Thermochimica Acta, 92 (1985) 265-268
Elsevier Science Publishers B.V., Amsterdam

NEW POSSIBILITIES OF CALVET'S CALORIMETRY. COMBINATION OF DSC AND TG.

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ABSTRACT

A DSC-111 calorimeter and an MTB-10-8 differential microbalance are used to build a new instrument that combines the characteristics of both devices.The kinetics of two simultaneous reactions can be studied on the new instrument if only one or both reactions involve a change in weight.FFT method was employed in order to obtain true DSC curves.

INTRODUCTION

A usual Calvet's calorimeter[1] is characterized by a large time constant because of the presence of a massive bloc for equalizing temperature.The instrument operates under isotermal conditions and it can be used for studying various solubility, mixing, adsorption, and other processes.Kinetic data are usually obtained by the TG or DTA techniques and checked by other methods.Simultaneous determination of the TG and DTA patterns and the composition of gases evolved in the reaction increases reliability of the results and also makes it possible the kinetics of several simultaneous reactions, the thermodynamics of gas adsorption, etc.

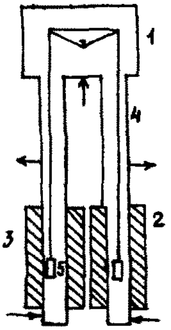
We examined the characteristics of a DSC-111 calorimeter(Setaram Soc., Lyon, France) and concluded that this instrument can be used as a basis unit for building a new device combining the characteristics of a calorimeter and a balance.

EXPERIMENTAL

The DSC-111 calorimeter was described in [2].The experimental enthalpy values were independed of the size and the shape of spiecimens, the nature of a gas, and the gas flow rate because of the small time constant, high sensibility and lengthy working zone, even if a crucible did not touch the wall.The device enables true specific heat with to be measured with uncertainty of 0.6%[3,4].
We combined a DSC-111 calorimeter and a differential microbalance (Setaram Soc., Lyon, France) by a vacuum tight joint(Fig.1).

Proceedings of ICTA 85, Bratislava

Block(3) is fixed.Block (2) can be turned to a horizontal for other thermal measurements.Balance(1) is moved in a vertical direction with the helpof a lift.A crucible with a sample is hanged up to a beam using a fine wire and balanced.The joint is then closed hermetically.If it is necessary the balance and the calorimeter are evacuated and/or filled by a gas.The balance is moved down until the crucible is in the central zone of the calorimeter.



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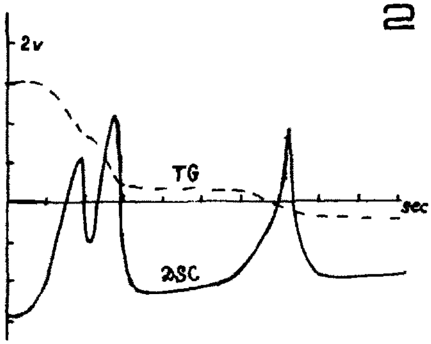

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The clearance between the crucible and the inner calorimeter wall is 1mm.Measured signals are stored using an IN-110 computer(Intertechnique Soc.,Plaisiz, France).The calorimeter is calibrated against melting heats of metals and using the electric technique. The experiment was carried out in He flow(0.5cm^3/sec) in a Pt crucible 0.5cm in diameter and o.5cm in hight.

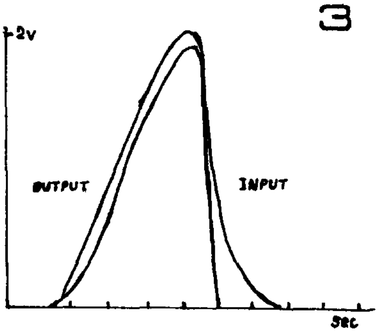
RESULTS AND DISCUSSION

In Figure 2, the DSC and TG curves are shown for a test mixture of Sn(26.4mg) and $CuSO_4 \cdot 5H_2O$(22.4mg).Tin melting and the last dehydration stage occurved simultaneously.It should be noted that the time constant of the calorimeter was approximately 20sec.The DSC curve was therefore distorted.Fast Fourie Transform(FFT) method was employed to obtain true DSC curves.For this purpose we stored synchronous spectra of initial calibrater signals and response signals in IN-110 memory.Then we determined friequency spectra of transfer functions for various temperatures.At last we used this function for restoring the true Sn melting DSC curve (Fig.3) for testing the procedure.We resolved the Sn melting and $CuSO_4 \cdot H_2O$

dehydration peaks by means of the equation [5]:

$$\frac{dW_i}{d\tau} = \alpha\frac{dm}{d\tau} + \beta W + (\gamma + \delta_m)\frac{dW}{d\tau} \quad , \quad (1)$$

where m, W and W_i are the mass, the total rate of weight variations and the rate for one of the reactions, respectively.



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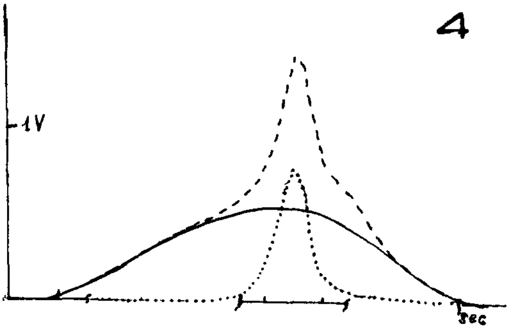

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The parameters $\alpha, \beta, \gamma, \delta_m$, and are determined by the DSC unit characteristics and the thermodynamics of reactions.The data was computed by a Basic program according to equation (1) which was only modified to describe linear heating.For testing purposes we used the dehydration enthalpy.We determined the Sn melting curve (Fig.4) and calculated the heat of melting (61.9J/g).

CONCLUSION

Combined DSC and TG method enables one to study the thermodynamics and the kinetics of complex processes when they involve a change in mass.For accurate calculations of the kinetic parameters, DSC curves should be reduced to their true shapes.

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