

## A NEW METHOD FOR THE DETERMINATION OF HEAT OF VAPORIZATION BY QUANTITATIVE DIFFERENTIAL THERMAL ANALYSIS

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### ABSTRACT

A method is described which allows to determine the enthalpy of vaporization by a simple DTA experiment. The measurements are performed in a commercially available quantitative DTA instrument.

Experimental results of measurements with several organic and inorganic liquids are presented which have vapor pressures at room temperature varying from 150 Torr to less than 1 Torr. The typical accuracy of such measurements is  $\pm 2\%$ .

### INTRODUCTION

There are two commonly used methods for the determination of the enthalpy of vaporization:

The direct measurement of the heat of vaporization or condensation by means of calorimeters.

The calculation from vapor pressure data by means of the Clausius–Clapeyron equation.

Both methods are time-consuming and it is obvious that attempts were made to find an easier and faster method with the aid of quantitative DTA, specially since DTA is already used as a routine technique for the determination of boiling points<sup>1</sup>.

There are several methods for the determination of heats of vaporization described in the literature<sup>2,3</sup>. All these methods are very similar in principle: The sample is weighed into a sample cup which has a pinhole in the cover. The temperature is then scanned across the boiling point and the area of the boiling endotherm is used for the evaluation.

There exist several modifications of this method, e.g., holding the temperature isothermal at the boiling point or placing a small ball on the hole in the lid to reduce the evaporation losses.

But there are two major sources of errors which are common to all these methods:

(1) Unknown sample loss between the weighing-in and the measurement: The amount of compound corresponding to the boiling endotherm is not exactly known.

(2) A constantly changing baseline due to the increasing weight loss and therefore a change of the heat capacity of the sample.

Measurements made with one of these methods can therefore yield only approximate results and the error often exceeds 10%.

An attempt was made to eliminate the first of these errors by installing a device for puncturing the sample pan lid after the pan has been introduced into the instrument<sup>3</sup>. But as a simple, general method this system is unsatisfactory since it needs a modification of the instrument.

To solve these problems we have developed a new, simple method which will be presented in the following.

#### EXPERIMENTAL

All measurements were done with a Mettler TA2000 System with the DTA-20 to +500°C measuring cell. This unit allows calorimetric measurements with a typical accuracy of  $\pm 2\%$ . Its temperature accuracy is better than  $\pm 0.5^\circ\text{C}$ , over the entire temperature range, and it has the capability of holding the temperature isothermal at a preselected, defined temperature with fluctuations smaller than a few  $1/1000^\circ\text{C}$ .

It will be seen later on that these are important instrumental specifications for this method. The samples are weighed into standard aluminium pans with the aid of a Hamilton microliter syringe and then closed. Previously the cover of the pan is punctured so that the hole has a slightly greater diameter than the diameter of the needle of the syringe (about 0.5 mm). Again this will turn out to be important later on. The sample cup is then placed in the measuring cell which was previously kept isothermal at  $25^\circ\text{C}$ , for instance. The upper limit of the instrument is set to the temperature at which the heat of vaporization is to be measured. The heating rate is chosen at say  $20^\circ\text{C min}^{-1}$  and the heating program is started. The temperature increases now at the chosen heating rate until the upper temperature limit is reached at which the temperature remains isothermal.

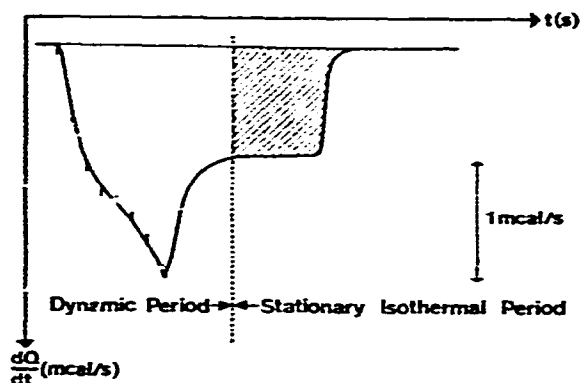


Fig. 1. DTA curve of the vaporization of 2.21 mg of 1-butanol. Heating rate  $20^\circ\text{C min}^{-1}$ ; isothermal at  $100^\circ\text{C}$ .

Figure 1 shows the DTA curve of such an experiment. The area under this curve can be divided into two sections: A dynamic one and an isothermal one; the latter is hatched in the figure. Both portions correspond to a certain amount of heat. In the dynamic region the situation is rather complex since two components contribute to this heat: The heat necessary to raise the heat capacity of the sample and the heat required for the partial evaporation of the sample. The analytical description of this area is therefore very difficult.

In the isothermal region the situation is easier to understand. The sample evaporates at a well-defined temperature with a constant rate of evaporation. The heat flowing to the sample is used for the evaporation of the sample and the hatched area in Fig. 1 corresponds therefore to the heat necessary to evaporate a certain amount of compound.

A problem arises from the fact that the amount of sample evaporated during isothermal conditions is not known. But this difficulty can be overcome easily: The experiment is repeated with exactly the same experimental conditions but with a different sample mass and only the difference of the two areas is evaluated.

For this purpose the sample cup is removed from the measuring cell and a sample with a greater mass is weighed in. The compound is introduced with a microliter syringe through the hole in the same sample cup as used before. This procedure is very important since the conditions of the experiment must exactly be the same as for the preceding one, especially the pinhole diameter. The sample cup is again placed into the measuring cell which is at the same isothermal temperature as before. For each of these experiments, the time elapsed between weighing-in and starting the temperature program is the same. The weight loss occurring between these two operations is still unknown, but since it is not dependent on the sample mass, this weight loss is exactly the same for both experiments.

The temperature is now programmed as before and the second experiment is recorded exactly on the first one. Figure 2 shows the two resulting DTA curves superimposed.

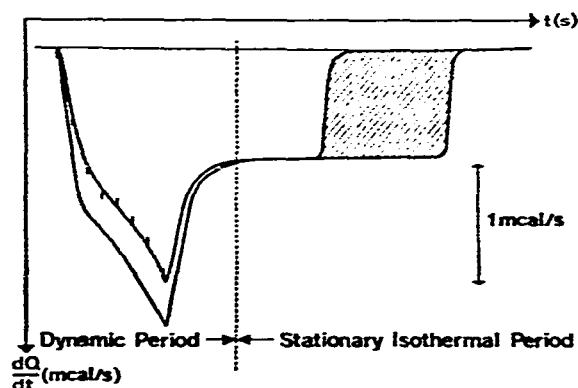


Fig. 2. DTA curves of the vaporization of 2.21 and 5.08 mg of 1-butanol. Heating rate  $20^\circ\text{C min}^{-1}$ ; isothermal at  $100^\circ\text{C}$ .

The unknown losses of the two samples until stationary isothermal conditions are reached, are identical under identical conditions. Therefore the hatched area in Fig. 2 which represents the difference between the two isothermal parts of the curves corresponds to the heat necessary to evaporate the difference of the two sample masses. This difference of the sample masses is known and the area can be measured accurately. (For the manual evaluation this area can be approximated by a rectangle.) Thus the heat of vaporization can now easily be calculated.

#### RESULTS AND DISCUSSION

A series of determinations of the heat of vaporization of compounds with different vapor pressures were carried out using the described method. Figure 3 shows the vapor pressure curves of the substances used.

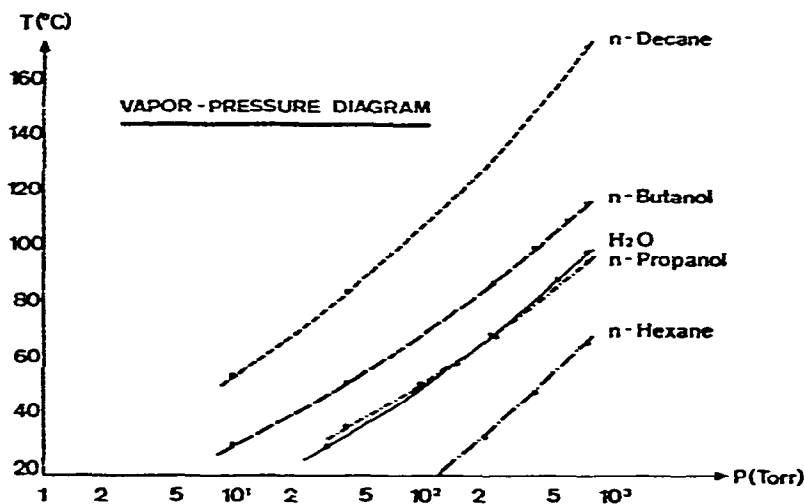


Fig. 3. Vapor-pressure diagram of the compounds used.

Figure 4 shows the results of the measurements of water. Measurements were performed at 70, 80, 90 and 100°C. All results are within a 2% error limit. Figure 5 shows the results of the n-decane measurements. Two measured values are slightly outside the 2% error limits, all the others are well within these limits. Figure 6 shows the results of 1-butanol, Fig. 7 of 1-propanol and Fig. 8 of n-hexane, all of which are within the  $\pm 2\%$  limits.

Thus, the described new method makes it possible to determine the heat of vaporization with a simple and easy DTA experiment with a typical accuracy of  $\pm 2\%$ . The time needed for such a determination is between 30 and 60 min.

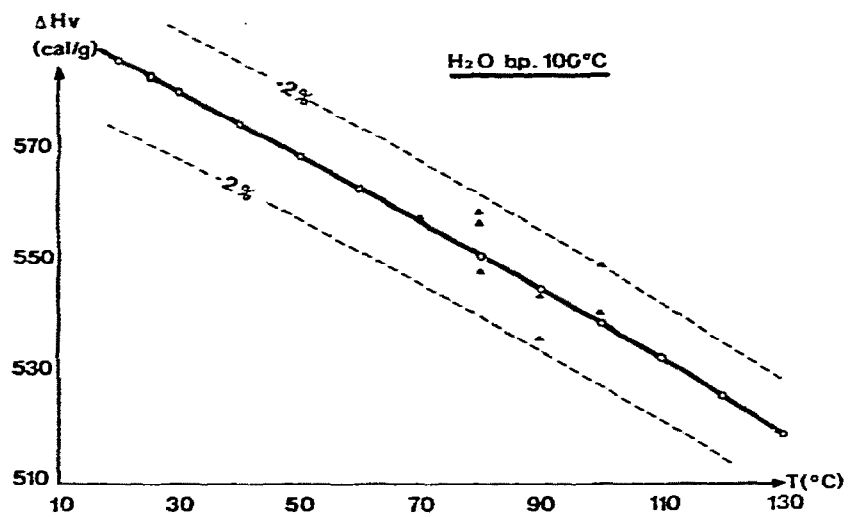


Fig. 4. Heats of vaporization of water. ▲ = Measured values; ○ = literature values.

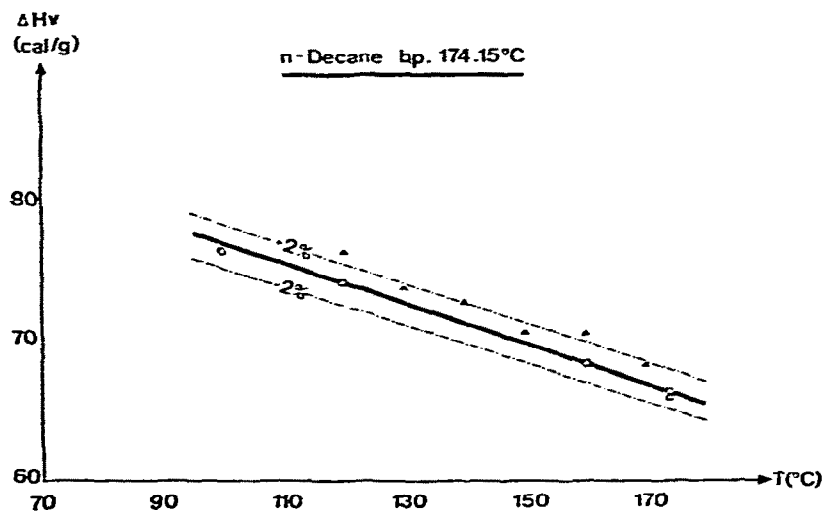


Fig. 5. Heats of vaporization of n-decane. ▲ = Measured values; ○ = literature values.

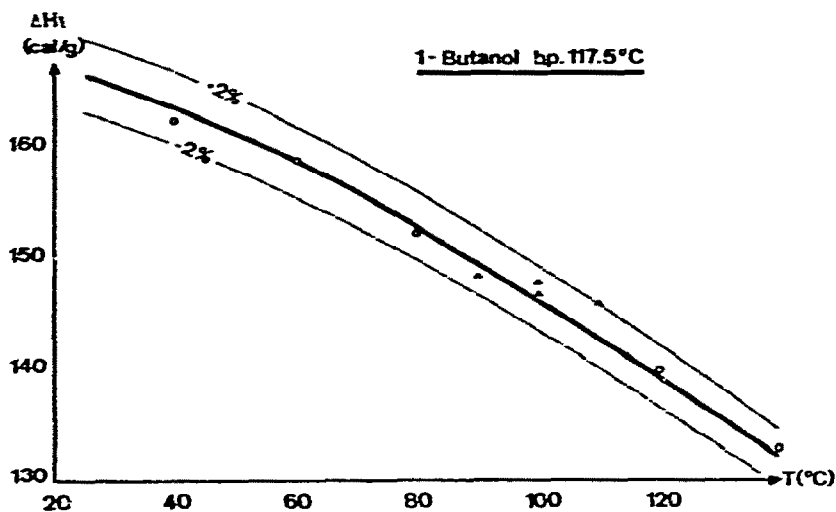


Fig. 6. Heats of vaporization of 1-butanol.  $\blacktriangle$  = Measured values;  $\circ$  = literature values.

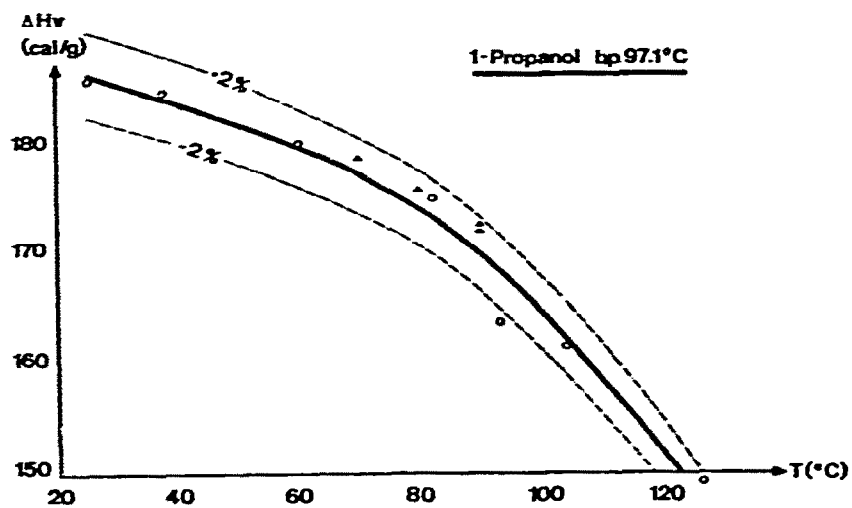


Fig. 7. Heats of vaporization of 1-propanol.  $\blacktriangle$  = Measured values;  $\circ$  = literature values.

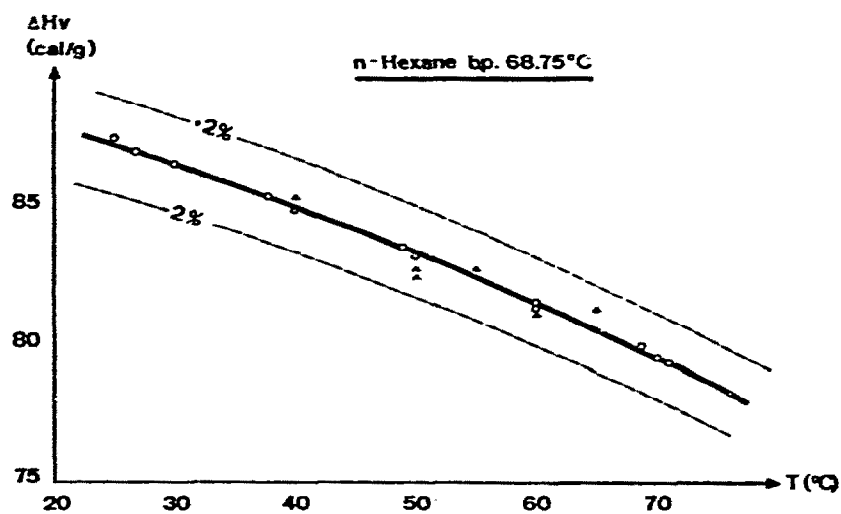


Fig. 8. Heats of vaporization of n-hexane. ▲ = Measured values; ○ = literature values.

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