AN AUTOMATED CALORIMETER FOR SOLID SUBSTANCES*

J.Zubillaga, A.López-Echarri and M.J.Tello

Depto. de Física.Facultad de Ciencias,Universidad
del País Vasco. Apto.644,Bilbao, Spain.

ABSTRACT

An automated low temperature adiabatic calorimeter for solid
samples is described. It operates in the 10-370 K temperature range
with an stablished accuracy of 0.1% in C_p measurements. Data are
also presented of the heat capacity in $(C_nH_{2n+1}NH_3)_2ZnCl_4$, with
n=2,4. Thermodynamic functions of new phase transitions and thermal
relaxation results are also shown.

INTRODUCTION

In the last few years microcomputer automated calorimeters
using the adiabatic technique have been described /1,2,3/ and the
calibration results show similar accuracy features than those found
in the manually operated ones. Here we describe an automated system
for data acquisition and process control of an adiabatic calorimeter
whose calibration results have been previously presented /4/. The
computer programs allows a simple operation mode for pulse measure-
ments as well as a continuous heating/cooling method specially indi-
cated when C_p anomalies near solid-solid phase transitions are found.
Moreover, thermal relaxation analysis can be easily performed.

AUTOMATIC SYSTEM

Fig.1 is a scheme of the data acquisition and the control
system. The microcomputer (HP9836) is primarily interfaced with the
multiplexer-actuator (HP8497A) for the main operation functions and
data acquisition. Only the temperature data is obtained directly
from an independent DVM, as the multiplexer thermal noise has been
found inadequate for the required accuracy. 1 mK sensibility is
then achieved by an averaging program which smoothes the DVM origi-
nal data. A digital-analog converter provides the heater power
supply in the range 0-40 mA.,while time measurements are obtained
from the computer internal clock.

The four element adiabatic jacket is also controlled by PID's

---

amplifiers. However an additional DC signal which favours the adia-
batic control can also be programmed both for heating and equilib-
rium intervals. Periodic controls of the vacuum detectors, rotatory
and difussion pump refrigeration,etc., assures a safe operation
mode.

Finally, the microcomputer speed also permits a simultaneous
data process for a rapid determination of the C_p results. The final
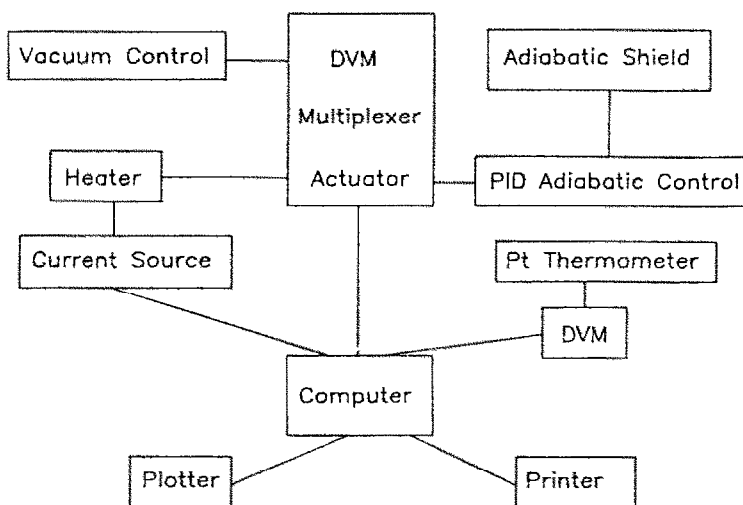most important data are then recorded on a magnetic disc.

Fig.1 Automatic System Block Diagram.

OPERATION MODE

Once the desired temperature is reached and the adiabatic con-
trol is assured, a continuous check of the sample temperature takes
place. Simultaneous time measurements determine the calorimeter
temperature drift. Values of $10^{-6} - 10^{-7}$ ºC/sec. are commonly found
when thermal equilibrium is attained. Then a heating period starts
and power mesurements are periodically performed as well as the
above refered operation controls. The initial and final temperature
are fixed trough the extrapolated temperature drift before and af-
ter the heating pulse.

An alternative heating/cooling method can also be used for Cp
measurements. This method is notoriously improved when automatic
data acquisition is available.

RESULTS

Fig.2 shows the measurements results for the phase transition found in $(C_4H_9NH_3)_2ZnCl_4$. The heating rates used as well as the thermodynamic functions values are included in the figure. The same calorimetric technique have showed a new phase transition at T=234 K in $(C_2H_5NH_3)ZnCl_4$. Experimental investigations are now in progress in order to clarify the physical mechanisms present in these new phase transitions found in both layer compounds.
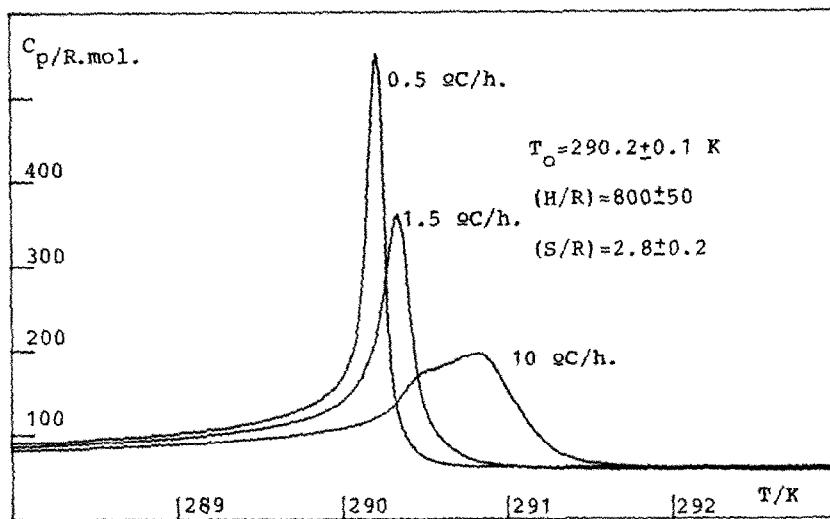

Fig.2 $(C_4H_9NH_3)_2ZnCl_4$ specific heat near the phase transition.

In fig.3 we can see the characteristic shape of the relaxation T -t curve after a heating pulse. Although this result must be strongly dependent on the sample characteristics and on the heat exchanger helium gas content, it provides a relative measurement of the sample thermal relaxation and conductivity. As we can expect a different thermal behaviour among the calorimeter vessel and the sample, we can crudely aproximate the observed relaxation to a sim- ple sum of exponential functions each one being related with each system. The found relaxation times are shown in the figure, the first one in good agreement with the observed equilibrium time of the empty vessel.
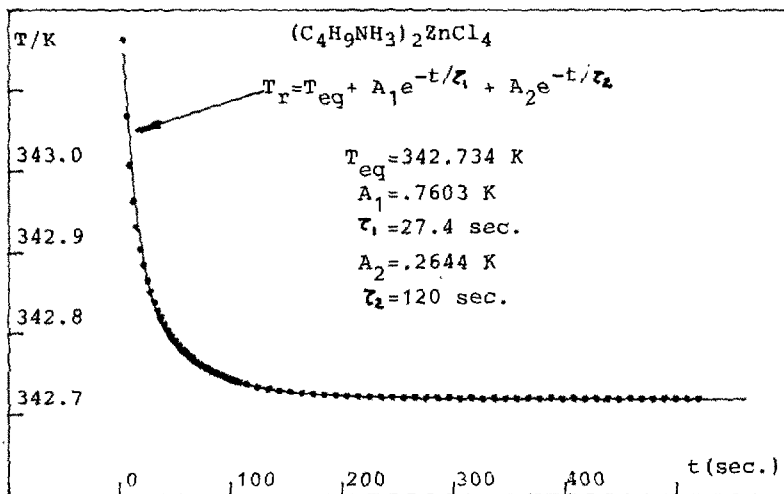
Fig.3 Sample + vessel thermal relaxation.

REFERENCES

1 E.Gmelin and P.Rödhammer, J.Phys.E:Sci.Instrum. 14(1980)223
2 P.C.Lanchester and D.P.Baker, J.Phys.E:Sci.Instrum. 14(1981)805
3 S.J.Collocott,Aust.J.Phys. 36(1983)573
4 A.Lopez-Echarri and M.J.Tello, J.Phys.D:Appl.Phys. 14(1981)71