

A Heat of Vaporization Calorimeter for Work at 25°C and for Small Amounts of Substances

INGEMAR WADSÖ

Thermochemistry Laboratory, University of Lund, Lund, Sweden*

An accurate heat of vaporization calorimeter designed for work at 25°C and for liquid compounds in the vapor pressure range 0.5–200 mm Hg (25°C) is described. An adequate amount of substance for each run is about 100 mg and the time required for a complete experiment is usually less than 45 min. The calorimeter has been tested on a number of hydrocarbons, carbon tetrachloride, and water. The results indicate an accuracy of $\geq \pm 0.02$ kcal/mole.

By modern combustion and reaction calorimetric methods it is possible to obtain accurate heat of formation data for most kinds of substances. When using these enthalpy values it is very often essential to have heat of vaporization (ΔH_v) data available which will make it possible to consider the thermochemical properties in the gaseous state. There is also an obvious direct interest in this type of data. For pure compounds as well as for compounds in solution,** ΔH_v data are expressions for the intermolecular binding properties in the actual condensed states.

Very few accurate heat of vaporization data are available, however, at the present time, especially at the standard temperature of 25°C. It is thus quite a common situation that accurate combustion or reaction calorimetric data have to be combined with rather crude ΔH_v data, usually arrived at from vapor pressure measurements at different temperatures or simply by employing more or less empirical rules.

Several types of vaporization calorimeters have been described in the literature but most of them were designed for work at temperatures higher than 25°C and they usually require a considerable amount of substance. To meet a specific need in connection with reaction calorimetric work a simple vaporization calorimeter was built and tested a few years ago.¹ The calori-

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** ΔH_v for a compound in solution (= –heat of solvation, $-\Delta H_{\text{sol}v}$) is preferably obtained by a combination of heats of vaporization and heats of solution ($\Delta H_{\text{sol}a}$): $\Delta H_{\text{sol}v} = \Delta H_{\text{sol}a} - \Delta H_v$.

meter was designed for small amounts of substance, *ca.* 150 mg per run, and was preferably suited for work at room temperature and for liquid compounds having vapor pressures in the range 1–100 mm Hg at 25°C. The apparatus has since been used for a number of measurements in connection with combustion and reaction calorimetric work at this laboratory. During the course of that work some drawbacks attached to the apparatus were revealed which called for changes in the construction. Among the imperfections which gradually appeared can be mentioned corrosion effects, tendency to gas leakage, sensitivity to mechanical abrasion and rather irregular "zero effect" (heat effect in connection with the carrier gas flow).

In this paper a calorimeter construction is described which has been gradually developed out of the apparatus described in Ref. 1. The precision working range has been extended to compounds with vapor pressures (at 25°C) ranging from 0.5–200 mm Hg. The precision and the dependability have been improved.

DESCRIPTION OF THE CALORIMETER

Principle. The principle of the present construction is essentially the same as for the prototype.¹ Heat absorbed by the substance during the evaporation process 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 (determined by weighing the calorimeter before and after the experiments) and from the measured amount of supplied electrical energy, the heat of vaporization can be calculated. In order to achieve smooth evaporation a small amount of carrier gas (nitrogen) is leaked into the system through a capillary tube.

Construction. Although the principle of the calorimeter remains unchanged the actual construction is quite different compared to the earlier design. No ampoule technique is used and the disc construction has been abandoned in favour of a construction without any loose parts, which will guarantee a regular performance as well as a low sensitivity to mechanical abrasion. All parts exposed to the investigated substance are of silver.

In the present design as well as for the preceding models it has proved necessary to have a minor flow of carrier gas through the calorimeter in order

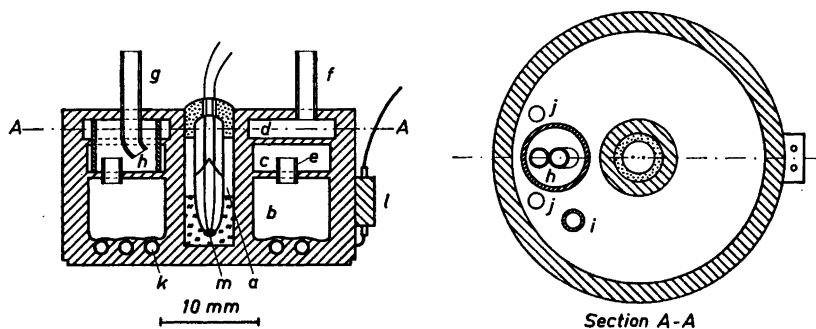


Fig. 1. Construction of the calorimeter.

to avoid irregular boiling phenomena. The rate of flow of the carrier gas is controlled by a capillary tube.

The calorimeter construction is shown in Fig. 1. The calorimeter body is made up of a hollow cylindrical silver vessel containing a central bore, *a*, and a cavity divided into three compartments (*b*, *c*, *d*) by means of two 0.6 mm silver plates soldered to the calorimeter body. Compartment *b*, which is the evaporation chamber, is in contact with the cavities *c* and *d* by means of a short silver tube, *e*, and two holes (*j* in Fig. 1 b). From *d* there is a gas outlet tube, *f*. Carrier gas is introduced into the evaporation chamber, *b*, through gas inlet tube, *g*, via the back suction trap, *h*. Substance is filled into the evaporation chamber through the tube, *i*. (Fig. 1 b).

In the bottom of the calorimeter there is a flat spiral, *k*, formed from a thin-walled steel tube which contains a manganin heating element (0.1 mm, 50 Ω). The spiral tube is covered by a thin layer of low-melting silver alloy ("Castolin") which is silver-plated. The manganin wire is soldered to 0.4 mm copper wires (the joints are kept inside the steel tube) which lead to the contact, *l*. The central bore, *a*, contains a thermistor, *m*, (Victory 32A47, 2 k Ω) with the bead kept in paraffin oil. The top of the thermistor is sealed to the metal by means of epoxy resin (Araldite).

Fig. 2 shows the calorimeter placed in a chromium-plated brass can forming the calorimeter jacket. The can is placed in a water thermostat, 25.00°C, where the temperature variation is kept lower than 10⁻³°C. The calorimeter is supported by a thin-walled lucite ring. The thermostated carrier gas coming from the copper tube, *n*, passes through a glass capillary tube, *o*, before entering the calorimeter. Short 2 mm PVC tubes are used as connections between the different metal and glass tubes. Soft spun, insulated copper wires from the heater and from the thermistor are connected to the energy supply circuit and Wheatstone bridge, respectively, over the screw contact, *q*. Above the calorimeter there are two lid constructions made from 0.2 mm aluminium foil. The jacket can is covered by a lid made from a 20 mm polystyrene foam.

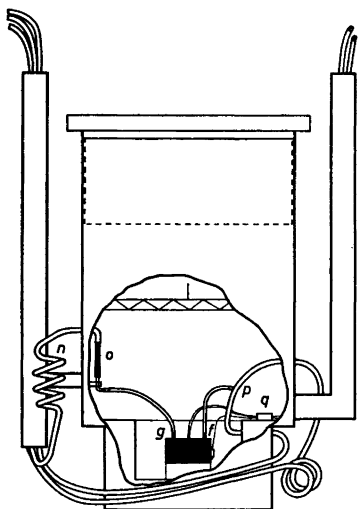


Fig. 2. The calorimeter placed in a metal can which is submerged in a water thermostat.

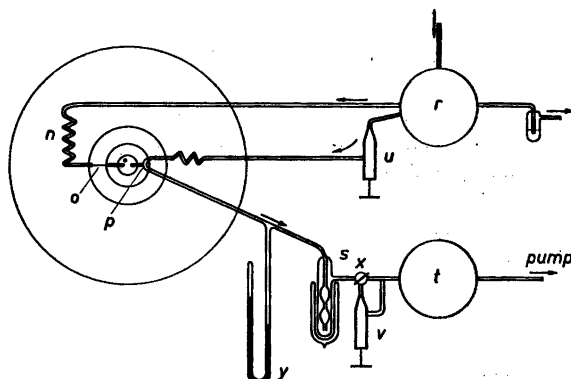


Fig. 3. Schematic view of the calorimetric assembly.

Fig. 3 shows a schematic view of the calorimetric assembly. Carrier gas from the nitrogen tank, *r*, (pressure 1 atm.) is thermostated in the copper tube, *n*, before entering the capillary tube, *o*. The gas passes the calorimeter, the T-junction, *p*, a cooling trap, *s*, and is finally taken up by the vacuum system, *t*. The rate of evaporation is governed by the vacuum maintained in the calorimeter but also by the bore of the capillary tube, *o*: Low pressure and a large capillary will promote a high evaporation rate. With a given capillary tube the rate of evaporation can be controlled by adjusting the calorimeter pressure. Pressure, as measured by the manometer, *y*, ranges from 400–10 mm Hg. This is achieved by allowing a suitable leakage of nitrogen through the needle valve, *u*, to the vacuum system, *t*. It was found suitable to use two capillary tubes of different bores. The tubes can be characterized by the nitrogen flow rate at a certain pressure difference (100 mm Hg). For the more volatile compounds (vapor pressures down to *ca.* 15 mm Hg) a narrow capillary tube with a flow rate of about 0.15 ml/min (atm. pressure) was employed. For less volatile compounds a capillary tube with a flow rate of about 3 ml/min. was used. Neither the bore of the capillary tube nor the rate of evaporation is critical (*cf.* below, *corrections*).

An adequate rate of vaporization for compounds having very high vapor pressures (above *ca.* 150 mm Hg) was obtained by reducing the suction capacity of the vacuum system by means of the needle valve, *v*.

The temperature of the calorimeter is observed by means of the thermistor which forms one of the arms in a conventional DC Wheatstone bridge. Current through the thermistor is kept at 0.2 mA. A Sullivan Spot Galvanometer (T 2005/M) with a sensitivity of 600 mm/ μ A is used as a null detector. This sensitivity corresponds to a temperature change of $1.5 \times 10^{-4} \text{ }^\circ\text{C}$ or a change in the energy content of the calorimeter equal to 6×10^{-4} cal.

Procedure. Before the start of an experiment the calorimeter was evacuated for 15 min (the calorimeter was connected to the capillary tube and to the vacuum system. Needle valve, *v*, was closed). The calorimeter was charged with 50–150 mg of substance. A slow stream of nitrogen was then passed through the calorimeter for about 10 sec in order to secure saturated vapor in the entire calorimeter.

After weighing, (all three silver tubes extending from the calorimeter were closed by PVC caps) the calorimeter was placed in the jacket can and connected to the gas tubes. The temperature of the calorimeter was adjusted to that of the thermostat and the system was left for 15 min.

The vaporization was started by connecting the vacuum system, *t*, to the calorimeter 3-way stopcock, *x*, and applying a suitable constant voltage over the heater. By regulating the needle valve, *v*, the temperature of the calorimeter was kept constant (and equal to that of the thermostat). The evaporation time was usually taken to about 15 min. The electrical energy supplied to the heater was determined by measuring current and time and using a predetermined heater resistance value. (The resistance value of the heater was not significantly affected by the heat effect during an experiment.)

The experiments were continued until about 75 % of the substance was evaporated. Electrical current was switched off and the stopcock, *x*, was closed. The calorimeter and the tube system were allowed to be filled with nitrogen (partly through the capillary tube but mainly through the needle valve, *u*) and small additional amounts of electrical energy were supplied to the calorimeter in order to reach the starting temperature. The calorimeter was disconnected, the gas tubes closed by stoppers, and the amount of substance evaporated determined by weighing.

Corrections. A few corrections have to be added to the obtained vaporization value.

1. When carrier gas is passed through the calorimeter at its equilibrium temperature, a small cooling effect is observed. This effect is believed to be due to the sum of several factors (working in both directions): gas expansion after the capillary tube, gas friction inside the calorimeter and an equilibrium temperature of the calorimeter (= the temperature at which the experiments were performed) which was slightly higher, about 7×10^{-3} °C, than of the surroundings due to the heat effect from the thermistor current. As could be expected, this "zero effect" varied with the pressure and with the bore of the capillary tube. The correction due to this zero effect was in all cases small; its influence on the ΔH_v value was 0—40 cal/mole (see Table 1). In the calorimeter described earlier¹ the observed effect was of opposite sign and considerably larger.

2. In the earlier construction the ampoule technique ensured negligible evaporation during the equilibration time between the weighing procedure and the start of the experiments. In the present design a small amount of substance was lost before and after the evaporation experiment. This undesirable substance loss occurred mainly during connection and disconnection of the calorimeter to the gas tube system. For each substance, one or more separate control experiments were undertaken. In these, the charged calorimeter was weighed, connected to the tube system, left for a 15 min equilibration period, disconnected, and then reweighed. The weight loss varied with the vapor pressure of the substance as well as with the type of substance. As the leakage effects are small (except for very volatile substances; see Table 1), and the reproducibilities in the control experiments satisfactory, these corrections do not usually affect the accuracy in the determinations.

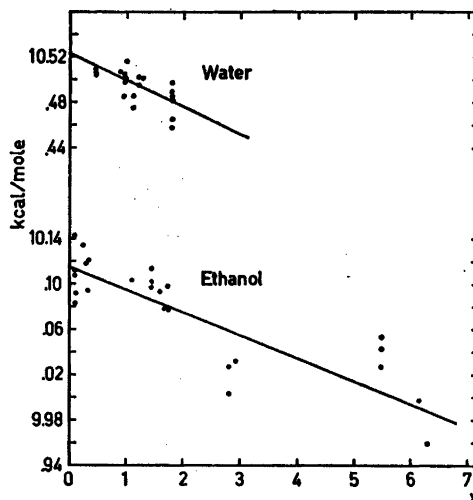


Fig. 4. Determination of heats of vaporization (kcal/mole) for water and ethanol performed at different ratios mole carrier gas/mole evaporated substance (x). (The heat of vaporization value for ethanol given in the following paper is not an extrapolated value but is the mean of the determinations performed at $x < 0.3$.)

3. When, at the end of an experiment, the pressure inside the calorimeter is raised to atmospheric pressure, most of the carrier gas will enter the calorimeter through the gas outlet tube (f , Fig. 1). Unless a sufficient amount of substance is present in compartments c and d at the end of the experiment the gas phase will be unsaturated and will accordingly have a density different from that at the start of the experiment. When correcting for this gas phase density difference it was assumed that at the end of an experiment compartment d (0.8 ml) contained pure nitrogen whereas compartment c was believed to contain enough substance (mainly brought there as droplets by the carrier gas *) to provide a gas phase density identical with that at the start of the experiment.

4. It has been noted that for some compounds (especially the lower alcohols and water) a comparatively high ratio carrier gas/evaporated substance resulted in slightly low values. For some compounds, *e.g.* the hydrocarbons, no such effect could be observed. Assuming that the presence of carrier gas will somehow affect the measurements the ΔH_v values obtained should be extrapolated to a zero ratio value. As an example, measurements on water and ethanol performed at different ratios ($= x$) are recorded in Fig. 4.

It has been found that it is possible to perform the measurements at such a low ratio carrier gas/evaporated substance that an extrapolation procedure will not be necessary. However, as the origin of the observed ratio-effect is unknown (*cf. Discussion*) experiments are frequently run at several ratio values.

TESTING OF THE APPARATUS

The calorimeter has been extensively tested on a number of hydrocarbons, on carbon tetrachloride and on water, all compounds having well established ΔH_v data at 25°C.

* This is in agreement with experiences from earlier constructions where compartments corresponding to c were accessible for inspection.

The hydrocarbons (of commercial puriss. grades) were purified by treatment with sulphuric acid,² followed by repeated fractional distillation through a 25-plate column. Carbon tetrachloride (Merck *p.a.*) was further purified by distillation. As judged by gas chromatography (Pye Argon Chromatograph, Apiezon column) the purities of the hydrocarbons and of carbon tetrachloride were better than 99.9 %. Freshly glass distilled water was used.

Results from the test experiments are given in Table 1 and Fig. 4 and are expressed in units of the defined calorie (1 cal = 4.1840 J) and the true mass. Measurements refer to the isothermal (25.00°C) process liquid → vapor at saturation pressure.

DISCUSSION

The simple hydrocarbons with their well-known heats of vaporization are at present the obvious choice as "general test substances" in vaporization calorimetry. Inspection of Table 1 shows that hydrocarbons with vapor pressures at 25°C ranging from 0.4 to 190 mm Hg have been tested and that results are in excellent agreement with the literature data. In separate experiments it was shown that a tenfold change in vaporization rate (caused by change in pressure or capillary size) did not significantly change the obtained values. Outside the vapor pressure range covered by these compounds the precision of the calorimeter will rapidly decrease, although it is believed that for many purposes acceptable results can be obtained. At higher vapor pressures evaporation effects in the fore- and after-periods will increasingly interfere. For compounds with pressures lower than about 0.5 mm Hg the rate of evaporation attainable will be undesirably low.

Carbon tetrachloride was chosen as a test substance because of its high gas density. (*cf. corrections*, 2 and 3). As seen from Table 1 the result agrees with the well verified literature value.

Table 1.

Substance	Vapor pressure at 25°C, mm Hg	Evaporation time, min.	Mean values for			Number of experiments	± σ cal/mole	ΔH_v , cal/mole		
			Amount of substance evaporated mg	Correction terms				This work	Literature	
				zero effect cal/mole	leakage mg					gas density mg
3-Methylpentane	189.8	12	140	0	1.3	0.48	6	8	7 216	7 235 ^a
Cyclohexane	97.5	15	140	13	0.7	0.22	6	5	7 886	7 895 ^a
Methylcyclohexane	46.3	15	130	11	0.7	0.14	5	7	8 452	8 451 ^a
Octane	14.0	15	90	17	0.3	0.05	7	8	9 919	9 915 ^a
Decane	1.4	15	60	31	0	0	9	17	12 272	12 276 ^a
Undecane	0.4	30	40	38	0	0	6	20	13 488	13 464 ^a
Carbon tetrachloride	109.6	13	310	8	1.4	0.60	7	6	7 752	7 746 ^b
Water	23.8	20	100	0	0	0	23	—	10 521 ^c	10 514 ^d

^a Literature values for the hydrocarbons are the API values.³

^b Hildenbrand and McDonald.⁴

^c Obtained by extrapolation to zero ratio mole carrier gas/mole evaporated substance; *cf.* Fig. 4. Mean value for all determinations is 10.493 cal/mole. ^d Ref. 5.

Water has an accurately known ΔH_v value at 25°C and is a compound with extreme properties in contrast to the hydrocarbons which here makes it to a desirable test object.

The heat of vaporization value given for water was obtained by linear extrapolation (method of least squares) to zero value for the ratio carrier gas/evaporated substance (*cf. corrections*, 4, and Fig. 4). As seen from Fig. 4 the extrapolation correction for water is very small and hardly significant compared to the values measured at a low ratio value. The heat of vaporization value for water obtained is in very good agreement with the accepted literature value.

No explanation can at present be given for the origin of the ratio-effect. It has so far been most marked for highly associated compounds (to some extent being associated also in the gaseous phase) like water and the lower alcohols, but the effect is in opposite direction to what might possibly be expected: At a high carrier gas flow the vaporization process might proceed at such a rate that a significantly unsaturated vapor was obtained. Such an effect, however, would result in a less associated vapor which should give a too high vaporization value. Actually a too low value is obtained. For water (as well as for methanol and ethanol) identical results were obtained if argon was used as carrier gas instead of nitrogen.

Beyond the experiments on water and alcohols the ratio-effect has been looked for in measurements with hydrocarbons, esters, bromides, amines, and ketones but in no case has such a marked ratio dependency as for the lower alcohols and water been noted.

As judged from the test experiments the precision of the described calorimeter is ≥ 20 cal/mole for compounds in the vapor pressure range investigated. The method seems to be free from significant systematic errors.

A comment on vaporization calorimetry. During the course of this work it has repeatedly been found that it is comparatively easy to obtain very reproducible results in vaporization calorimetry. Our experience is, however, that systematic errors with an origin often hard to explain can equally easily be introduced. As in other types of calorimetry an extensive use of test substances is the superior guard against these types of errors.

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