

Design and Testing of a Vaporisation Calorimeter. Enthalpies of Vaporisation of Some Alkyl Cyanides

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An enthalpies of vaporisation calorimeter for work at 25°C has been designed and tested. Results of test experiments indicate an accuracy of about $\pm 0.25\%$. The calorimeter has been used for a study of ΔH_v for a series of alkyl cyanides.

The enthalpy of formation data of liquid and solid substances which can be obtained from combustion measurements reflect the complexity of the condensed state. In order to study properties such as bond energies, resonance energies, *etc.*, a knowledge of enthalpies of formation in the ideal vapour state is needed. Obviously, enthalpies of vaporisation data are indispensable for such investigations.

In connection with the investigation on ΔH_c of some alkyl cyanides^{1,2} it was felt necessary to build a vaporisation calorimeter for small samples.

In the present paper, a new semi-microcalorimeter for measurements of ΔH_v of liquid compounds is described. The amount of substance necessary for ΔH_v determination is in the range of 0.1 g to 1 g.

DESCRIPTION OF THE CALORIMETER

Principle. The basic principle of the present calorimeter has been used in several earlier constructions^{3,4} where, however, the instruments were designed for comparatively large quantities of substance.

The present calorimeter basically consists of an inverted U-tube which contains the compound to be investigated only (in liquid and gas phases). A suitable amount of liquid substance is vaporised from one end of the tube and condensed in the other. The vaporisation end (the calorimetric vessel) is heated electrically in order to keep the temperature constant, while the other end (the condensation bulb) is suitably cooled. The heat supplied to

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maintain the constant temperature of the calorimetric vessel, together with the amount of vaporised substance, is used for ΔH_v calculation.

In contrast to the earlier calorimeters of a similar type the present method is based on the complete vaporisation of the compound from the calorimetric vessel. The amount of compound necessary for measurement is, thus, considerably reduced.

Vaporisation vessel. The calorimetric vessel is made of brass and consists of several parts (Fig. 1). The cylindrical part *a* has a threaded part for connection to the vaporisation tube. The piston *b*, which is equipped with twelve vertical grooves, is pressed into the cylindrical body *a*. The calorimetric vessel is closed by means of lid *c*, which is sealed with Araldite epoxy resin. Screw *e* serves to attach the U-shaped glass tube, joined to ring *d* with epoxy resin, to the body of the calorimeter over a lead amalgam packing, *g*.

The U-tube can be joined to the vacuum system by means of tube H (Fig. 2). Through this tube the substance can be introduced into the vaporisation system and condensed in bulb I. The system can be sealed and detached in a vacuum.

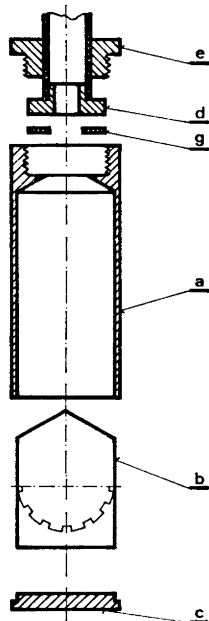


Fig. 1. Construction of the calorimetric vessel.

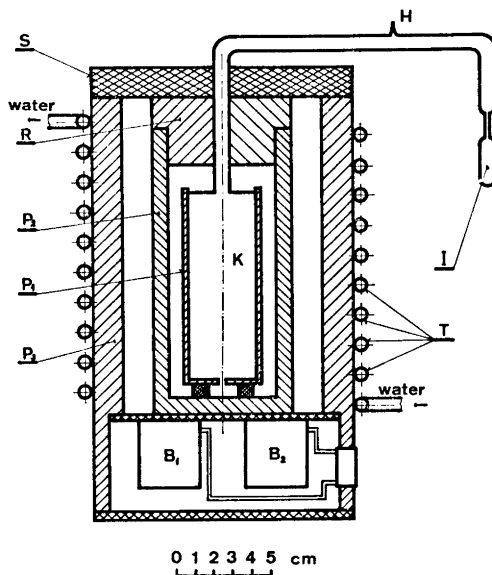


Fig. 2. Schematic view of the calorimetric assembly.

Calorimeter. The calorimeter consists of three cylinders P_1 , P_2 , P_3 (Fig. 2). The measuring part of the calorimeter, P_1 , is made of copper. There is a copper resistance thermometer wound in a groove on the lower part and a heater in another groove on the upper part of the cylinder. The thermometer is con-

nected in a Wheatstone bridge and controls the heater by means of an electronic device. The surface is coated with a layer of heat-hardened varnish, aluminium-metalized in a vacuum.

Cylinder P_1 is located in the centre of the cylindrical brass jacket P_2 . The space between the walls is 10 mm. There is a platinum resistance thermometer and a heater wound around the surface of jacket P_2 . The thermometer forms part of a Wheatstone bridge and controls the function of the heater by means of proportional control system. The temperature of jacket P_2 is kept constant within $\pm 5 \times 10^{-4}^\circ\text{C}$. In the upper part of jacket P_2 there is an opening through which the vaporisation vessel can be inserted into jacket P_1 . Insert R is a two part copper ring which fits tightly around the glass tube of the vaporisation system in order to minimize uncontrolled heat exchange between the surroundings and the calorimeter.

The duraluminium cylinder P_3 is divided into two parts. In the upper part, the calorimetric jackets are placed. The lower cavity contains two boxes B_1, B_2 made of permalloy in which 2×3 calibrated manganine resistors (100Ω) are placed. They form two Wheatstone bridges together with resistance thermometers on the measuring (P_1) and thermostating (P_2) jackets, respectively. As the bridges are supplied with alternating current they are — together with preamplifiers — enclosed in shielding boxes B_1, B_2 to avoid capacity coupling between the two bridges. The temperature of jacket P_3 must be kept about 0.3°C lower than the temperature of jacket P_2 . Therefore, a copper tube T is wound around the surface, and the temperature is kept constant by circulating thermostated water.

Electronic equipment. The electronic equipment consists of two identical parts; one of them is used for the calorimetric cylinder P_1 and the other for jacket P_2 . The bridges are supplied with alternating current; the voltage on the bridge is 0.2 V. The signal is used for the control of the heaters and can also be recorded. The signal from the P_2 bridge serves thus as a steering signal for the control of the heater on P_2 . At the output side of the measuring part of the electronic system an electronic power relay is connected with two parallel contacts. One of the contacts connects and disconnects a lead storage battery with the calibrated heater on jacket P_1 . The parallel contact serves for switching on and off an electronic stop watch (pulse counter Universal Counter Tesla BM-52).

PROCEDURE

Sample filling. The sample is introduced into the vaporisation system by the filling system shown schematically in Fig. 3. The sample is transferred into bulb B, the system is evacuated to about 10^{-1} mmHg and valve V_4 is closed. Ampoule A is filled with granulated charcoal and when cooled by liquid nitrogen, a vacuum in the order of 10^{-4} mmHg is obtained. The sample in B is cooled and heated several times in this vacuum for degassing. Finally, the sample in B is heated to room temperature, bulb I in the vaporisation system C is cooled down, and a suitable amount of the sample is condensed in I. The vaporisation system C is separated from the filling system by melting

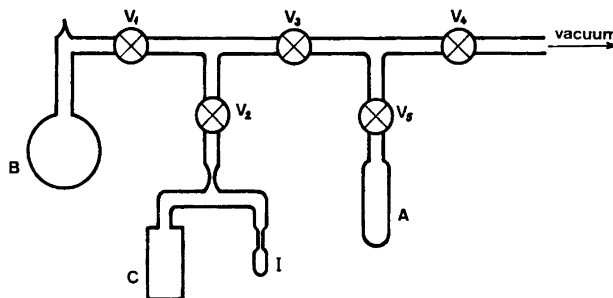


Fig. 3. The filling system.

off the connecting tube under vacuum. The sample is distilled into the calorimetric vessel by heating the glass part and by cooling the brass part.

Measurement. The calorimetric vessel is now filled with the sample. The calorimetric vessel fits into the copper cylinder P_1 . Jacket P_2 is then closed by the two parts of lid R and covered by styrofoam lid, S (Fig. 2). The calorimeter is then heated to the equilibrium temperature (25°C). The temperature of the surrounding air is kept at 25.3°C to avoid a condensation of the sample in the glass tube before the beginning of the measurement. When the temperature in the calorimeter has come to the equilibrium, bulb I is cooled to a suitable pre-determined temperature. The sample is vaporised from the calorimetric vessel K and condensed in bulb I. The vaporisation in the calorimeter causes a temperature drop which is compensated by the calibrated heater. The usual on and off periods of the heater are from 2 to 5 sec during the measurements. When the last residues of the sample are being vaporised the rate of switching on of the heater slows down and the heating periods become very short, about 0.2 sec.

When the sample has condensed completely in bulb I, and when no further vaporisation takes place in the calorimeter, the total heating time is shown on the screen of the counter. The final temperature is identical with the equilibrium temperature before the experiment. The calorimetric vessel K is removed from the cylinder, and the sample is distilled back into the brass body. Using this procedure, the experiment can be repeated several times on the same sample.

After the final experiment, the sample is condensed in bulb I and thermostated at 24.5°C , while keeping the temperature of the vaporisation vessel and the U-tube approximately 0.5°C higher. Then bulb I is cut off, the hole is closed by a rubber stopper and the bulb and its content are weighed, emptied and weighed again. From the amount of the substance and from the energy supplied by the heater the enthalpy of vaporisation, ΔH_v , is calculated (eqn. 1):

$$\Delta H_v = Q/g \text{ kJ/mol} \quad (1)$$

Q is the heat supplied by the heater and g the weight of the sample.

Testing of the instrument. The calorimeter was tested by measurements on water, methanol, benzene, and carbon tetrachloride. For these compounds well established ΔH_v data at 25°C are available.

Table 1. Comparison of the ΔH_v values at 25°C for water, methanol, benzene, and carbon tetrachloride.

	This work	ΔH_v (kJ/mol)	Other results
Water	44.04 ± 0.10		43.99 ± 0.02 ⁸ 44.02 ± 0.08 ¹¹ 43.98 ± 0.02 ⁵
Benzene	33.90 ± 0.10		33.87 ± 0.05 ³
Methanol	37.42 ± 0.10		37.70 ± 0.18 ⁴ 37.40 ± 0.05 ⁷ 37.28 ± 0.08 ⁹ 37.43 ± 0.02 ⁵
Carbon tetrachloride	32.54 ± 0.10		32.43 ± 0.08 ¹¹ 32.41 ± 0.02 ⁸

Water redistilled in glass was used. The other test substances were of *p.a.* grade. The test compounds were dried by molecular sieves and were further purified by fractional distillation.

The results of the test experiments are summarised in Table 1. Experiments were performed on two or three independent samples. The weight of the samples varied from 93 mg to 400 mg for water, and from 250 mg to 1200 mg for the other compounds. For each sample, four experiments were performed.

Enthalpies of vaporisation of alkyl cyanides. As a part of a study on formation enthalpies of some alkyl cyanides ^{1,2} measurements of their ΔH_v values were made. Results are summarised in Table 2. Each value is an average of eight determinations with two independent samples.

Table 2. Enthalpies of vaporisation of some cyanides at 25°C.

Compound	ΔH_v kJ/mol
Allyl cyanide	40.01 ± 0.10
<i>cis</i> -1-Propenyl cyanide	38.91 ± 0.15
<i>trans</i> -1-Propenyl cyanide	40.04 ± 0.15
<i>trans</i> -2-Butenyl cyanide	44.77 ± 0.15
<i>cis</i> -1-Butenyl cyanide	43.22 ± 0.15
<i>trans</i> -1-Butenyl cyanide	44.89 ± 0.15
Cyclopentyl cyanide	43.43 ± 0.20
1-Cyclopentenyl cyanide	44.98 ± 0.20
Cyclohexyl cyanide	51.92 ± 0.25
1-Cyclohexenyl cyanide	53.55 ± 0.20

DISCUSSION

A robust construction of the vaporisation vessel, made from brass, was chosen. The vaporisation vessel serves not only as a container of the liquid to

be investigated but has an important heat distributing function. Stirring is thus not necessary and yet reasonably fast evaporation rates can be achieved. The results of the test experiments suggest that there is no significant deviation from the equilibrium condition at the given temperature. The liquid in the vaporisation vessel is in intimate contact with the bottom of the vessel. A sample of 1 cm³ forms a layer 2 mm high if the amount which condenses on the walls and in the grooves is not considered.

The minimum amount of the substance to be investigated is limited by the precision of the temperature measurement and by the heat capacity of the calorimetric vessel. The heat capacity of the calorimeter (*i.e.* calorimetric vessel and cylinder P₁) was about 130 J/deg. With the difference between the initial and final temperature of the calorimeter of 0.001°C, the error of the measurement would be 0.1 % for a heat quantity of 130 J. This amount of energy is consumed when about 50 mg water or about 400 mg of a hydrocarbon are vaporised. Usually, larger samples were used, especially during the test experiments.

The calorimeter with the condensation vessel is a closed system containing the substance to be measured only, in liquid and vapour phase. The total volume of the system is about 25 cm³. In order to establish the true amount of the substance vaporised from the vaporisation vessel accurately, it is necessary to keep a small temperature difference between the calorimetric vessel and the U-tube, especially for volatile compounds. For the same reason, the temperature of the condensation bulb should not be kept much lower than the equilibrium temperature when cutting it off for weighing. If this type of calorimeter is used at higher temperatures it becomes even more important to observe these conditions. The error introduced when measuring the enthalpy of vaporisation at temperature T_0 and determining the amount of substance vaporised at temperature T_1 can be expressed by the equation:

$$\% \text{ error} = \frac{(d_{T_0} - d_{T_1}) \times V}{g} \times 100 \quad (2)$$

where d_{T_0} and d_{T_1} are saturated vapor densities at the respective temperatures, V is the volume of the instrument, and g is the amount of the substance to be investigated in the calorimeter.

A calorimeter, which was based partly on the present design, has recently been used by Polak and Benson.⁵ They used a different approach to determine the amount of substance vaporised. The amount of substance present in vapour phase at the start of vaporisation was calculated from the known liquid density, the state equation of the substance in vapour phase, and the total volume of the calorimetric system. The advantage of this procedure lies in the fact that measurements can be made at different temperatures by only once filling the calorimeter with a sample.

For proper function of the calorimeter, it is important that the heating intervals are of approximately the same duration as the intervals during which the heater is shut off. This condition can be achieved by suitable temperature choice of the condensation bulb. A proper vaporisation rate for most of the measurements reported here is about 0.5 W which corresponds to a cooling

rate of about 0.004°C/sec. At this vaporisation rate the electrical heat effect was chosen to be about 1 W. Under these conditions, the temperature of the calorimeter varies regularly $\pm 0.02^\circ\text{C}$ around the experimental temperature.

A necessary condition for obtaining a stable vaporisation rate is that the volume of the condensation bulb be kept several times larger than the volume of the liquid which will condense in it. Otherwise, the vaporisation rate will slow down proportionally to the decrease in the cooled vapour's volume in the condensation bulb.⁴

Results of the test experiments indicate a precision of $\pm 0.15\%$, expressed as twice the standard deviation of the mean. The standard deviation was calculated from eight experiments on two independent samples. Comparison of results from the test experiments with the literature data (Table 1) has not indicated any significant systematic error. However, an uncertainty of $\pm 0.1\%$ was added to the standard deviation to account for eventual errors.

Enthalpies of vaporisation of some alkyl cyanides were measured (Table 2). Values of CH_2 increments can be derived from ΔH_v of propenyl cyanides and butenyl cyanides. The increment is 4.31 kJ/mol for the *cis*-compounds and 4.85 kJ/mol for the *trans*-compounds. It is interesting to note that for the *trans*-compounds the increment value is close to the normal value of 4.95 kJ/mol.¹⁰ For *cis*-cyanides, similarly as for n-alkyl cyanides,¹¹ the CH_2 increment is significantly lower. Enthalpies of vaporisation of the *cis*-isomers are somewhat lower than for the *trans*-isomers which probably is due to the lower dipole-dipole interactions.

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REFERENCES

1. Konicek, J., Prochazka, M., Krestanova, V. and Smisek, M. *Collection Czech. Chem. Commun.* **34** (1969) 2249.
2. Prochazka, M., Krestanova, V., Konicek, J. and Smisek, M. *Collection Czech. Chem. Commun.* **35** (1970) 727.
3. Osborne, N. S. and Ginnings, D. C. *J. Res. Natl. Bur. Std.* **39** (1947) 453.
4. McCurdy, K. G. and Laidler, K. L. *Can. J. Chem.* **41** (1963) 1867.
5. Polak, J. and Benson, G. C. *J. Chem. Thermodyn.* **3** (1971) 235.
6. Rossini, F. D., Wagman, D. D., Ewans, W. H., Levine, S. and Jaffe, J. *Selected Values of Chemical Thermodynamic Properties, Circular of National Bureau of Standards 500*, U.S. Government Printing Office, Washington D.C. 1952.
7. Green, J. H. S. *Chem. Ind. (London)* **1960** 1215.
8. Hildebrand, D. L. and McDonald, R. A. *J. Phys. Chem.* **64** (1959) 1521.
9. Wadsö, I. *Acta Chem. Scand.* **20** (1966) 544.
10. Howard, P. B. and Wadsö, I. *Acta Chem. Scand.* **24** (1970) 145.
11. Wadsö, I. *Acta Chem. Scand.* **20** (1966) 536.

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