

MICRO CONDUCTION CALORIMETERS TO MEASURE ENTHALPIES OF VAPORIZATION

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ABSTRACT

Details of the construction of micro-conduction calorimeters for measuring enthalpies of vaporization (or sublimation) are described. Accuracy and precision of the calorimeters were tested by the use of a few standard reference compounds. Experimental results showed that the enthalpies of vaporization could be measured for compounds of vapor pressures of 10 Pa to 10 kPa at 298 K with uncertainty less than 0.2 per cent. Results of enthalpy of vaporization measurements for some compounds are also given. Since calorimetric cells of these calorimeters were composed of glass and PTFE, the calorimeters made it possible to measure the enthalpies of vaporization for metal corrosive compounds.

INTRODUCTION

Enthalpy of vaporization (or sublimation) of a compound is one of the most important properties in thermochemistry, because thermochemical properties of the compound at the ideal gas state is always obtained by combining the enthalpy of vaporization value with other thermochemical quantities.

For example, since the standard enthalpy of formation of a compound in the condensed state contains both chemical binding forces within the molecule and the forces between molecules, if we want to discuss about the chemical binding forces alone, it is necessary to eliminate the intermolecular forces from the considerations. In order to arrive at our purpose, the standard enthalpy of formation of the compound at the condensed state must be transformed into that at the hypothetical ideal gas state, wherein no intermolecular forces exist, by the use of its enthalpy of vaporization value.

As other examples of the use of enthalpy of vaporization, there are practical calculations of the enthalpy changes for gas phase reactions, based on the reaction enthalpies at the condensed phase at 298 K, and evaluations of the solvation enthalpies of liquid (or solid) solutes into the solvents.

Although number of attractive compounds for chemists has progressively increased, owing to the difficulties of their synthetic procedures or to their high price, quantity of each compound being available for the measurements seems to be limited. On the contrary, if an apparatus demands a large amount of samples at a time, it is not so easy task to obtain such amount of pure compound to fit for the measurements. Therefore, it is desired to reduce mass of the samples required for the measurements as small as possible.

Many kinds of vaporization calorimeters have been reported (ref.1,2). Among them only a few ones can be operated by the use of a small amount of samples less than 1 g. For example, Wadsó's calorimeter needs 40 to 200 mg samples for a single run (ref.3), and Morawetz's calorimeter requires less than 100 mg samples for the whole runs (ref.4). An isothermal twin micro-calorimeter designed by Sunner et al demands about 10 mg samples for each run (ref.5).

In most of these calorimeters, calorimetric cells are made of metals to attain rapid thermal equilibrium. However, the use of metals as the construction elements of the cells is occasionally inadequate, because metals may decompose unstable compounds to be measured, and may be attacked by corrosive compounds. If these decomposition of the samples or corrosion of the cells take place, it leads to errors into the final calorimetric results.

As another source of error brought into the experimental results, there is a surface condition of the cells. If the surface of a cell is in different conditions before and after the evaporation process, it leads to errors in mass of the samples being evaporated, as long as the mass is measured by differential weighings. These fluctuations of masses of the cell have often been observed in high humid seasons in Japan. Therefore, it is desired to reduce the quotient (surface area of the cell)/(mass of the sample to be evaporated) to eliminate error induced by the surface conditions of the cell.

In contrast with an isothermal or an adiabatic calorimeter, a conduction calorimeter makes it possible to use poor thermal conductivity materials as the construction elements of the cells, because time constant of the calorimeter is relatively large, and because heat capacities of the cells do not, at least in principle, give any influences on the final heat effects.

Considering these conditions, two kinds of twin micro-conduction calorimeters (I and II) to measure the enthalpies of vaporization (or sublimation) were constructed. Essential part of Calorimeter I was the same as that of LKB-2107 adsorption calorimeter (ref.6). For the calorimeter, two types of evaporation cells were designed by the use of greaseless glass stopcocks. As the surface areas of the cells were evaluated to be about 50 cm², an attempt was made to reduce their surface areas, and Calorimeter II was designed to be adopted for the small cells.

In this paper, details of the construction of these calorimeters are described and results of calibration and test experiments using some standard reference compounds are given.

1. CALORIMETER I

Main part of Calorimeter I is similar to that of an adsorption calorimeter designed previously (ref.6).

1.1 Calibration Heater

As a calibration heater, Nikrothal LX wire (Kanthal AB, 0.09 mm in diameter

and 50 cm in length) was used. At both ends of the wire, copper current leads (0.15 mm in diameter and 12 cm in length) were soldered on. The heater wire was wound non-inductively onto a silver bobbin which was made to fit the central hole of the aluminium plate of the calorimetric unit.

To make the wiring of current and potential leads of the calibration heater, furnished inside the calorimetric unit, following assumptions are made:

- 1) heats evolved in the current leads on the aluminum plate would completely transfer into the plate,
- 2) a half of heats evolved along the current leads lying between the aluminum plate and terminals, to which the leading wires were connected, would flow into the plate and the rest would conduct to the heat sink via terminals,
- 3) heats flowing from the plate to the heat sink through the leading wires can be ignored compared with the heats conducting through thermopiles.

According to these assumptions, the current leads which came from the bobbin were tightly cemented onto the surface of the plate until they left it. To either current lead, another copper wire of smaller diameter (0.05 mm), used as a potential leads, was connected at the point where the current lead just left the aluminum plate. Other ends of these three wires were respectively soldered onto the terminals which had been fastened on the heat sink with good thermal contact. The fourth copper wire (0.15 mm), used as the other potential lead, was soldered on the terminal to which another current lead had been joined.

To obtain effective resistance of the calibration heater, current leads were connected to a 100 Ω standard resistor (YEW, 2972, inaccuracy $\pm 0.01\%$) in series, and potential drops across the heater and the resistor were compared by the use of a potentiometer (YEW, 2722, inaccuracy $\pm 0.05\%$) streaming various currents less than 10 mA. Thus, the effective resistance of the calibration heater for calorimetric unit 1, for example, was found to be 100.493 Ω .

Since the resistance of the copper leading wires that had to be included into the effective resistance of the calibration heater was found to be 0.130 Ω at 295 K, the overall temperature coefficient of the heater resistance was calculated to be $+0.18 \text{ m}\Omega \cdot \text{K}^{-1}$, or 18×10^{-6} part per Kelvin, where the temperature coefficients of copper and Nikrothal were taken to be $+4.3 \times 10^{-3}$ and $-4 \times 10^{-6} \text{ K}^{-1}$, resp. Under usual experimental conditions, therefore, variation of the effective resistance of the calibration heater caused by the change of temperatures was not taken into consideration.

1.2 Calorimetric Cell

Two types of calorimetric cells were designed for Calorimeter I as shown in Fig. 1. Both cells were made of an L-shaped greaseless glass stopcock POR/5/RA supplied from Young Co. U. K. The stopcock can be closed at the throat by PTFE O-ring seals mounted on a plug rod which moves vertically without rotation by the screw knob turning.

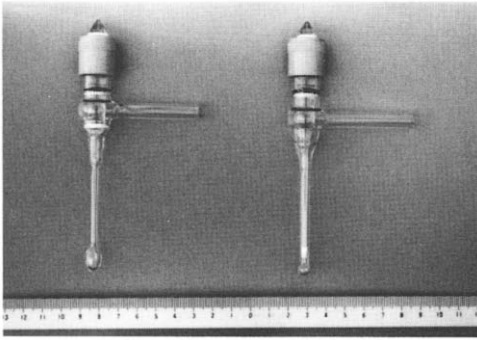


Fig. 1. Calorimetric cells for Calorimeter I. Left: Cell A, right: Cell B

One of the glass tubes aligned axially with the plug rod was replaced with a thin tube of smaller diameter, and its end was bulged to be used as an evaporation chamber.

Cell A consisted of the stopcock without its closing elements improved, and the evaporation chamber could be closed by the lowest O-ring on the plug rod. As Cell A was designed so that its closing elements was situated at the outside of the heat sensible part of the calorimetric unit, when it was installed into the calorimeter, only small part of the heats produced by the stop plug operation would transfer to the calorimetric unit. Experimental results showed that the heat effects caused by each opening and closing the stop plug were less than -0.3 and $+0.3$ mJ, respectively. Since these heat effects were small enough compared with the heats of vaporization measured under the usual experimental conditions (10-20J), and since they were cancelled each other in each evaporation procedure, the effects were not to count into the correction for the observed heat of vaporization values.

When Cell A was used for the measurements of high vapor pressure compounds, it was observed that a part of the sample vapor condensed on the inside wall of the cell which was situated at the outside of the heat sensible part of the calorimetric unit during thermal equilibration, because samples were always confined in an air free space as shown below. For such compounds, therefore, Cell B was employed in spite of some larger heat effects caused by the stop plug operation.

Cell B was made of the same stopcock as that for Cell A, but a little larger bore tube was fused to make an evaporation chamber. The evaporation chamber was made so that the end of the tube was little bulged, and the neck of the bulb was

shrunk to fit with a stop plug. A small glass rod being capable of inserting into the tube without any contact was fused to the end of the plug rod, and the other end was knotted to fasten a small PTFE tip used as a stop plug of the evaporation chamber.

When Cell B was installed into the calorimeter, since the closing elements of the evaporation chamber was completely entered into the hole of the calorimetric unit, all of heats produced by the stop plug operations would transfer to the calorimeter. As it was expected that heat effects detected by the calorimeter possibly vary according to the initial extent of closing the stop plug, care was taken that the screw knob was always turned to the same extent after the tip just touched upon the neck of the evaporation chamber. The heat effects thus detected were found to be -15.1 and $+20.1$ mJ for each opening and closing the stop plug, respectively, and their arithmetic sums were added to the observed enthalpy values for corrections.

1.3 Recorder and Integrator

Output signals from each calorimetric unit were connected to an opposite direction, and the differential signals were supplied to a recorder (Hitachi, QPD-54). The non-linearity of the recorder was tested by reading the traces of the pen deflections supplying various potentials from the potentiometer (YEW, 2722) calibrated against a Weston standard cell (Shimadzu, CSC-1, inaccuracy ± 50 μ V). Experimental results showed that its non-linearity did not exceed ± 0.1 %.

Areas under the voltage-time curves were integrated as a function of time by the use of a ball and disk integrator (Disk Instruments, 245-D) equipped on the recorder, and the areas were expressed as the number of counts, α , of the integrator. The linearity of the voltage-time products against α was examined by supplying several potentials for various time intervals to the recorder. However, no deviation exceeding the non-linearity of the recorder was observed.

2.4 Time Interval Measurements

Time intervals streaming the electric currents to the calibration heater were measured by an electronic digital stop-watch (Seiko, S-023) calibrated against JJY. Inaccuracy of the watch was found to be less than 2×10^{-6} part per second.

An electric contact of the watch, used for starting and stopping, was connected to the relay which could be activated in an instant through a double-pole double-throw switch. One of the two poles of the switch was used for switching the current from the dummy resistor (100.481Ω) to the calibration heater and vice versa, and the other was used to activate the relay. The switch was operated manually, and the time intervals streaming the currents to the calibration heater could be measured at the same time. The schematic diagram of the circuit is shown in Fig. 2.

In this type of the relay circuit it is possible to exist time lag in switching between the current switching from the dummy resistor to the calibration

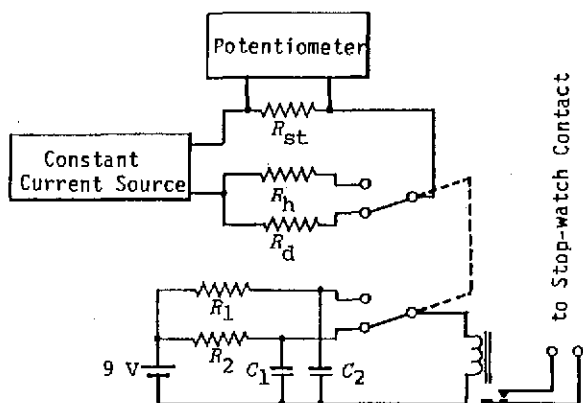


Fig. 2. Schematic diagram of switching circuit. R_{st} : standard resistor; R_h : calibration heater; R_d : dummy resistor; R_1, R_2 : 10 k Ω ; C_1, C_2 : 33 μ F.

heater and the contact making to start the stop-watch, and vice versa. However, synchroscope observation showed that there was only a time lag less than 5 ms.

1.5 Determination of Calorimeter Constants

The calorimeter constants, ϵ , is defined as the electrical energy supplied to the calibration heater divided by the area under the voltage-time curve. To obtain the ϵ values, either cell was installed into the calorimetric unit, and its side tube was connected to a high vacuum system by the aid of a screw-cap joint with a PTFE insert (Young Co., DSY/O/1). After the cell was completely evacuated, the plug of the evaporation chamber was closed, then the whole calorimeter system was left until it attained to thermal equilibrium.

When the equilibrium was established, the electric current was streamed to the calibration heater for desired durations, and voltage signals from the thermopiles were recorded and integrated as a function of time.

Table 1 shows ϵ values obtained for the respective cells installed in the same calorimetric unit, as examples. For both cells, almost the same ϵ values were obtained. But, the fact that Cell B gave a little larger ϵ values than Cell A is attributed to the heat losses caused by the heat conduction through a thick glass wall and plug rod of Cell B.

2. CALORIMETER II

Calorimeter II was designed so that the calorimetric cell could have as small surface area and light weight as possible. In order to stabilize the calorimeter rapidly, it was also designed so that the whole calorimeter could be immersed in a water thermostat controlled ± 0.2 mK. Water in the thermostat was strongly stirred to reduce the thermal resistance of the liquid layer formed on the surface of the heat sink. Absolute inaccuracy of thermostat temperature, determined by a calibrated Pt-resistance thermometer (Tinsley, 51875A) was found to be ± 5 mK.

TABLE 1. Examples of calibration constant determinations for Calorimeter I

i/mA	t/s	E_{el}/J	S/α	$E_{\text{el}} \cdot S^{-1} / \text{mJ} \cdot \alpha^{-1}$
Cell A				
4.6007	1800.0	3.8287	129.021	29.675
4.6007	3600.1	7.6577	258.104	29.669
4.6007	4500.2	9.6721	322.533	29.678
8.6113	899.9	6.7065	255.933	29.676
8.6114	1200.1	8.9434	301.419	29.671
8.6113	1800.1	13.4137	451.883	29.684
11.4845	900.0	11.9290	401.826	29.687
11.4843	1200.0	15.9048	535.950	29.676
$\epsilon = (29.677 \pm 0.006) \text{mJ} \cdot \alpha^{-1}$				
Cell B				
10.0883	900.1	9.2057	310.014	29.695
10.0981	900.0	9.2226	310.626	29.690
10.0968	960.1	9.8360	331.342	29.685
10.0771	1800.0	18.3686	618.532	29.697
$\epsilon = (29.691 \pm 0.005) \text{mJ} \cdot \alpha^{-1}$				
$R_h = 100.493 \Omega$				

2.1 Calorimetric Unit

The calorimetric unit was composed of a central block, four pieces of thermo-modules, and two heat conduction blocks. The central block was machined from a square aluminum rod to be a size of $12 \times 15 \times 30 \text{ mm}^3$. At the center of a $12 \times 30 \text{ mm}^2$ surface, a 11 mm hole was drilled in 10 mm depth by the use of an end-mill to be a flat bottom.

Two pieces of thermo-modules (Marlow Industries, MI-1023) were slightly greased and were stuck on each $15 \times 30 \text{ mm}^2$ surface of the central block. Then, the block and thermo-modules were sandwiched with heat conduction blocks (made of copper, 20 mm in height), to assemble a calorimetric unit. Two sets of the units were symmetrically placed on the top surface of a copper column (60 mm in diameter and 60 mm in height), used as a heat sink, to sit the hole of the aluminum block upwards. Another copper column of similar size was placed on the units, and both columns were screwed so as to coincide their axes and to contact them with the heat conduction blocks tightly. Then, both heat sinks were covered with a copper sleeve to keep the heat sinks in good thermal contact and water tight.

2.2 Calibration Heater

A calibration heater, made of Nikrothal LX wire (0.05 mm), was settled in the double spiral grooves formed on a silver disk (11 mm in diameter and 0.8 mm in thickness). The disk was pressed into the central hole of the aluminum block backwards. In the wiring of the current and potential leads of the calibration heater, the same assumptions were made as those for Calorimeter I.

2.3 Calorimetric Cell

Calorimetric cells were made of a glass tube of 5 mm outer diameter by means

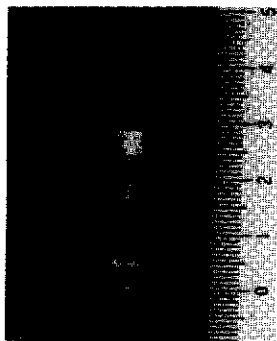


Fig. 3 Calorimetric cell for Calorimeter II

of a molding technique, as shown in Fig.3. The bottom of the cell was polished to be a flat surface to fit well on the silver disk when it was installed into the hole. The outlet tube of the cell was somewhat shrunk at the middle, and above the shrink, a 3 mm female screw was molded to be able to screw the stop plug. Outside the shrink, a horizontal groove was ground to situate an O-ring used for the connection to a vacuum system. The outlet tube also had two pins to prevent the cell turning in a course of the stop plug operation.

A stop plug, made of PTFE, had a 3 mm male screw and a pin to connect to an operation rod by a bayonet joint. On the male screw, three vertical slots were caved to let the evaporated vapor escape when the stop plug was loosened. Mass and surface area of the cell was about 1.5 g and 4 cm², respectively.

Typical examples of the calibration constant determinations for Calorimeter II are shown in Table 2.

3. METHOD OF OPERATION

Since the methods of operation of the calorimeters are almost the same, the procedures for Calorimeter I are described here.

Samples were introduced into the calorimetric cell either by means of vacuum distillation or of direct injection by the use of a long needle syringe. When the samples were introduced by the syringe, the cell was connected to a vacuum system and the liquids were degassed according to the standard method. Then the stop plug of the cell was closed, and the cell was removed from the vacuum system and weighed. After the cell was installed into a central hole of either calorimetric unit, it was again connected to the vacuum system, and inner space above the stop plug was evacuated. Then the whole calorimeter system was left

TABLE 2. Examples of calibration constant determinations for Calorimeter II

i/mA	t/s	E_{el}/J	S/α	$E_{\text{el}} \cdot S^{-1} / \text{mJ} \cdot \alpha^{-1}$
4.5992	900.0	1.0602	50.760	7.0321
6.0652	899.8	1.8434	262.108	7.0329
6.9302	899.9	2.4069	342.395	7.0296
6.0549	1800.0	3.6751	522.548	7.0330
6.0549	1800.2	4.8144	684.490	7.0336

$$\bar{\epsilon} = (7.0322 \pm 0.0019) \text{mJ} \cdot \alpha^{-1}$$

$$R_h = 55.690 \Omega$$

until it attained the thermal equilibrium.

After the calorimeter arrived at the equilibrium, evaporation was started by opening the stop plug. The rate of evaporation was regulated by the extent of lowering the temperatures of a cold trap placed between the cell and a vacuum holder. If a suitable area under the voltage-time curve was obtained on the recorder, the stop plug was closed to terminate the evaporation, and the calorimeter was left until it recovered thermal equilibrium. Then, the cell was taken out from the calorimeter and weighed after keeping it in a desiccator for 1 ks.

Two methods were employed for evaluating enthalpies of vaporization. In the first method, the evaporation was started after the calibration heater was switched on and was stopped before the current was shut off. The enthalpies of vaporization were evaluated as the ratio of the decrease in the area caused by the evaporation to the area which would be recorded when the electric energy was supplied without any evaporation effect (ref.7).

In the second method, the evaporation was conducted without electric current supplied, and only voltage-time curves caused by the evaporation were recorded. The enthalpies of vaporization were evaluated as the products of the areas under the voltage-time curves and ϵ values determined previously.

Since no difference was observed between the enthalpy values evaluated by these two methods, the second method was used for most experiments.

4. MATERIALS

Cyclohexane, decane, and dodecane supplied from Tokyo Kagaku Seiki Co, were used as the standard reference materials to test the calorimeters. These hydrocarbons were the standard materials for gas chromatography, and their purity was certified to be better than 99 mole per cent by the dealer. Since gas chromatographic analyses showed that their purity was better than 99.9 mole per cent, they were used without further purifications.

Dithiaalkanes, butylamine, and bicyclo[2,2,1]hepta-2,5-diene (norbornadiene) were obtained from Tokyokasei Co, and were purified either by means of fractional distillations or by the use of a preparative glc. Purity of the final best fractions of these compounds was found to be better than 99.9 mole per cent by glc. Each (+)-, and (-)-fenchone was supplied from Tokyokasei Co and Fulka AG. The glc analysis showed that there was no difference in the kinds and total amount of impurities contained in each compound from different sources. Purity of both fenchones was estimated to be better than 99.9 mole per cent, and no purification procedures were applied except drying.

Tetracyclo[2,2,1,0^{2,6},0^{3,5}]heptane (quadricyclene) was kindly gifted from Prof. Shima in our department, and its purity judged by glc was found to be about 99.8 mole per cent.

Di-*tert*-butyl carbonate and bicyclo[2,2,2]octa-2,5,7-triene (barrelene) were synthesized in the laboratory by the methods described by Choppin and Rogers

(ref.8) and by Zimmerman et al (ref.9), respectively. The carbonate was purified by repeated sublimations under reduced pressures, while barrelene was refined by the use of the preparative glc. Both samples showed no impurity peaks on glc.

Oxaalkanes were synthesized from their corresponding alkanols and alkyl bromides by the aid of phase transfer catalyst (ref.10). Although final purification of the compounds were carried out by the use of preparative glc, it was unsuccessful to remove whole impurities from a few compounds. Purity of such compounds, denoted asterisk in table 4, was estimated to be about 99.5 mole per cent

Water content in the purified samples was determined by a glc technique (ref. 11), and was found to be less than 0.01 mass per cent for all compounds.

5. RESULTS AND DISCUSSION

Typical experimental results for the test compounds measured by Calorimeter I are summarized in Table 3. Enthalpy of vaporization values given in the table correspond to the enthalpy differences between real gases and liquids under the saturation pressures, because the liquids in the evaporation cells are always in equilibrium with their vapors in the air free space throughout the evaporation

TABLE 3. Enthalpies of vaporization of standard reference compounds at 298.15 K measured by Calorimeter I.

Cell	$m_{\text{evap}}/\text{mg}$	S/α	$\epsilon \cdot S/\text{J}$	$\Delta_{1D}^{\text{gH}}/\text{kJ}\cdot\text{mol}^{-1}$	
				obsd.	lit. ^a
Cyclohexane					
B	17.09	226.40	6.722	33.08	33.00 <i>b</i>)
B	26.01	343.32	10.194	32.97	33.03 <i>c</i>)
B	27.53	363.54	10.793	32.98	
B	32.53	429.66	12.752	32.99	
B	39.02	574.0	15.362	33.12	
				(33.03±0.07)kJ·mol ⁻¹	
Decane					
B	25.21	387.41	9.128	51.49	51.36 <i>d</i>)
A	26.39	320.82	9.52	51.34	51.35 <i>b</i>)
B	28.68	348.35	10.343	51.29	
B	32.56	395.83	11.752	51.33	
A	32.58	397.48	11.796	51.52	
				(51.39±0.10)kJ·mol ⁻¹	
Dodecane					
A	38.29	464.64	13.789	61.38	61.29 <i>d</i>)
A	42.21	510.70	15.156	61.16	61.30 <i>e</i>)
A	47.94	581.70	17.263	61.21	
A	51.79	627.19 <i>a</i>)	18.613	61.21	
				(61.27±0.10)kJ·mol ⁻¹	

When Cell B was used, heat effect correction -0.005 J should be added to the observed $\epsilon \cdot S$ values.

a) Wane area caused by evaporation in a course of streaming 10.6105 mA through the calibration heater 100.493 Ω for 6598.2 s.

b) ref. 12; *c*) ref. 13; *d*) ref. 14; *e*) ref. 15.

process. Uncertainties given are twice the standard deviations of the means. As can be seen in the table, there are no differences between the observed and literature values.

In these experiments though the amounts of samples being evaporated were 20 to 50 mg, it was experienced that the optimum amount to be evaporated was 20 to 30 mg. When a large amount of a sample was introduced in the cell in the beginning of the experiments, irregular results, probably due to bubbling of liquids, were occasionally observed. On the contrary, if the amount taken is too small, errors caused by weighing of the sample would increase, in spite of special care taken. Thus, the calorimeter can be operated with uncertainties of ± 0.2 per cent, and it has the advantage of being used for the measurements of low vapor pressure compounds, whose enthalpies of vaporization could not be obtained by Wadsö's calorimeter being used for the routine works in our laboratory. In addition, the calorimeter can be used for the measurements of metal corrosive compounds, because all components of the cells which will contact with the compounds to be measured are composed only of glass and PTFE.

One of the defects of the calorimeter is its long time constant, and a half-value period has been found to be about 0.2 ks. However, the fact that the recorder takes about 4 ks to recover its original position after heat is added to the calorimetric unit limits the number of measurement times in a day.

In order to decrease the time constant, and to increase the sensitivity, Calorimeter II was designed. Since the central block of the calorimetric unit was designed to be its heat capacity as small as possible, and the block was surrounded by four thermo-modules, the time constant could be reduced to be one third, and its sensitivity was increased four times compared with those of Calorimeter I (see ϵ values in Tables 1 and 2). Moreover, as the surface area and mass of the cells are respectively made to be less than ten per cent than those of Calorimeter I, fluctuations of mass of the cells before and after the evaporation procedures are expected to be reduced, and the Calorimeter II is now under testing.

Examples of enthalpies of vaporization measured by Calorimeter I are collected in Table 4. For dithaalkanes, the observed values are poorly agreed with the literature ones, except for a few compounds, because most of the literature values are those which have been obtained either by temperature dependencies of vapor pressures or by the estimation from their chemical formula. For butylamine the observed value is excellently agreed with reported values (ref.16, 17).

As an example to measure enthalpy of sublimation, di-*tert*-butyl carbonate was used. Employing Cell A, the carbonate sublimed smoothly, and its enthalpy of sublimation could be obtained with uncertainty of ± 0.3 per cent.

In order to discriminate the chirality of liquids, Dr. Atik measured enthalpy of vaporization values for (+)- and (-)-fenchone by the use of Calorimeter I. As has been expected, the difference is only 0.33 kJ mol^{-1} .

For norbornadiene and for quadricyclene, some larger enthalpy of vaporization values were observed than literature values which were obtained by non-calorimetric methods. Enthalpy of vaporization for barrelene, measured by the use of both Wadsö's calorimeter and Calorimeter I agreed each other within uncertainties.

TABLE 4 Enthalpies of vaporization at 298.15K measured by Calorimeter I

Compound	Cell	$\Delta_{1m}^{\text{lg}} / \text{kJ}\cdot\text{mol}^{-1}$	
		observed	lit.
2,2-dithabutane	B	37.77±0.09	38.4 <i>c</i>)
3,4-dithahexane	B	45.17±0.06	45.44 <i>d</i>)
4,5-dithaoctane	A	53.77±0.12	54.14 <i>e</i>)
5,6-dithadecane	A	62.27±0.20	64.5 <i>f</i>)
2,7-dimethyl-4,5-dithaoctane	A	57.17±0.14	61.9 <i>f</i>)
2,2,5,5,-tetramethyl-3,4-dithahexane	A	52.47±0.15	53.2 <i>f</i>)
6,7-dithadodecane	A	71.09±0.21	
5-oxahendecane*	B	53.23±0.05	
3-oxadodecane	A	60.34±0.10	
4-oxadodecane	A	58.84±0.11	
5-oxadodecane	A	58.18±0.11	
3-oxatridecane	A	65.89±0.10	
7-oxatridecane*	A	64.10±0.10	
butylamine	B	35.66±0.16	35.6 <i>g</i>);35.65 <i>h</i>)
di- <i>tert</i> -butyl carbonate	A	65.44±0.22 <i>a</i>)	
(+)-fenchone	A	51.09±0.05 <i>b</i>)	
(-)-fenchone	B	51.42±0.05 <i>b</i>)	
bicyclo[2,2,1]hepta-2,5-diene	B	34.69±0.06	32.9 <i>i</i>)
tetracyclo[2,2,1,0 ^{2,6} ,0 ^{3,5}]-heptane	B	37.91±0.04	37.0 <i>i</i>)
bicyclo[2,2,2]octa-2,5,7-triene	B	42.85±0.08	42.77 <i>j</i>)

a) enthalpy of sublimation, *b*) measured by Dr. Atik, *c*) ref.18. *d*) ref. 19, *e*) ref.20, *f*) ref.21, *g*) ref. 16, *h*) ref. 17, *i*) ref.22, *j*) measured by Wadsö's calorimeter

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