Figure 4: Example of successive drops of sample and calibrant at 550°C

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

$$\overline{Cp} = \frac{\left([H]_{T_0}^{T_2} - [H]_{T_0}^{T_1}\right)}{(T_2 - T_1)} \qquad\qquad T = \frac{(T_1 + T_2)}{2}$$

- Cp 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 Cp 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 Cp variation.

If the enthalpy variation is represented by the following relation:

$$[H]_{T_0}^{T} = A_0 + A_1 T + A_2 T^2 + A_3 T^3 + A_4 T^{-1}$$

the corresponding standard Cp variation is obtained:

$$Cp = A_1 + (2A_2)T + (3A_3)T^2 - \frac{A_4}{T^2}$$
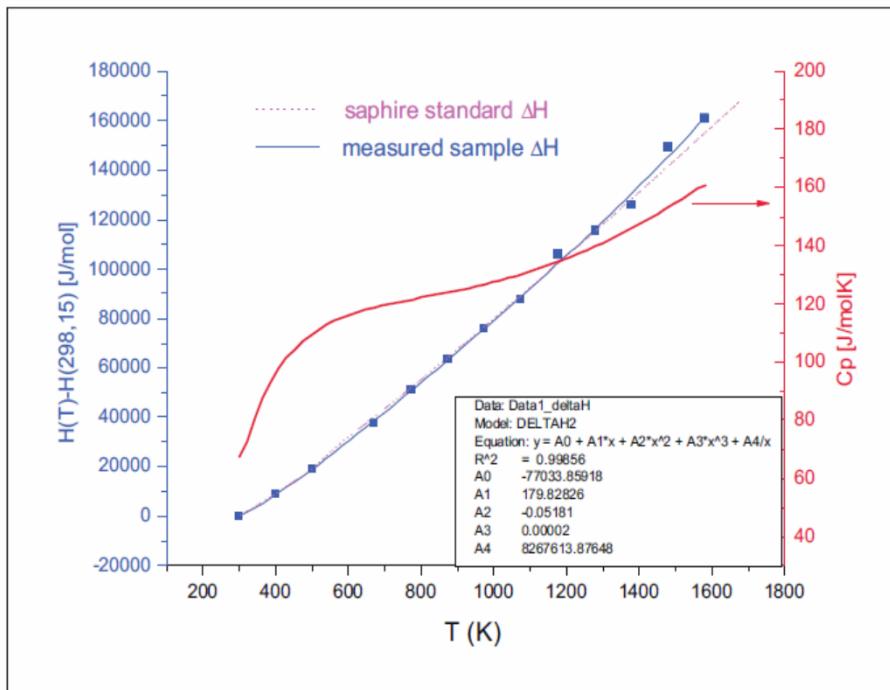
*Figure 5. Enthalpy of heating and Cp results for alumina
(from T. A. Guisard Restivo and B. Legendre, personal publication)*

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_2SO_4) packed bed configuration, being developed for high-temperature thermal storage. The thermophysical properties of the more particular hybrid system SiO_2/Na_2SO_4 have been investigated in the range from room temperature above the melting point of the salt, 884°C. The Na_2SO_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
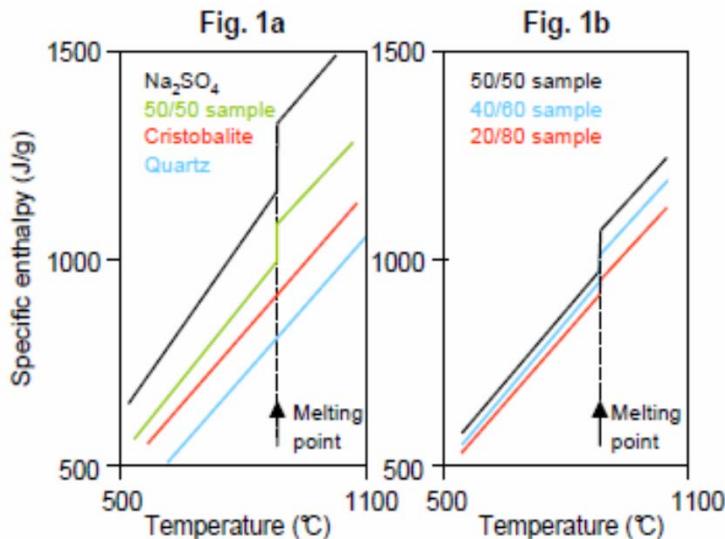
(from *W. Notter, Th. Lechner, U. Gross and E. Hahne Thermochimica Acta, 218 (1993) 455-463*)

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_2SO_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_2SO_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.

$$Fe_2O_3 + 2\ Al \rightarrow Al_2O_3 + 2\ Fe$$
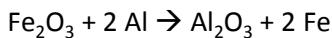
Although the reactants are stable at room temperature, when they are exposed to sufficient heat to ignite, they burn with an extremely intense exothermic reaction. Thermite contains its own supply of oxygen, and does not require any external source (such as air). To reach ignition, the mixture in a form of a pellet (about 50 mg) is dropped from room temperature to 1550°C. Sapphire is used as a calibrant.
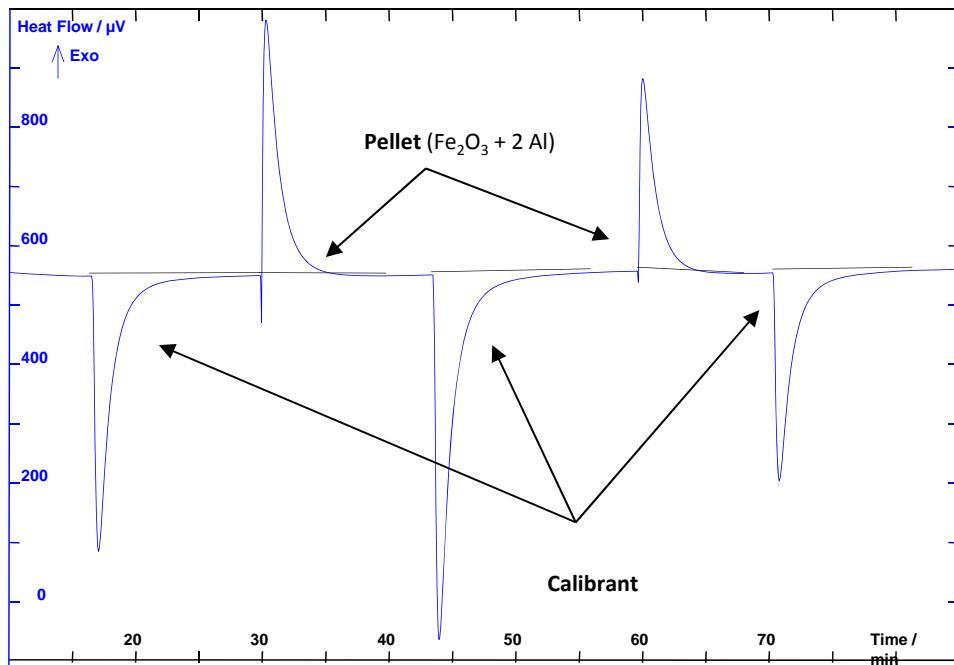

Figure 7. Drops of (Fe$_2$O$_3$ + 2 Al) pellets at 1550°C

According to Figure 7, the average value between the two pellets is – 2076.2 J/g or – 444.3 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 litterature data knowing the Cp variation of iron or by dropping a sample of iron at 1200°C without the aluminium bath.
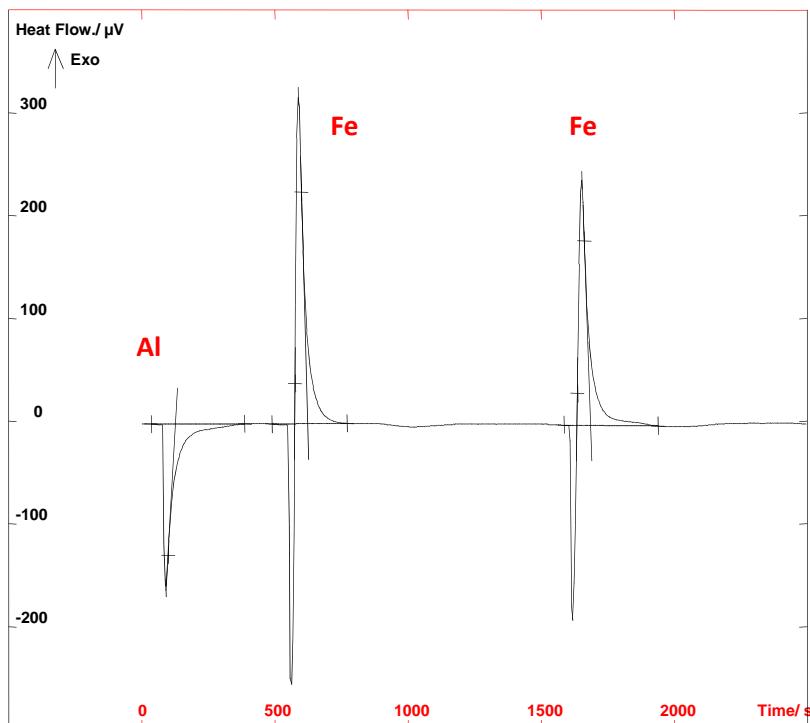The heat of dissolution is obtained by subtracting this value from the total measured heat.

Figure 8: Drops of aluminium and iron pellets in an aluminium bath at 1200°C

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 La_2O_3 in potassium silicate solvents (K_2O-$3SiO_2$) at 1760 K (Figure 9). Pellets of La_2O_3 with and without P_2O_5 are dropped in the calorimeter containing the molten silicate bath, in order to measure the effect of P_2O_5 on the heat of solution.

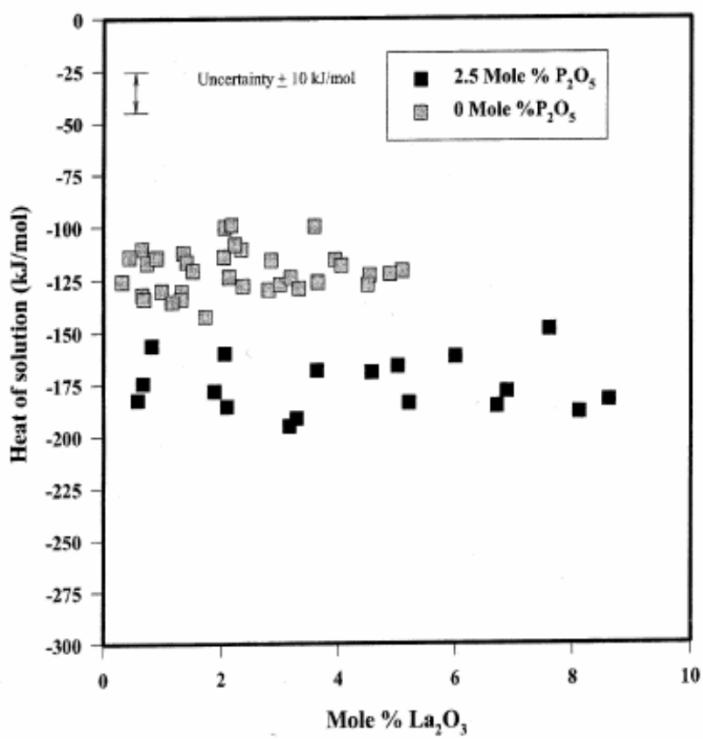Figure 9: H*eat of solution of La$_2$O$_3$ in potassium silicate solvents at 1760 K*
(from M.C. Wilding and A. Navrotsky, J. Non-Crystalline Solids 265 (2000), 238-251).

- 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 (AlNi$_3$, AlNi and Al$_3$Ni$_2$)
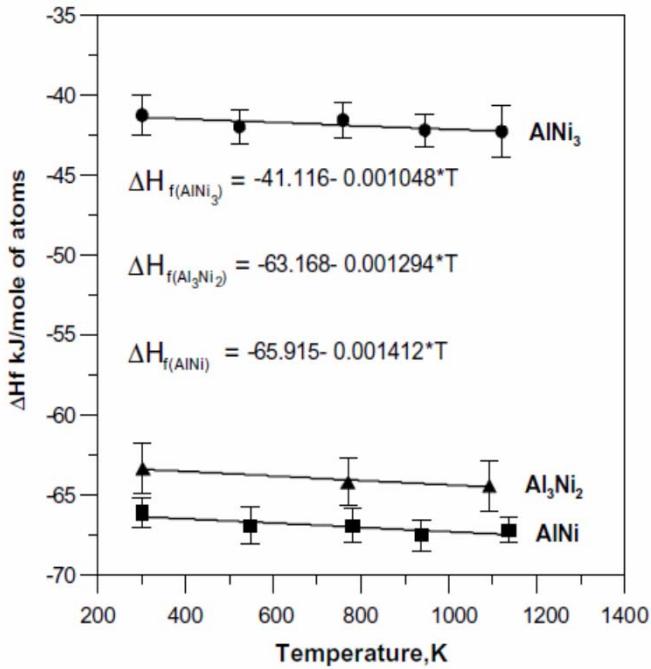

Figure 10: *Formation enthalpy of Al$_3$Ni$_2$, AlNi , AlNi$_3$ compounds as a function of temperature*
(from K. Rzyman, Z. Moser / Progress in Materials Science 49 (2004) 581–606)

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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 $AlNi_3$, $AlNi$ and Al_3Ni_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:

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

The corresponding enthalpy of formation of Al_3Ni_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

MHTC96 Drop
(RT to 1500°C)

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).

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