The determination of enthalpies of sublimation by means of thermal conductivity manometers

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The determination of enthalpies of sublimation by means of thermal conductivity manometers*

C. G. de Kruif and H. A. J. Oonk **

This paper describes an investigation into the suitability — for the determination of enthalpies of sublimation of low volatility substances — of thermal conductivity manometers which are operated according to the method described by Engelsman. By making use of the known vapour pressure-temperature relation of liquid mercury the characteristics of the manometers are obtained. They show deviations from linearity at higher pressures; in spite of this the most suitable manometers still have linear ranges of three to four decades. One of the thermal conductivity manometers (TCM) was used for the determination of the enthalpies of sublimation of benzophenone ($\Delta_s H = 22.60 \pm 0.10$ kcal mole^{-1}), benzoic acid ($\Delta_s H = 21.05 \pm 0.05$ kcal mole^{-1}), ferrocene ($\Delta_s H = 17.7 \pm 0.4$ kcal mole^{-1}) and trans-stilbene ($\Delta_s H = 24.40 \pm 0.15$ kcal mole^{-1}). As the measurements on ferrocene fell outside the linear range of the manometer, it was necessary to introduce a correction coefficient derived from the measurements on benzophenone and benzoic acid in order to obtain satisfactory results.

The characteristics of the manometers

The enthalpies of sublimation of low volatility compounds are generally not determined directly but are derived from the measured relation between vapour pressure and temperature with the help of the Clausius-Clapeyron equation. In this method a quantity proportional to vapour pressure suffices, so that use can be made of manometers such as the thermal conductivity manometer. The design of the thermal conductivity or Pirani manometers is based on the principle from the kinetic theory of gases that the conduction of heat, by a Knudsen

Apart from the usual metal wire we employed NTC***) beads, with and without glass-coating, and made a mutual gas, from a hot wire to its envelope is proportional to the vapour pressure [1].

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comparison of the properties of these different filaments. A NTC bead of 1 mm diameter is depicted in Fig. 1.

We designed a number of Pirani manometers of which the constructional details are given; the electrical circuit and the manner of operation are described on page 457. The manometers are operated in a so-called "constant temperature" mode [2] and by application of the *Engelsman* [3] procedure (s. the next section), the quantity proportional to vapour pressure is found from double difference measurements which are expected to be free from systematic errors.
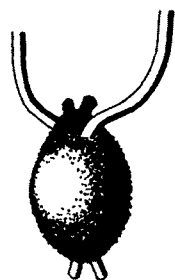

|6 3579.7| Fig. 1. The NTC bead (enlarged).

In order to verify the assumed proportionality between the quantity measured and the vapour pressure we investigated the characteristics of the manometers by making use of the known vapour pressure of liquid mercury. In our opinion mercury is the only low volatility substance that can be used as a standard, especially because its vapour pressure and enthalpy of vaporization have been determined fairly consistently by a variety of techniques. The characteristics obtained (s. page 458) reveal an unexpected deviation from linearity at higher vapour pressures. An explanation for this behaviour, which may be obscured in an ordinary Clausius-Clapeyron plot, is given on page 458.

In conclusion it can be said that the manometers in combination with the adopted measuring procedure can successfully be used for the determination of the enthalpies of sublimation of low volatility compounds.

The Engelsman procedure [3, 4]

The manometer filament is made one of the arms of a Wheatstone bridge and its watt input is measured under a number of varying circumstances. The watt input is necessary to maintain the filament at a certain temperature and its magnitude is equal to the sum of the losses due to radiation, conduction through the support leads and to heat conduction by the vapour molecules.

At zero pressure ($P = 10^{-6}$ Torr or lower) the conduction by the vapour molecules vanishes. The watt input is measured at the same thermostat temperature T for two filament temperatures T_1, the higher one, and T_2. The difference of these two watt inputs is called the zero point of the manometer:

$$W_0 = W'_{T_1} - W'_{T_2} \ . \tag{1}$$

Engelsman assumed W_0 to be independent of T and found this to apply over a temperature range of four degrees. In contrast with this we find a slight dependence of W_0 on T whose sign and magnitude are determined by the material and by constructional details, (s. below). At the presence of vapour the watt inputs are again measured for the filament temperatures T_1 and T_2:

$$W = W_{T_1} - W_{T_2} \ . \tag{2}$$

As relation with vapour pressure can be shown that the difference $W - W_0$ is given by

$$W - W_0 = cP/\sqrt{T} \tag{3}$$

in which

$$c = (T_1 - T_2) \frac{\alpha}{2} A \frac{(\varkappa + 1)}{(\varkappa - 1)} \sqrt{\frac{R}{2\pi M}} \ . \tag{4}$$

α is the accommodation coefficient, A the surface area of the filament, $\varkappa = C_p/C_v$ and R the gas constant.

After rearranging the pressure P is found as

$$P = \frac{W - W_0}{c} \sqrt{T} \ . \tag{5}$$

Substitution of Eqn. (5) in the Clausius-Clapeyron equation

$$\frac{d \ln P}{d(1/T)} = - \frac{\Delta H}{R} \tag{6}$$

yields

$$\frac{d \{\ln(W - W_0) + \frac{1}{2} \ln T\}}{d(1/T)} = - \frac{\Delta H}{R} \ . \tag{7}$$

Consequently, the slope of a plot of $\{\ln(W - W_0) + \frac{1}{2}\ln T\}$ against $1/T$ has the value of $-\Delta H/R$. If the temperature interval is too great, the influence ΔC_p has to be taken into account.

Manometers constructed

General

We constructed a number of manometers which are named Pirani I, III, IV, V and VI. The general design of all the manometers is the same; the differences are brought about by the choice of the filament. The considerations leading to the construction of each manometer are given in the thesis. The relevant properties of each filament are given in Table 1. It should be noted that, unlike the other manometers, Pirani VI does not have a NTC as filament but a straight platinum wire. Moreover the isolation valve of this manometer consists of an O-ring in a seat which can be opened and closed by squeezing or extending a metal bellows in a pivot (this system proved to be the most satisfactory).

The measurements presented at the end of this paper were conducted with the Pirani I manometer which is shown in Fig. 2 and constructed as follows:

A Philips NTC type B 8.32006P/1K is sealed to pyrex glass. A piece of kovar pipe, 10 mm in diameter and with a length of 30 mm, is sealed via G 28 to pyrex; the other side of the kovar
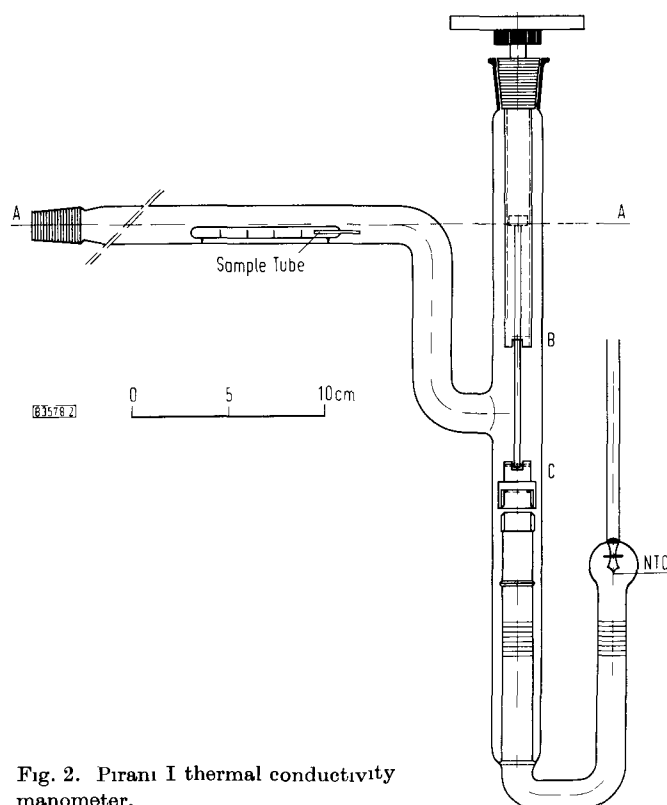
Fig. 2. Pirani I thermal conductivity manometer.

Fig. 3. Electrical circuit of self-balancing Wheatstone bridge.

Fig. 4. Block diagram.

pipe is provided with a screw thread and a cap nut. This cap nut can be turned by a spindle fitted to a ground joint, made of metal. In this way the measuring chamber can be isolated from the vacuum system. During the sublimation process, i.e. the introduction of the compound to be measured into the manometer, the cap nut and spindle are moved from position C to position B by turning the manometer around the axis AA'.

Experimental

Electrical circuit

The filament resistor is made one of the arms of a Wheatstone bridge whose balance can be observed on a galvanometer (Kipp AL 1). An operational amplifier, the output of which serves as a power supply to the bridge, is connected, parallel with this galvanometer. The complete electrical diagram is given in Fig 3. In this figure R_1 and R_2 denote Bleeker standard resistors (100 Ω) which have the same value within experimental error (1:10⁵). R_3 and R_4 are parts of a resistance box; they are inserted by means of a heavy relay with a very low and constant contact resistance. The resistor R_5 consists of two parallel standard resistors of 100 Ω each. The respective values of the filament resistor (R_{NTC}) are determined by measuring with a digital voltmeter (dynamco measurements 2010, full deflection 1099.99 V, sensitivity 10 μV, input resistance 10^{10} Ω) the voltage across R_{NTC} relative to R_5. The voltmeter signal is serialized and printed on a typewriter. The watt input in the filament resistor is now given by
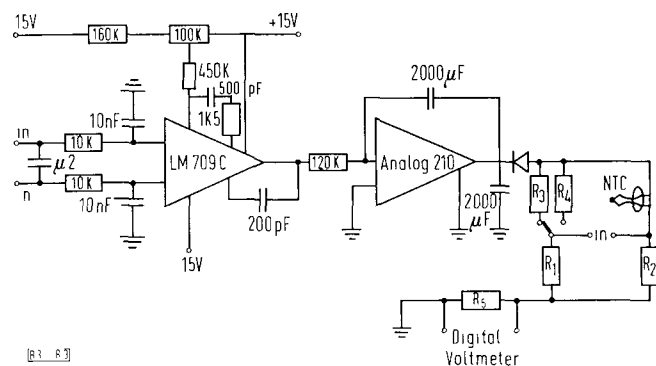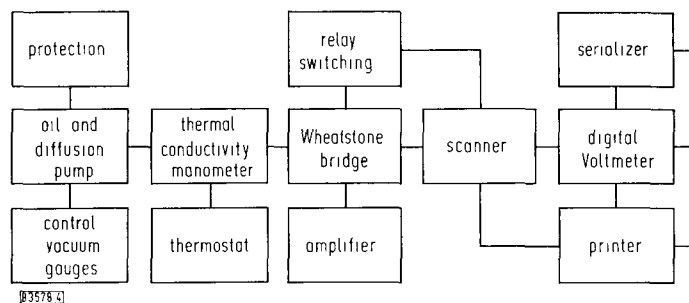
$$W = \frac{V_5^2}{100^2} \, R_{NTC} \ .$$

Thermostat and vacuum system

The manometers are immersed in a thermostat (LKB Precision Thermostat) with a temperature constancy of one millidegree. The temperature measurements are better than 0.01 degree indicated by mercury thermometers which are calibrated against a platinum resistance thermometer of the Kamerlingh Onnes Laboratorium, Leiden.

The vacuum system consists of an oil diffusion pump backed by an Edwards rotation oil pump. The obtainable vacuum, measured with a Bayard Alpert ionization manometer, is about 10^{-6} Torr. – Fig. 4 gives a block diagram of the experimental set-up.

Operation

After being degassed at 100 to 150 °C the manometer is immersed in the thermostat bath. The watt input at "zero pressure" (W_0) is determined as a function of thermostat temperature. Thereafter a small amount of the substance to be measured is sublimed out of the inserted sample tube into the measuring chamber. After closing the measuring chamber the watt input is measured; as there is always an increase in pressure due to degassing, the watt input is extrapolated to the time of closing. During the time required to attain equilibrium at another thermostat temperature the measuring chamber is opened. After having measured the watt input at a representative number of thermostat temperatures, the substance is sublimed into the cold trap. Finally a new determination of W_0 is made to detect a possible drift.

Table 1. Filament properties of the manometers constructed.

manometer	manufacturer and type number	nominal resistance at 25 °C	material of support leads	length and diameter of support [cm]
Pirani I	Philips B 32006P/1K	1 kΩ	Pt/Ir (90/10)	0.6/0.005
Pirani IV	Philips B 32002P/1K	1 kΩ	Pt-ribbon	5/0.3 × 0.0002
Pirani V	Fenwall Elec. Inc. GA 51T2	100 kΩ	Pt/Ir (90/10)	0.3/0.0024
Pirani VI	Drijfhout	33 Ω	straight Pt-wire	10/0.002

Manometer characteristics, experimental results

The characteristics of the manometers have been obtained with the help of mercury whose the enthalpy of vaporization, consistently determined by a variety of techniques, has the value at 25 °C (see the thesis):

$$\Delta H = 14.680 \pm 0.005 \text{ kcal mole}^{-1} \ .$$

In addition the absolute vapour pressure is reasonably well known; it can be expressed by the following equation:

$$R \ln P = -\frac{3695}{\Theta} + 14.680 \left(\frac{1}{\Theta} - \frac{1}{T} \right) -$$

$$- 1.711 \left(\frac{\Theta}{T} - 1 + \ln \frac{T}{\Theta} \right) +$$

$$+ 1.696 \cdot 10^{-3} \left(\frac{T}{\Theta} - \frac{\Theta}{T} - 2 \ln \frac{T}{\Theta} \right) \frac{\Theta}{2} \ ,$$

with

$\Theta = 298.16$ K and P in Torr.

In the procedure adopted, see Eqn. (3), the relation between $(W - W_0)$ and P is given by

$$(W - W_0) = c \frac{P}{\sqrt{T}} \ .$$

Instead of applying the Clausius-Clapeyron equation to this relation it is convenient to make use of the known vapour pressure of mercury by plotting the measured value of $(W - W_0)$ against the calculated value of $P/\sqrt{T}$. The plot should then satisfy two requirements:

1.) the line should intersect the origin. In the time interval between completion of the measurement of W and the determination of W_0, the latter may have drifted as mentioned in the preceding section. If this is the case, intersection of the origin will not occur and erroneous results are obtained;

2.) a straight line should be obtained.

Fig. 5 gives the $(W - W_0)$ vs. $P/\sqrt{T}$ plots obtained for the respective manometers. For Pirani IV two curves are given: the lower curve shows the decrease in sensitivity as a result of halving the difference in filament temperatures (T_1 and T_2).

It can be seen from Fig. 5 that the characteristics do intersect the origin as expected. As for the second requirement: straight lines are shown only in a limited region of $(W - W_0)$ starting from zero. So, Pirani I is linear to 70 µW, this has been established in other measurements, whereas the upper Pirani IV characteristic is linear up to 50 µW.
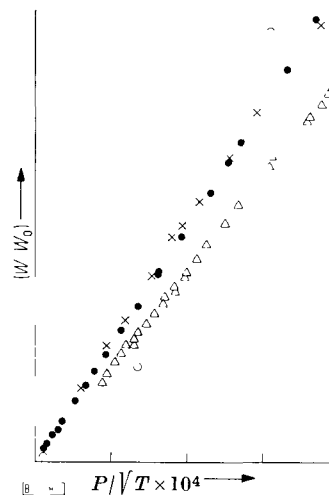

Fig. 5. Characteristics of the manometers; watt input $(W - W_0)$ against $P/\sqrt{T}$ for mercury.

△ Pirani I ordinate 12.5 µW/div; abcissa 1.25 Torr K$^{-1/2}$/div.
○ Pirani IV ordinate 80 µW/div; abcissa 1.25 Torr K$^{-1/2}$/div.
× Pirani V ordinate 10 µW/div; abcissa 0.4 Torr K$^{-1/2}$/div.
● Pirani VI ordinate 100 µW/div; abcissa 5 Torr K$^{-1/2}$/div.

We found that the deviation from linearity is connected with the manometer and not with the nature of the substance to be measured. A survey of the properties of the manometers is given in Table 2.

The sensitivity is defined here as a 0.1 µW input change divided by the corresponding pressure change in Torr (referred to mercury). One tenth of a µW is chosen as it is an average measuring error for short time measurements. The reciprocal value given in Table 2 can be interpreted as the lower limit of the manometers.

Conclusions, discussion

From the last two rows of Table 2 it follows that the manometers should be used each in a particular pressure range. For instance, Pirani IV is a suitable manometer for the determination of enthalpies of sublimation in the range, referred to mercury, from $2 \cdot 10^{-6}$ to 10^{-3} Torr, whereas the range of Pirani I is from $3 \cdot 10^{-5}$ to $2 \cdot 10^{-2}$ Torr. These three-decade ranges are exceeded by Pirani VI which has a suitable range of four decades, from 10^{-5} to 10^{-1} Torr. In this respect Pirani V, the only manometer with a glasscoated NTC as filament, compares unfavourably with the rest in having a two-decade range.

Table 2. Sensitivity and linearity of the manometers when operated at the temperatures indicated.

manometer	Pirani I	Pirani IV		Pirani V	Pirani VI
temperature	94 °C	97 °C	97 °C	92 °C	93 °C
resistance	210 Ω	210 Ω	210 Ω	5 kΩ	43.6 Ω
temperature	126 °C	126 °C	106 °C	127 °C	147 °C
resistance	130 Ω	130 Ω	170 Ω	2 kΩ	49.6 Ω
reciprocal sensitivity [Torr/0.10 µW]	$3 \cdot 10^{-5}$	$2 \cdot 10^{-6}$	$4 \cdot 10^{-6}$	$8 \cdot 10^{-5}$	$9 \cdot 10^{-6}$
linear up to	70 µW	50 µW	25 µW	14 µW	650 µW

As for the sensitivity of the manometers the following can be noticed The use of ribbon-shaped support leads increases the sensitivity of the instrument, e g for Pirani I to Pirani IV by a factor 15 It is expected that flattening of the wire of Pirani VI will also increase its sensitivity The sensitivity of Pirani V is probably reduced as a consequence of the glass-coating which lowers the accommodation coefficient and also the effective surface area

The decline in linearity at higher pressures can in our opinion be ascribed to surface cooling of the filament resistor Except for Pirani VI the filament resistor is a NTC which consists of a drop of semiconducting material sintered between two Pt/Ir support leads As a result of the sintering process the NTC has a very rough and relatively large surface area The electrical resistance of the NTC, compare Fig 1, is determined mainly by the region between the two support leads The Joule heat is also evolved in this area Because sintered material is a poor heat conductor there is a temperature gradient to the surface of the NTC, which increases with pressure In other words, the surface temperature is lowered and the contribution of the pressure dependent term to the watt input drops below the value that would correspond with the inner NTC temperature The decrease in linearity range of Pirani V and the increase in linearity range of Pirani VI, both compared with Pirani I, fit this explanation well For the former the heat conductivity is decreased by the glass-coating, whereas for the latter it is increased as the resistor is all-metal

In conclusion it can be remarked that thermal conductivity manometers, on account of the findings of this investigation, are expected to be suitable for the determination of enthalpies of sublimation provided that their properties are recognized and accounted for

The enthalpy of sublimation of benzophenone, benzoic acid, ferrocene and trans-stilbene

The scope of this part is to provide confirmation of this suitability by giving the results of the measurements of the enthalpies of sublimation of benzophenone, benzoic acid, ferrocene and trans-stilbene These compounds have in common that their enthalpies of sublimation have been measured by a number of investigators employing a number of different techniques including the one used by us As a consequence the reader will be in a better position to assess the possibilities of properly handled thermal conductivity manometers

The results of the measurements, obtained with the Pirani I manometer, are gathered in Table 3, along with the results of the investigations given in the literature As the vapour pressure of ferrocene falls outside the linear range of the manometer, the measurements on benzophenone and benzoic acid were extended to higher pressure regions this yielded a correction coefficient with the help of which the value of the enthalpy of subli mation for ferrocene could be obtained

Benzophenone

Both the enthalpies of sublimation $(\Delta_s H)$ and of vaporization $(\Delta_v H)$ can be determined at room temperature as the metastable liquid can be kept for long periods of time The difference between the values can be compared with calorimetrically determined values for the enthalpy of melting, which are 4 25 ± 0 3 kcal mole^{-1}, loc cit by Neumann [5] as the average of the determinations by six investigators and 4 34 ± 0 02 kcal mole^{-1} measured with the adiabatic calorimeter of our laboratory by Van Miltenburg

The least-squares values of the slopes of Clausius Clapeyron plots are given in the rows 1, 2 and 3 of Table 3 The average of 22 60 ± 0 10 kcal mole^{-1} is in close agreement with the values obtained by Neumann and Volker [5] and by Volmer and Kirchhof [6]

The enthalpies of vaporization of the metastable liquid given in rows 7 and 8 do not agree within experimental error The difference $\Delta_s H - \Delta_v H$ is just in favour of the TCM values − The deviating value obtained by Wolf and

Table 3   Survey of the enthalpies of sublimation and vaporiza tion (only row 7 and 8) of benzophenone, benzoic acid, ferrocene and trans stilbene When no reference is given the results were obtained by the author (TCM = thermal conductivity mano meter)

	com pound	technique	temp (range) [°C]	value kcal mole^{-1}	Ref
1	benzophenone	TCM	25 − 30	22 56 ± 0 10	
2		„	23 − 31	22 71 ± 0 15	
3		„	22 − 27	22 52 ± 0 15	
4		effusion	25	22 72 ± 0 10	[5]
5		„	25	22 50 ± 0 10	[6]
6		„	40	18 70 ± 0 20	[7]
7		TCM	22 − 28	18 2 ± 0 2	
8		effusion	27 − 55	18 70 ± 0 2	[5]
9	benzoic acid	TCM	24 5 − 36 5	20 98 ± 0 10	
10		„	24 8 − 38 6	21 20 ± 0 20	
11		„	20 6 − 38 6	21 00 ± 0 10	
12		„	22 4 − 30 9	21 16 ± 0 24	
13		„	28 8 − 22 1	21 07 ± 0 12	
14		„	28 8 − 22 1	21 04 ± 0 01	
15		dynamic	25	18 5 ± 1 6	[8] *)
16		isoteniscope	25	20 8 ± 0 1	[9] *)
17		tensimeter	25	23 3 ± 0 6	[10]*)
18		transpiration	25	22 55 ± 0 06	[11]*)
19		TCM	25	19 6 ± 0 1	[12]*)
20		effusion	25	20 3 ± 0 2	[7] *)
21	ferrocene	spectrosc	25	17 57	[13]
22		effusion	25	17 53 ± 0 10	[13]
23		TCM	25	17 30 ± 0 30	[13]
24		Bourdon	25	18 1	[14]*)
25		effusion	25	20 5	[15]*)
26		spectrosc	25	16,64	[16]
27		effusion	25	17 36 ± 0 13	[16]
28		TCM	25	17 7 ± 0 4	
29	trans stilbene	„	22 0 − 42 0	24 44 ± 0 22	
30		„	22 0 − 45 0	24 40 ± 0 15	
31		„	30 − 42	20 68 ± 0 08	[3]
32		effusion	56	21 7 ± 0 2	[7]

* Note These values are reduced to 25 °C

Weghofer [7] in an effusion experiment is 20% too low. Perhaps this value is the result of a systematic error as, in comparable measurements they also find values which deviate in the same direction.

Benzoic acid

Benzoic acid was measured several times (rows 9 to 14 in Table 3) to test the reproducibility of the manometer. These tests, which were performed four times with rising thermostat temperatures and two times with falling temperatures, were made with benzoic acid because of the extremely low gas desorption of the samples. For the measurements of rows 9, 10 and 11 zone-refined samples were used and for those of 12, 13 and 14 we used zone-refined samples from Aldrich Chemicals. The average value is 21.05 ± 0.05 kcal mole^{-1}. The values of the other investigators were reduced to 25 °C with the help of $\Delta_s C_p$ of $-$ 10.4 cal mole^{-1}K^{-1} which can be calculated from data given by *Stull* [17] and by *Furukawa* [18].

It is not our intention to discuss the discrepancies in the various results, with the exception of that of row 19. The experiment of row 19 was performed with a thermal conductivity manometer having the same NTC as filament resistor as our Pirani V. We have shown that the latter has a restricted linear range which if not recognized may yield too low values for ΔH.

In our opinion benzoic acid is not suitable as a standard substance for enthalpy of sublimation mea-surements so far. This contrasts with other kinds of calorimetric measurements in which benzoic acid has proved to be a useful standard. The reason for this is the dimerization of the acid in the vapour phase which has not yet been fully investigated. We have indications that it is less than 1% at room temperature, so we take it that our value of $\Delta_s H$ is close to the enthalpy of sublimation of the monomer.

Ferrocene

In our experiment it appeared that the vapour pressure of ferrocene is so high that measurements could not be made within the linear range of the manometer. We therefore decided to extend the measurements on benzophenone and benzoic acid to higher pressures (in fact higher watt inputs) and to derive from them a correction coefficient. As a first approximation we assumed that this coefficient is a linear function of watt input counted from 70 μW (Pirani I manometer has a linear range up to 70 μW).

The calculation is shown in Table 4. The average of the two values obtained is given in Table 3, row 28; it fits well with the average of the literature values, given in the rows 21 to 27. The experiments of rows 24 and 25 were performed at higher temperatures and the values obtained were reduced by us to 25 °C with $\Delta_s C_p$ of $-$ 12 cal mole^{-1}K^{-1} given by *Andrews* [16].

Trans-stilbene

In order to compare our results with those of *Engelsman* [3], who introduced the procedure followed here, we made a measurement of the enthalpy of sublimation of trans-stilbene. The results of our two independent measurements are given in the rows 29 and 30 of Table 3. The two values found do not agree with the value of *Engelsman*, row 31; the latter may however be low as a result of nonlinearity of the manometer[****] and as a result of the observed high rates of pressure increase.

The value of *Wolf* and *Weghofer* [7] is given in row 32 of Table 3. That value is obtained in an effusion experiment (along with benzoic acid and benzophenone) in which a number of different cells is used. Unfortunately they do not specify which cell is used for the listed enthalpy of sublimation values. Their values for benzophenone and benzoic acid are 3.9 and 2 0 kcal mole^{-1} lower than ours. So their value of 21.7 kcal mole^{-1} for trans-stilbene is probably too low as well.

[****] Note: Engelsman used a manometer very similar to Pirani V.

Table 4. Calculation of the enthalpy of sublimation of ferrocene.

compound	$\Delta_s H$ Table 3	Watt input minus 70 μW	$\Delta_s H$ obtained (at temp.)	deviation with correct value	correction coeff. kcal mole^{-1} per μW difference
benzoic acid	21.05 ± 0.05	60	20.50 ± 0.10 36 °C	$-$ 0.55 ± 0.10	0.0092 ± 20%
benzophenone	22.60 ± 0.10	80	20.91 ± 0.10 36 °C	$-$ 0.70 ± 0.10	0.0087 ± 14%
benzophenone	22.60 ± 0.10	63	20.91 ± 0.10 35 °C	$-$ 0.70 ± 0.10	0.0110 ± 14%
	↓	+	+		0.0097 ± (max) 20%
ferrocene	17.80 ± 0.35	135	16.49 ± 0.10 20 °C		
ferrocene	17.62 ± 0.40	255	15.15 ± 0.10 25 °C		

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