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An Adiabatic Calorimeter for Measuring Heats of Vaporisation at 25° C

INGEMAR WADSÖ

*Thermochemistry Laboratory *, University of Lund, Sweden*

An adiabatic calorimeter for measuring heats of vaporisation at 25°C has been constructed. It has been designed preferably for compounds having vapour pressures between 1 and 100 mm Hg at 25°C. An adequate amount of substance for each run is 150 mg. The accuracy has been checked by remeasuring some well-known heats of vaporisation. The results indicate an accuracy of 0.5 % or better.

By combustion and reaction calorimetry it is possible to obtain very accurate heat of formation data for most kinds of substances. Unfortunately, there are many thermochemical precision data which at present cannot be used to their full extent, because of a lack of heat of vaporisation data. Calorimetric data have been obtained for many hydrocarbons, but are lacking for other substances, with very few exceptions. As a rule, heats of vaporisation data must be obtained indirectly from vapour pressure measurements by use of Clausius-Clapeyron's equation, or simply from empirical rules [1].

Several types of calorimeters for measuring heats of vaporisation have been described in the literature (see, *e.g.*, Ref.[2]). However, most of them were designed for work at a temperature higher than 25°C, and values obtained have therefore to be recalculated to the standard reference temperature. Also, in all of the methods, it is necessary to use a considerable amount of substance. It was therefore undertaken to design and build a simple but accurate calorimeter for the determination of heats of vaporisation at 25°C, using small amounts of substance.

The apparatus described in the present paper is of a very simple design and requires only *ca* 150 mg of substance per determination. The accuracy is 0.5 % or better, which for most purposes is quite satisfactory. However, the method in its present form is limited to substances having vapour pressures at 25°C in the range 1—100 mm Hg.

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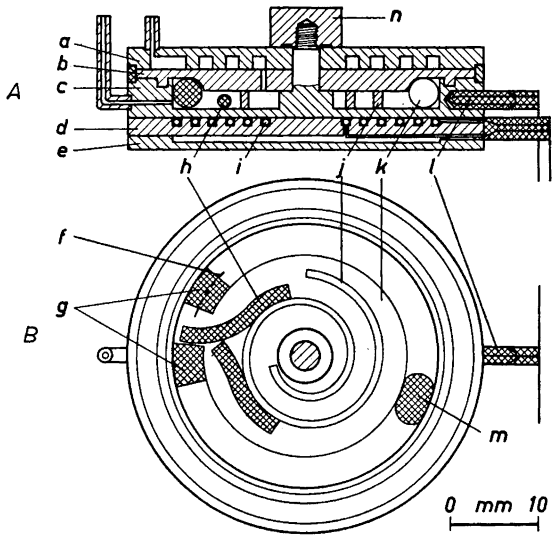

Fig. 1. A. Section through the calorimeter.
B. Disc *c* seen from above. For explanations see the text.

Principle. The evaporation of the substance is caused by a flow of nitrogen kept under reduced pressure *. The heat taken from the calorimeter is compensated electrically in such a way as to keep the temperature of the calorimeter constant and equal to that of the surrounding thermostat. From the amount of substance evaporated, as determined by weighing, and from the amount of supplied electrical energy, the molar heat of vaporisation can be calculated.

Construction. The construction of the calorimeter is shown in Fig. 1. The calorimeter body consists of five gold plated brass discs, *a*—*e*. The liquid substance to be vaporised is introduced into an ampoule placed in the cavity between discs *b* and *c*. The ampoule, *k*, consists of a bent thin-walled teflon tube, inner diameter 4 mm, closed in both ends by silicone rubber stoppers, *g*. One of these stoppers holds a capillary teflon tube, *f*, length 10 mm, inner diameter *ca* 0.3 mm. The ampoule is divided into two parts by means of a silver wool pellet, *m*. At the start of an experiment the liquid is kept between the pellet and the capillary tube, but when the pressure inside the calorimeter is lowered, the liquid will be pressed out from the ampoule and absorbed on glass fibre wicks, *h*.

The carrier gas passes from the gas inlet tube through the evaporation chamber into a spiral groove between discs *a* and *b*. The heat loss accompanying the vaporisation is compensated by electrical energy generated in the heating element *i*, which is a spiralized manganin wire lacquered and nylon spun (resistance 40 Ω), lying in a spiral groove in disc *d*. An air gap between disc

* This "carrier gas technique" has been used previously, *e. g.* by Coon and Daniels [3].

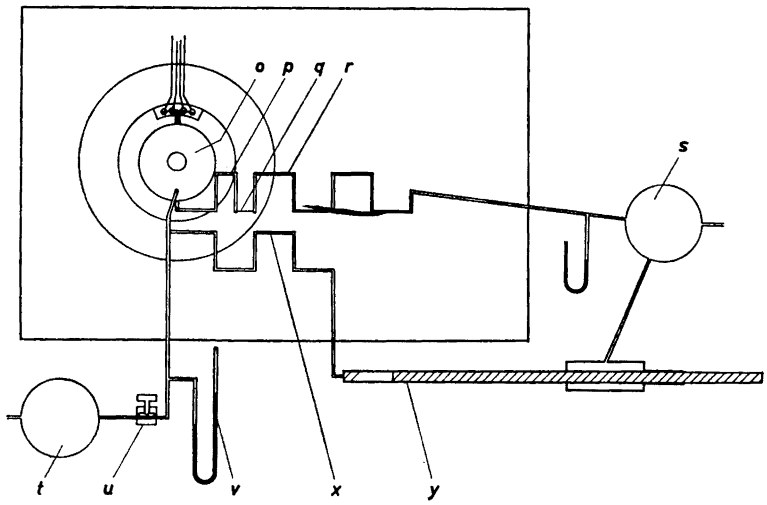

Fig. 2. Schematic view of the calorimetric equipment.

d and the bottom disc *e* prevents the bottom surface from being overheated. The saturated carrier gas is allowed to reach thermal equilibrium in the spiral duct in disc *a* before passing through the outlet tube. To ensure a good thermal contact between the gas mixture and the calorimeter, *ca* 50 mm of the spiral duct is filled by loosely packed silver wool. To improve the thermal conductivity between the discs *b* and *c*, a gold spiral, *j*, is introduced in the evaporation chamber.

A thermistor, *l*, is inserted in a drilled hole in disc *c*. The thermistor was a Stanthel, type F 2311, 2000 Ω, sealed off with a microflame *ca* 5 mm from the top, with subsequent cooling of the thermistor bead. Electrical connections from the thermistor and the heater consist of 0.4 mm platinum wires dipping into mercury cups.

In order to obtain a vacuum tight system silicone rubber gaskets had to be used between discs *a* and *c*, and between the nut *n* and disc *a*.

The calorimeter is placed on three polystyrene pegs inside a chromium plated brass can, fitted with a thin-walled lid. The can is placed in a bigger brass vessel and the space between the two cans is filled by copper chips. The outer can is immersed in a water thermostat kept at 25°C by means of a standard mercury contact thermometer fitted with an electronic relay.

The carrier gas is brought to 25°C by passing it through a copper tube (*r* in Fig. 2) inside the thermostat. In order to keep the gas flow at a suitable rate, the gas is passed through a capillary tube, *q*.

Heat effects due to the expansion of the carrier gas, after having passed the capillary tube, are avoided by allowing the gas to pass through a small silver tube, *p*, in contact with the copper chips between the two cans, before it reaches the calorimeter, *o*.

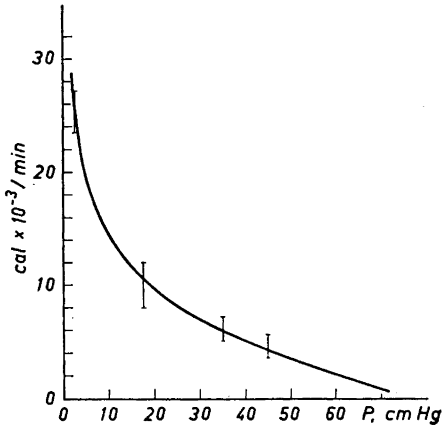

Fig. 3. The "zero" effect *versus* the pressure as shown by the manometer *v*.

By altering the pressure inside the calorimeter the flow of the carrier gas through the capillary tube, and thereby the evaporation rate, is changed. The pressure can be regulated by means of a screw clamp, *u*, and a "leakage valve", *y*. The valve consists of a metal tube and polystyrene rod as shown in Fig. 2. The rod is close fitting but movable to allow variation in the leakage from the nitrogen tank *s* to the vacuum tank *t*. By moving the rod of this valve it is possible to regulate the pressure inside the calorimeter within very small limits. The pressure in the nitrogen tank is kept slightly higher than atmospheric so that no air can reach the calorimeter by leakage through the end of the metal tube.

The temperature of the calorimeter is observed by means of the thermistor which forms one of the arms in a conventional D.C. bridge circuit. A Sullivan Spot Galvanometer (T 2001/D) with sensitivity 0.005 μA/mm, was used as a zero point instrument. The sensitivity corresponded to a temperature change of 0.0002°C, equivalent to a change in energy content of 0.002 cal.

Procedure. The ampoule was charged with *ca* 150 mg of substance and placed in the evaporation chamber. Discs *a* and *b* were fastened to discs *c*, *d* and *e*, by means of the central screw and the nut *n*. A slow stream of nitrogen was forced through the calorimeter in order to remove adsorbed water. The gas inlet and outlet tubes were closed by stoppers and the calorimeter was weighed to the nearest 0.01 mg. After being cooled to a temperature slightly below 25°C, the calorimeter was placed in the thermostat and the two gas tubes were connected to the metal tubes *p* and *x* by means of PVC tubes. The temperature of the calorimeter was raised to that of the thermostat, after which the system was allowed to equilibrate for 15 min. The vaporisation was started by opening the screw clamp *u*. A suitable voltage was applied to the heater, and by regulating the vaporisation with the leakage valve, the temperature of the calorimeter was kept equal to that of the surroundings.

By using a storage battery of high capacity (144 Ah), and by passing the current through a dummy heater circuit for *ca* half an hour before the experiment started, the variation in the current during a run was insignificant.

The current through the heater was determined by measuring the potential drop over a 10 Ω standard resistance in series with the heater, by use of a Rubicon High Precision Type B Potentiometer.

An appropriate time for the evaporation varied between *ca* 10 min for substances having vapour pressures of 100 mm Hg, to *ca* 60 min for substances having vapour pressures of 1 mm Hg. During this time *ca* 100 mg of the substance evaporated.

The experiment was finished by switching off the electrical current and closing the clamp *u*. The calorimeter was then filled with nitrogen to atmospheric pressure and the temperature was adjusted to that of the thermostat by addition of a small amount of electrical energy. The calorimeter was closed by the stoppers and the amount of substance evaporated was determined by reweighing the calorimeter. From the known resistance of the heater, and from the measured current and time, the supplied electrical energy could be calculated.

Zero effect.. When a stream of nitrogen was passed through the calorimeter, furnished with an empty ampoule, a small evolution of heat was observed, which included heat of friction and heat of expansion of the carrier gas. This heat effect could be determined by measuring the speed of the galvanometer spot when passing the zero position. As could be expected, the effect varied with the pressure (as shown by manometer *v*), that is, with the ve-

Table 1. Heats of vaporisation of some hydrocarbons.

Substance	mmoles	Q, cal	q, cal	ΔH_v, kcal/mole
*Cyclo*hexane	1.338	10.601	0.011	7.93
	1.250	9.832	0.010	7.87
	1.081	8.513	0.009	7.88
	1.020	8.087	0.008	7.94
	1.062	8.358	0.010	7.88
			Mean	7.89 ± 0.02
Methyl*cyclo*hexane	1.272	10.689	0.028	8.43
	1.193	9.958	0.026	8.37
	1.145	9.502	0.024	8.32
	1.220	10.334	0.026	8.49
	1.058	8.972	0.024	8.50
			Mean	8.42 ± 0.04
n-Octane	0.9055	8.972	0.038	9.95
	0.8329	8.204	0.035	9.89
	0.7419	7.375	0.031	9.98
	0.7648	7.594	0.031	9.97
	0.6523	6.440	0.038	9.93
			Mean	9.94 ± 0.02
Mesitylene	0.6372	7.050	0.16	11.32
	0.6909	7.676	0.17	11.36
	0.6376	7.074	0.15	11.32
	0.6657	7.406	0.16	11.37
	0.6902	7.748	0.13	11.42
			Mean	11.36 ± 0.04

locity of the nitrogen stream through the calorimeter. In Fig. 3 the mean of this "zero" effect is plotted against the pressure. Each value in the figure is a mean of five to ten separate experiments. The uncertainties, expressed as the standard deviation of the mean, are indicated by the lengths of the vertical lines. The correction due to "zero" effect amounts only to *ca* 0.1 % for compounds having a vapour pressure of 100 mm Hg, but is as much as 2 % for compounds having vapour pressures of 2 mm Hg. Heat effects due to adsorption and wetting of the interior part of the calorimeter are negligible as judged from available data in the literature [4].

The vapour of the substance leaves the calorimeter with a directed velocity and thus has acquired some kinetic energy, which corresponds to a small amount of energy withdrawn from the system. The carrier gas has almost exactly the same kinetic energy when entering the calorimeter as when leaving it, and can thus be left out of consideration. The kinetic energy of the vapour can easily be estimated. The vapour velocity is calculated to be less than 5 m per sec, and thus the correction must be in the order of 10^{-4} cal, which is insignificant.

The accuracy of the method seems mainly to be limited by the uncertainty in the weight determinations and in the "zero" effect experiments. The ampoule technique worked satisfactorily; before the experiment the weight of the calorimeter was found to be constant. After a run, however, a small vapour leakage was observed for compounds having high vapour pressures. By graphical extrapolation over the short time between the finish of the experiment and the weighing, this error could be corrected for. Corrections applied were always less than 0.2 %.

The weight difference has to be corrected in order to obtain a value of the true mass evaporated. Therefore, it is necessary to consider the amount of nitrogen replaced by the ampoule content before the experiment, and by the remaining liquid and its vapour after the experiment. As the total cavity of the calorimeter is as small as 1.5 ml, these corrections are quite small, being 0.4 % for compounds having vapour pressures in the order of 100 mm Hg.

The "carrier gas technique" makes it possible to control the speed of the vaporisation accurately and in a very simple manner. Attempts to work without carrier gas were not successful as no constant rate of vaporisation could be obtained.

The apparatus, in the simple design described here, seems to be unsuitable for compounds having vapour pressures lower than 1 mm Hg. These demand either a long time of evaporation, in which case errors from the lack of adiabatic conditions will be very significant, or a high gas velocity, in which case the results will be strongly influenced by a high uncertainty in the "zero" effect.

The calorimeter has been tested on four hydrocarbons. Each compound was purified by fractional distillation through a 25-plate column until the purity, as judged by gas chromatographic analysis (Pye Argon Chromatograph), was better than 99.5 %. The results * of the measurements are given in Table 1.

* Uncertainties are given as the standard deviation of the mean. Uncertainties due to the "zero" effect are included.

The following symbols have been used:

Q electrical energy supplied
q amount of energy due to the "zero" effect
ΔH_v heat of vaporisation at 25°C

As seen in Table 2, the results obtained in this work, are in very good agreement with accurate values found in the literature [5]. The method seems therefore, not to be impaired by any significant systematic errors.

Table 2. Comparison between literature data and values obtained in this work.

Compound	Vapour pressure in mm Hg at 25°C	ΔH_v, kcal/mole	
		Ref [5]	This work
*Cyclo*hexane	96	7.89_5	7.89 ± 0.02
Methyl*cyclo*hexane	45	8.45_1	8.42 ± 0.04
n-Octane	14	9.91_5	9.94 ± 0.02
Mesitylene	2.5	11.34_5	11.36 ± 0.04

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