

SOLUTION CALORIMETRY IN ZERO GRAVITY*

SPACELAB EXPERIMENT PROPOSAL

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ABSTRACT

Starting in 1980 scientific experiments can be carried out at zero gravity in the Spacelab. There the possibility exists of performing non-contact measurements on freely suspended samples. This is of particular interest, if the samples otherwise would react with crucible materials. A solution calorimeter without crucibles with molten metals as solvent is proposed in order to measure the enthalpies of formation of alloys containing reactive metals. Solvent and solute sample are placed in an ultrasonic field and mixed. The heat of solution is measured by a differential platinum resistance thermometer. The proposed calorimeter permits an automatic sequence of numerous measurements.

INTRODUCTION

Starting in 1980 the so-called "Spacelab" will be available for scientific experiments. The zero gravity (appr. 10^{-4} terrestrial gravity) present in the Spacelab permits the application of support-free measuring techniques, that is, non-contact measurements on levitated samples. In this manner, errors can be avoided, which arise from contact of the sample with container materials, especially at high temperatures¹. The application of this principle to a calorimeter allows the measurement of heat changes of such materials, which under terrestrial conditions react with the container material and therefore prevent exact caloric measurements. Taking as an example the determination of the enthalpies of formation of alloys containing reactive elements, the application of this calorimeter will be described in more detail.

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DEFINITION OF THE EXPERIMENT AND UNDERLYING PRINCIPLES

Calorimetrically measured enthalpies of formation are indispensable to determine exactly the thermodynamic functions of state of composite phases. Exact thermodynamic functions of state are needed on one hand for the computation of equilibria²⁻⁵, i.e., in metals research for the computation of phase diagrams. On the other hand, they are important for a detailed study of the chemical bonds in the composite phases.

In calorimetric determinations of the enthalpies of formation, the phase of interest is brought to an exactly definable final state and thereby the heat change is measured. Then, the mixture of the components is brought to the same final state in which the heat change is also measured. The difference of the two heat changes is the required enthalpy of formation.

The various calorimetric methods differ mainly in the exactly defined final state^{5, 6}. There are combustion calorimeters, in which the samples are burned in oxygen or fluorine. In other calorimeters the samples are dissolved in aqueous solvents. At higher temperatures metallic samples can be dissolved in molten metals.

These different methods are not equally accurate. Their accuracy depends strongly on the ratio between the magnitude of the measured effects and of their difference which is looked for. If the measured effects are substantially larger than the required difference, the accuracy may be poor. For metallic phases, solution calorimetry in molten metals (Fig. 1) is in most cases the best method. In some cases however, this method cannot be employed with sufficient accuracy. The elements in the center of the periodic table (Ti, V, Zr, Nb, Hf, Ta and several others) do not dissolve in a molten metal without reacting with any crucible material, even if they are dissolved in small concentrations. Since the attack of the crucible is usually combined with a large heat of reaction, even a weak attack suffices to disturb the measurement.

In these cases, the enthalpies of solution must be determined in an arrangement

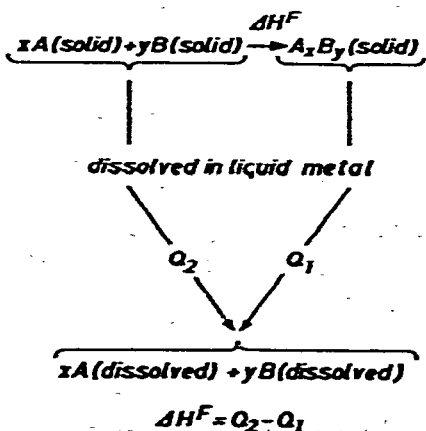


Fig. 1. The measurement of the formation enthalpy ΔH^F of a metallic phase A_xB_y .

without crucibles. At first sight, levitation melting offers a means of proceeding without crucibles. Calorimetry, however, cannot be carried out in this way, since the change in temperature can only partly be attributed to the heat of solution of the sample. In fact, a very much larger part can be assigned to fluctuations of the energy induced in the sample by the levitation field. On earth, a strong electromagnetic field is required to levitate metals. The energy induced in the levitated sample depends on its shape and resistivity. During the period of mixing, both these properties are altered in an incalculable manner. Thus, while the sample dissolves in the melt, the fluctuations of the energy induced in the sample become large and undefined.

Here the support-free measuring technique in the Spacelab can be advantageously applied. The main principles of the measurement are the same as with terrestrial conditions. Contrary to terrestrial conditions, two points have to be taken into account: Instead of the crucible a positioning system is needed, which stabilizes the sample against small residual accelerations. Secondly, the operation of the calorimeter should be automatized as far as possible, to get a maximum of measurements during the limited time of a mission.

OPERATING PRINCIPLE IN THE SPACELAB

The solvent and the solute sample are inserted in a tube furnace at constant temperature (Fig. 2) and freely suspended side by side. After the solvent metal has melted and thermal equilibrium is reached, the sample and solvent are brought together and allowed to mix. The heat of solution flows through the tube wall and produces a temperature difference between inner and outer surface of the tube. This temperature difference, averaged over the surface and integrated with time is proportional to the heat evolved.

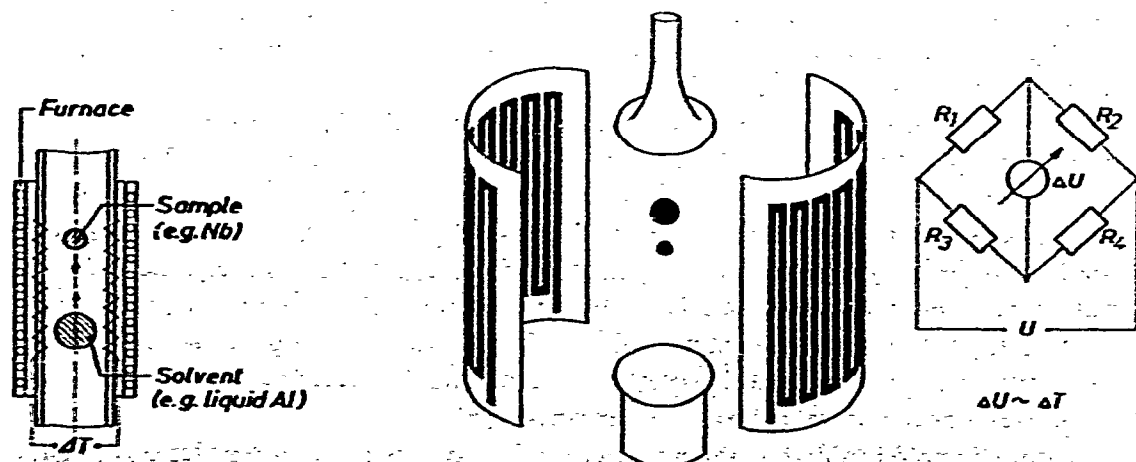


Fig. 2. Schematic representation of the solution calorimeter for freely suspended samples.

Fig. 3. Exploded view of the heat-flow-meter consisting of 4 platinum resistance thermometers (R_1 to R_4) vapour deposited on the surfaces of two half aluminum oxide tubes.

$$Q = k(T, \dots) \int \Delta T(t) dt$$

$k(T, \dots)$ is a quantity depending on temperature and the geometry of the apparatus. It has to be determined by calibration by known heats of solution. The temperature difference ΔT is measured by a differential platinum resistance thermometer, which consists of vapour deposited platinum films on the inner and outer surface of the furnace tube. The films are laser cut as shown in Fig. 3 and protected by a vapour deposited aluminum oxide film. The platinum resistances are connected to a Wheatstone bridge, the signal of which is proportional to the averaged temperature difference.

The tube furnace containing the measuring system must be controlled to a constant temperature of about 1200 K within ± 0.01 K. Since this will hardly be achievable, the measuring system must be constructed as a twin calorimeter, in order to compensate for fluctuations of the furnace temperature. Thus, the apparatus will be an isoperibolic differential heat flow calorimeter similar to the calorimeters developed by Tian and Calvet⁷.

The smallest expected heats of solution are of the order of 5 J/sample. This quantity should be measured within $\pm 1\%$. This means that disturbing energies should be calculable within ± 0.05 J.

POSITIONING OF THE SAMPLE

Since residual accelerations of about 10^{-4} g are present in the Spacelab, supporting fields are necessary to hold the samples in their prescribed positions. The strength of these supporting fields is determined on the one hand by the maximal disturbing acceleration. On the other hand, the heat produced by the supporting field in the sample and surrounding gas volume should be as small as possible. The critical phase in the experimental run is the time interval in which the sample is immersed in the liquid metal and dissolves. During this interval, the shape and the physical properties of the levitated body change indefinitely, thus giving changes of the heat produced by the supporting field.

For the operation of the solution calorimeter in the Spacelab, the supporting field must permit an automatic sequence of numerous measurements. There is the choice between an electromagnetic or an acoustic supporting field. Since samples and solvent metals differ in their diameters and physical properties, the supporting force of the field must either be nearly independent of these parameters (acoustic field), or it must consist of individual, locally adjustable partial fields (electromagnetic field).

Although the electromagnetic system is in principle applicable, it requires strong limitations on the material of the furnace and the electrical protection of the platinum resistance thermometers and thermocouples.

Acoustic positioning has the advantage of no constructional restrictions outside the acoustic cavity, but it can be less easily automatized⁸⁻¹¹. For this reason, the concept of a Spacelab calorimeter with acoustic positioning will be discussed next.

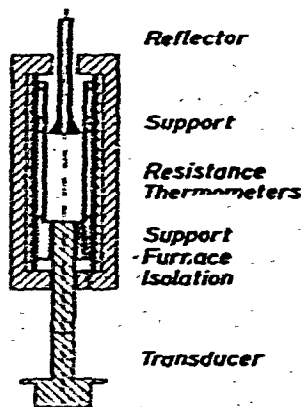


Fig. 4. Schematic representation of the solution calorimeter with an acoustic positioning system.

CONCEPTION OF THE SPACELAB CALORIMETER

In Fig. 4 the proposed apparatus is represented schematically. The acoustic positioning system with the transducer and reflector is in the centre of the tube furnace. The acoustic cavity is limited radially by an aluminum oxide tube on which are vapour deposited platinum resistors to measure the heat flow.

A measuring cycle proceeds as follows: Using a mechanical manipulator, the metal to be used as the solvent is brought as a solid into a pressure node of the ultrasonic standing wave. There the metal melts freely suspended. The solute sample is introduced in the same manner and positioned in a neighboring pressure node. After the temperature fluctuations have disappeared, both samples are brought together for mixing by means of a low frequency modulation of the ultrasonic standing wave. During and after this phase, the temperature difference is registered. After the temperature difference has reached zero again, the liquid sample is sucked away by a thin tube. Following this, the next reaction pair is introduced.

The problems, which are investigated at present, concern the selection of the type of manipulator, by which the acoustic field is least disturbed. In addition, the damping of sample oscillations and the combination of the two samples by means of low frequency modulation have to be studied more thoroughly.

The Spacelab calorimeter presented here is not restricted to the measurement of heats of solution of metallic phases. Generally, all heat effects in aggressive substances may be measured. Also thermal analysis or scanning calorimetry may be carried out in a similar way without contact of the sample with the apparatus.

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