Thermochimica Acta, 93 (1985) 317-320
Elsevier Science Publishers B.V., Amsterdam

MEASUREMENT OF THE THERMAL CONDUCTIVITY OF SOLID SUBSTANCES BY DSC.

G. Hakvoort[x] and L.L. van Reijen
Delft University of Technology, Chemistry Department, Netherlands
A.J. Aartsen, Du Pont de Nemours(Nederland) B.V., 's-Hertogenbosch

ABSTRACT

The thermal conductivity of solid samples can be measured with DSC by melting experiments with a pure metal (indium or gallium) on top of cylindrical pellets. Particularly samples with a low thermal conductivity, like plastics or porous substances, can be determined

INTRODUCTION

At our laboratory the catalytic activity of Ni/Al_2O_3 pellets, used for the highly exothermic methanation reaction, is investigated. One aspect concerns the temperature profile inside the pellet, which strongly depends on the thermal conductivity λ (ref.1). Measurement of λ has to be performed by measuring the heat flow through one side of a sample as function of a known temperature difference between that side and the opposite parallel side.

In a DSC cell of the Boersma type, both temperature and heat flow are measured at the contact area between sample and sensor. The temperature at the opposite side of the sample cannot be measured directly, but by applying a pure metal, placed on the sample, the temperature of that opposite side is known during the melting of the metal.

EXPERIMENTAL

A Dupont 910 DSC apparatus was used (see ref.1). Two kinds of experiments are to be made:

First the calibration factor (C.F.) is determined by melting indium or gallium, directly placed on the sensor, without using a cup, and measuring the DSC signal Δ (mV). In that case it is assumed that practically all heat of melting Q_m flows to the sensor and not to the gas phase, resulting in a calibration constant (C.F.), expressed in W/mV, according to:
$Q_m = \int Q'_{sensor}\, dt = (C.F.)\int \Delta dt$, giving: $Q'_{sensor} = (C.F.)\Delta$
The value of (C.F.) depends on the gas phase and varies a little with temperature. For gallium (melting temperature T_m = 30.0 °C)

Proceedings of ICTA 85, Bratislava

measured values of (C.F.) are (0.245 and 0.174) 10^{-3} W/mV in hydrogen en nitrogen respectivily. For indium (T_m = 156.6 °C) these values are (0.261 and 0.188) 10^{-3} W/mV.

Secondly two identical flat cylindrical pellets are directly placed on sample and reference side of the DSC cell. In some cases, when the thermal conductivity of the pellet is high, the thermal contact between sensor and sample has to be improved by applying a silicone paste. A flat piece of pure metal (indium or gallium) is placed on the top of the sample pellet (see fig 1A). The best results are obtained when the metal totally covers the sample pellet, having the same cylindrical diameter, and when the pellet dimensions are not too small: height 1-3 mm, diameter 2-4 mm. The weight of the piece of metal varies from 10 to 40 mg. Starting at low temperature, when the metal is solid, sample and reference are heated with a constant rate (2-10 °C/min). The sensor temperature T_s and the DSC signal Δ are recorded against time. During the melting the top of the pellet remains at constant temperature T_m, while the temperature of the lower side of the sample still increases with a constant rate. The resulting DSC plot is shown in fig. 1B.

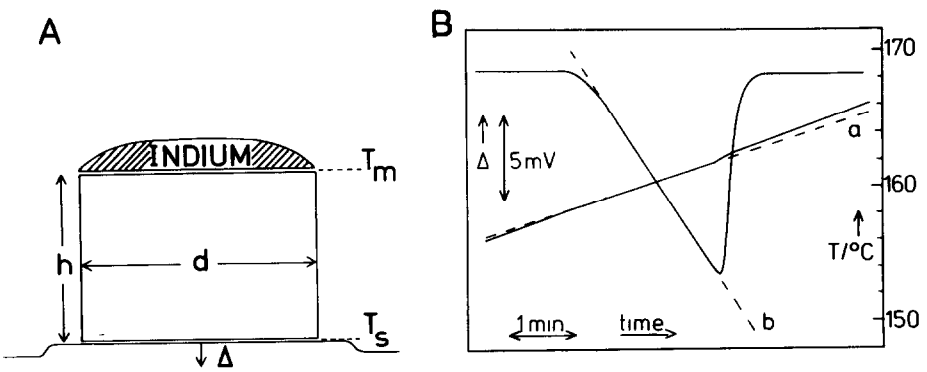

Fig. 1. Melting experiment with indium on top of a pellet.
A: sample geometry, B: DSC plot, a: T_s against time → dT_s/dt,
b: Δ against time → $d\Delta/dt$, $(dT_s/dt)/(d\Delta/dt) = dT_s/d\Delta = \beta_p$

RESULTS AND DISCUSSION

The following formulas can be derived for heat flow in one direction from sensor (x=0) to the top of the pellet (x=h):

$Q'_{sensor} = (C.F.)\Delta = A_s \cdot \{-\lambda(dT/dx)_{x=0}\}$

$A_s = \pi d^2/4$ = contact area between sensor and pellet.

Suppose there is a linear temperature profile inside the pellet:

$(dT/dx)_x = (T_m - T_s)/h$

This gives:

$\Delta = \lambda A_s (T_s - T_m)/h$ (C.F.)

$d\Delta/dt = \{\lambda A_s/h$ (C.F.)$\}(dT_s/dt)$

$dT_s/d\Delta = \beta_p = h$ (C.F.)$/\lambda A_s$

From fig. 1B the value of β_p can be determined, so

$\lambda = h(C.F.)/A_s\beta_p$ can be calculated.

In table 1 the results are given for a number of samples and compared with literature values. The following conclusions can be drawn:

- Samples with a thermal conductivity of 1 W/m.K or higher give only good results when the thermal contact between sample and sensor is improved by applying a special paste.
- Samples with low thermal conductivity, like plastics or porous materials, can be measured very well. Application of a contact paste is not strictly needed, provided that the contact faces of sample and sensor are sufficiently flat.
- The thermal conductivity of porous substances, like cork or polystyrene foam, depends on the gasphase. This dependance is not found for non-porous substances like pyrex glass.
- The thermal conductivity of the catalyst pellets is much greater for Ni/α-Al_2O_3 than for Ni/γ-Al_2O_3, though chemical composition and porosity are about the same. This is caused by the fact that α-Al_2O_3 consists of large crystals with a good thermal contact between the particles. In γ-Al_2O_3 particles and pores are very finely divided, giving a low thermal conductivity.

From these experiments it can be concluded that the Boersma type of DSC or DTA cell is a helpful instrument for measuring the thermal conductivity of solids.

TABLE 1. Thermal conductivity λ for solid substances in H_2 and N_2, as determined by applying Ga and In on top of the pellets.

Sample°	gasphase	Metal	λ (W/m.K)* measured A	measured B	lit.value (ref.2)
pyrex glass	nitrogen	Ga	1.02	1.14	1.14
"	"	In	1.12	1.24	1.30
"	hydrogen	Ga	-	1.12	1.14
quartz glass	nitrogen	Ga	0.94	1.42	1.37
"	"	In	0.96	1.45	1.54
PMMA	"	Ga	0.189	-	0.194
teflon	"	"	0.246	-	0.256
cork	"	"	0.082	-	-
"	hydrogen	"	0.185	-	-
polystyrene foam	nitrogen	"	0.103	-	-
"	hydrogen	"	0.328	-	-
catalyst pellet α	"	"	1.24	-	-
" γ	"	"	0.34	-	-

°PMMA = poly (methyl methacrylate); teflon = poly(tetrafluorethylene), cork: corkplate, density 659 kg/m^3; polystyrene foam, density 79 kg/m^3.
Catalyst pellet α : 6 wt % Ni on α-alumina, porosity 0.60;
γ : 6 wt % Ni on γ-alumina, porosity 0.63 (see ref. 1).
*A : without, and B : with use of a silicone compound for better thermal contact between pellet and sensor.

ACKNOWLEDGEMENT

The authors wish to thank Y. Timmerman for performing most of the experimental work and H. Doetsch of the KFA at Jülich for inspiring discussions. The research described in this paper has been supported by a NATO Research Grant for International Collaboration in Science.

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