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NEW EXPERIMENTAL VESSELS FOR CALORIMETRIC INVESTIGATIONS OF GASES AND LIQUIDS ON THE SETARAM C 80

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ABSTRACT

New experimental vessels for calorimetric investigations of gases and liquids on the SETARAM C 80 calorimeter are introduced and described : vessel for the measure of the vapour pressure of liquids and vessel for the determination of the thermal conductivity of liquids and gases.

INTRODUCTION

The last few years have seen a new interest of the scientific community for the calorimetric method. The calorimeter is becoming a complementary tool for DSC users, who are limited in the amount of sample to be investigated, with no possibility of mixing. For many years now, the SETARAM C 80 calorimeter has been used with different experimental vessels, allowing a broad range of measurements : thermal investigation under standard or high pressure (1), batch mixing (2, 3) (hydration, dissolution, wetting, reaction), flow mixing (titration).

In order to increase the facilities in the field of thermodynamic measurements, new experimental vessels have been designed especially for the investigations of liquids and gases : heat capacity of liquids, measure of the vapour pressure of liquids, thermal conductivity of liquids and gases. Only the two last vessels will be described in the paper. The determination of the corresponding thermodynamic parameters is made possible over a broad range of temperature. This is particularly interesting for gases because such data are not numerous above 100°C.

VAPOUR PRESSURE OF LIQUIDS

The vapour pressure of a liquid is the pressure exerted by the vapour when in equilibrium with the liquid phase. The vapour pressure, being a specific property of a compound, is widely used for practical calculations in physical chemistry and chemical engineering, and for the characterization of organic compounds. The tables of vapour pressures usually do not cover the full range of pressure and temperature, and some type of interpolation formula is necessary. To overcome this problem, a special calorimetric vessel has been designed for measuring the vapour pressure of liquids up to 200°C.

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The vessel is composed of a machined body, on which is fitted a special device for the filling of liquids and the regulation of the evaporation (Fig. 1).In the case of no volatile liquids, the sample is directly introduced in the vessel by means of a syringe, and then weight. If the liquid is volatile, the filling is done at the top of the vessel through a special inlet. When the equilibrium is reached in the vessel, a primary vacuum is run through a heated capillary located at the outlet of the vessel. When opening the evaporation control valve, the evaporation starts.

The determination of the vapour pressure of the liquid is reached by applying a counter-pressure of helium at the outlet of the heated capillary. This pressure is read very precisely by means of a manometer (precision 0.01 bar). The effect of the counter-pressure of helium is to reduce the flow of evaporation. By successive increases of this pressure, it is possible to stop the evaporation. The vapour pressure of the liquid is the corresponding pressure of helium. In this case, the calorimeter is used to detect an equilibrium, and not to measure an evaporation. With such an evaporation vessel, the precision of the method for the determination of the vapour pressure is better than 0.5 %.

The same experimental vessel can also be used to measure the heat of evaporation of a sample.

THERMAL CONDUCTIVITY OF LIQUIDS AND GASES

The thermal conductivity characterizes the capability of a compound to transmit heat. This transmission, operating at the molecular level, is very variable according to the materials. The determination of the coefficient of thermal conductivity, (in $W.m^{-1}.K^{-1}$) is important for all calculations of heat transfer, especially in chemical engineering. However, there are no many instruments commercially available for measuring especially the thermal conductivity of liquids and gases.

As a transmission of heat has to be measured, a calorimetric vessel to be adapted in the C 80 calorimeter is designed. The method of the coaxial cylinders is used, the fluid to be tested being located between the two cylinders (Fig. 2). The inner cylinder is made of copper, which has a high thermal conductivity. The outer cylinder is the wall of the vessel. Around this wall, is wound a heating coil. The whole device is set in a stainless steel cylinder, fixed at the top of the calorimetric block. The fluid (liquid or gas) is introduced in both vessels through a tube. In the case of gas filling, a purge of the vessels is previously run.

When the equilibrium is reached, a current is sent through the heating coil only in the measure vessel, in order to have a constant power dissipated by Joule effect. An exothermic deviation S of the calorimetric signal is recorded. In fact, the dissipated power goes for one part through the calorimetric detector and for another part through the liquid. The liquid transmits the corresponding heat to the copper cylinder, which, itself, with its high conductivity evacuates this heat to the environment. Depending on the thermal conductivity of the fluid, more or less heat will be transfered by the fluid to the copper cylinder.

Three pairs (λ, S) are needed for the calibration of the method at a given temperature. For the determination of gas thermal conductivity, hydrogen, methane and argon are chosen as standards (4). A calibration curve is drawn (Fig. 3) and the thermal conductivity coefficients of helium, air and nitrogen are calculated. The deviation with the litterature values is about 1 %, and the reproducibility of the measures is less than 1 %, even at high temperature (200°C). The good resolution of the method allows to differentiate the thermal conductivity coefficients of air and nitrogen which are very closed.

An identical calibration curve can be drawn for liquids. Also for liquids, the agreement is very good with litterature values, and the reproducibility is less than 1 %.

CONCLUSION

The different experimental vessels, described in this paper, give the possibility to measure with a good precision important thermal parameters, like vapour pressure, thermal conductivity, all needed for the calculations of heat transfer.

They increase largely the field of applications of the C 80 calorimeter for thermodynamic data evaluation. In a near future, the liquid specific heat measurement, the evaporation determination and the adsorption of liquids on powders will be described.

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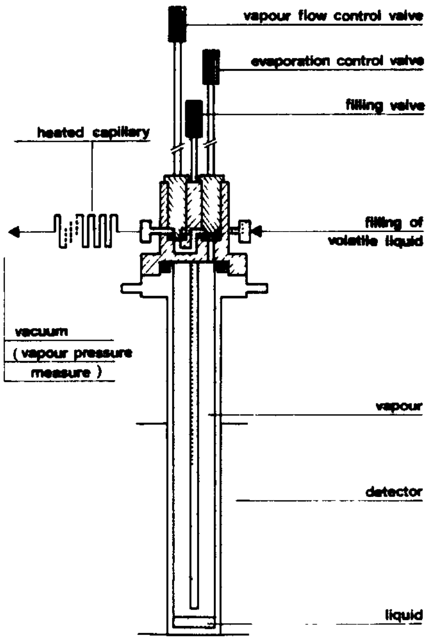

Fig. 1 : Cross-section of the vapour pressure determination vessel

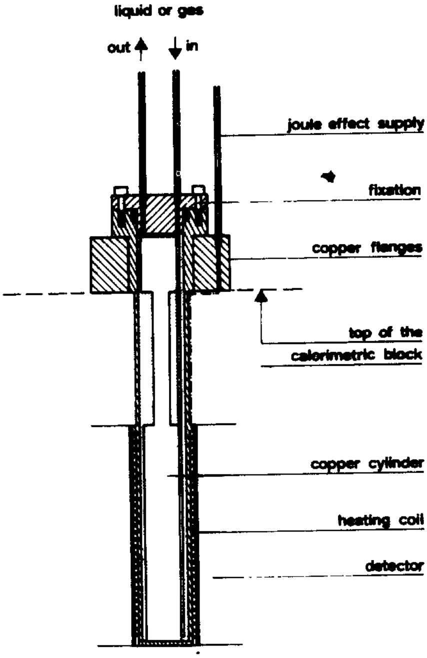

Fig. 2 : Cross-section of the thermal conductivity vessel

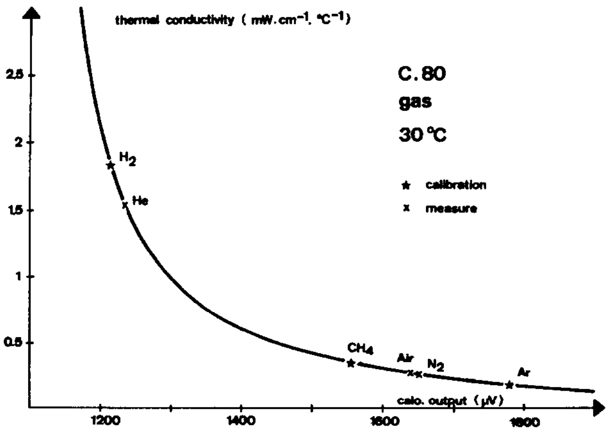

Fig. 3 : Thermal conductivity calibration curve for gases at 30°C