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# STANDARD ENTHALPY OF SUBLIMATION OF $[\text{Mo}(\eta\text{-C}_5\text{H}_5)_2(\text{CH}_3)_2]$ . A RE-EVALUATION OF $\text{Mo-CH}_3$ AND $\text{W-CH}_3$ BOND ENTHALPY CONTRIBUTIONS

*Molybdenum-methyl and tungsten-methyl bond enthalpy contributions in  $[\text{M}(\eta\text{-C}_5\text{H}_5)_2(\text{CH}_3)_2]$  complexes ( $\text{M}=\text{Mo}, \text{W}$ ) were re-evaluated as  $\bar{D}(\text{Mo-CH}_3) = 154.5 \text{ kJ mol}^{-1}$  and  $\bar{D}(\text{W-CH}_3) = 209.9 \text{ kJ mol}^{-1}$  by using previous thermochemical results and  $\Delta H_S^\circ[\text{Mo}(\eta\text{-C}_5\text{H}_5)_2(\text{CH}_3)_2] = 70.4 \pm 4.2 \text{ kJ mol}^{-1}$ , a value derived in this paper from pressure-temperature data obtained with a Knudsen cell. This cell, which is also described, was tested by comparing the measured  $\Delta H_S^\circ[\text{Fe}(\eta\text{-C}_5\text{H}_5)_2] = 72.60 \text{ kJ mol}^{-1}$  with other literature values.*

## 1 — INTRODUCTION

We have reported data on metal-ligand bond enthalpy contributions  $\bar{D}(\text{M-L})$  in  $[\text{M}(\eta\text{-C}_5\text{H}_5)_2\text{L}_2]$  complexes ( $\text{M}$  = transition metal;  $\text{L} = \text{H}$ , alkyl, aryl, halogen, etc.) from reaction-solution calorimetry studies [1]. The paucity of experimental values for standard enthalpies of sublimation of those complexes is one of the difficulties in the evaluation of  $\bar{D}(\text{M-L})$ . It is frequently necessary to estimate  $\Delta H_S^\circ$  values which sometimes causes a considerable loss of accuracy and precision in the final values of  $\Delta H_f^\circ(\text{g})$  and  $\bar{D}(\text{M-L})$ .

Among the experimental techniques leading to enthalpies of sublimation of compounds with vapour pressures between 10 and  $10^{-3}$  Pa at room temperature, the Knudsen effusion method is probably the most reliable. Moreover when a high-vacuum system is available it is simple to build an inexpensive «weighting method» Knudsen apparatus with a cell suitable for handling air sensitive substances. The description of such a Knudsen cell and auxiliary equipment, together with the tests performed by obtaining  $\Delta H_S^\circ[\text{Fe}(\eta\text{-C}_5\text{H}_5)_2]$  are given in the present paper. A value for  $\Delta H_S^\circ[\text{Mo}(\eta\text{-C}_5\text{H}_5)_2(\text{CH}_3)_2]$  is also reported. This value, taken with results obtained in previous thermochemical studies [2] allowed the recalculation of  $\bar{D}(\text{Mo-CH}_3)$ .

## 2 — EXPERIMENTAL

**KNUDSEN CELL AND OPERATION PROCEDURE** — Details of the Knudsen cell and auxiliary equipment are shown in figs. 1a-1d. The cylindrical bronze box 2 (1.8 cm height  $\times$  1.8 cm diameter) was filled to about 1/3 of its capacity with the finely powdered substance and the upper part of the spiral was greased with Apiezon N before screwing in bronze lid 3. This operation prevented loss of compound through the spiral path, during a run.

If the substance under study was oxygen sensitive the previous steps were carried out under pure nitrogen. Furthermore, use was made of bronze lid 4, which isolated the inside of the cell from atmospheric oxygen. This assembly (including or not lid 4) was then weighted to  $\pm 1 \times 10^{-5}$  g and introduced with a special tool into the vacuum chamber 3 (fig. 2) previously filled with nitrogen through tap

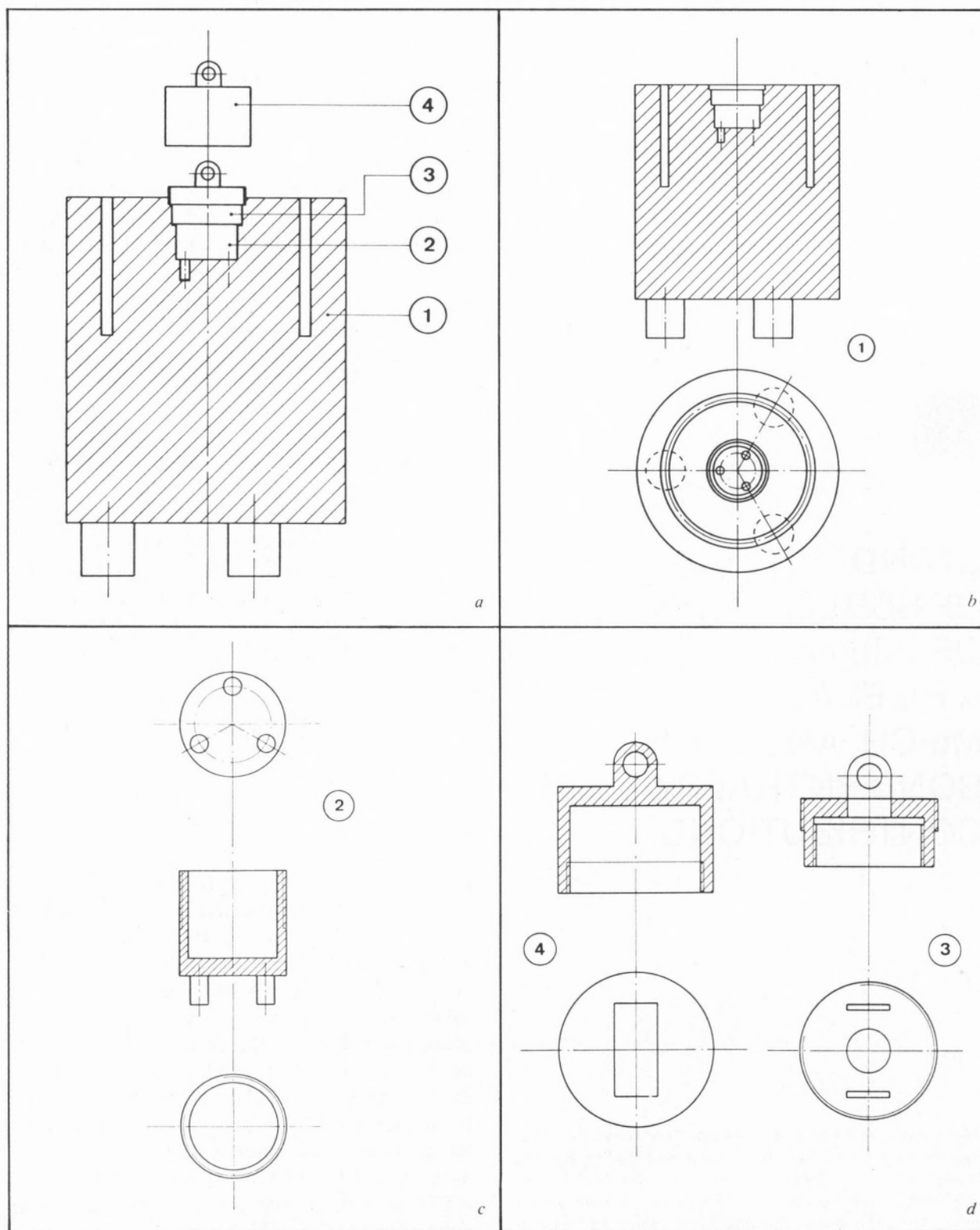


Fig. 1  
Brass block (1), cylindrical box (2), lid with the  
hole (3) and outer (insulating) lid (4)

2. Using a second tool, lid 4 was unscrewed and removed from the inside of the vessel.

The lower part the vacuum chamber, shown in detail in fig. 1b, consists of a cylindrical brass block with a central cavity where the Knudsen cell (2 + 3, fig. 1) fits tightly. The upper part is a glass tube ( $\approx 60$  mm internal diameter) with a tap and a flat flange joint in the top. The glass tube, which fits in the outer cavity of the brass block, was sealed with Araldite AV 138 M.

Before introducing the cell assembly into the vacuum chamber the bottom and lower sides of box 2 (fig. 1) were covered with a thin film of Apiezon N. This ensured a better thermal contact between the cell and the brass block [3]. The block and part of the glass tube were immersed in a water bath whose temperature is controlled to  $\pm 0.01$  K with a Haake ED «Unitherm» thermostat and measured with identical precision with a calibrated Amarell mercury thermometer.

The vacuum chamber was then connected to the vacuum line by using item 4 (fig. 2) which includes the small neoprene rubber tube 5 giving some flexibility to the system. The vacuum line and chamber were quickly evacuated and immediately filled with nitrogen. After about 45-60 minutes (time to achieve thermal equilibrium) the experiment was started. The high-vacuum is obtained with an Edwards vacuum system consisting of a ES 200 rotary pump, an E04 water cooled oil diffusion pump and a liquid nitrogen trap. A second trap is part of the vacuum line (item 6, fig. 2). A pressure of  $1 \times 10^{-3}$  Pa was reached in less than three minutes and a final constant pressure of  $8 \times 10^{-5}$  Pa was obtained in about twenty minutes.

The experiment ended by stopping the pumping and by filling the vacuum line and chamber with nitrogen. Item 4 (fig. 2) was then removed and lid 4 (fig. 1) was screwed in lid 3 (This step was unnecessary when the substance was not oxygen sensitive). The cell was taken out of the chamber and thoroughly cleaned to remove the Apiezon N from the bottom and wall of box 2 (fig. 1). The assembly was finally weighted and the difference between the initial and this second weight gave the mass of the evaporated substance.

Further details of the Knudsen cell and of the experimental technique are as follows.

Lid 3 has a central hole (0.7 cm diameter) covered

with a thin copper foil soldered to the body of the lid. In this foil a small circular effusion hole was drilled. Two lids 3 with different holes were used in the experiments. One hole had an area of  $(6.55 \times 10^{-3} \pm 10^{-5})$  cm<sup>2</sup> and the other an area of  $(4.09 \times 10^{-3} \pm 10^{-5})$  cm<sup>2</sup>. The thickness of the copper foils where these holes were drilled was  $11.5 \times 10^{-3}$  cm and  $8.90 \times 10^{-3}$  cm respectively. A metallurgical microscope and a planimeter were used to obtain the areas.

The thickness values were measured with a micrometer.

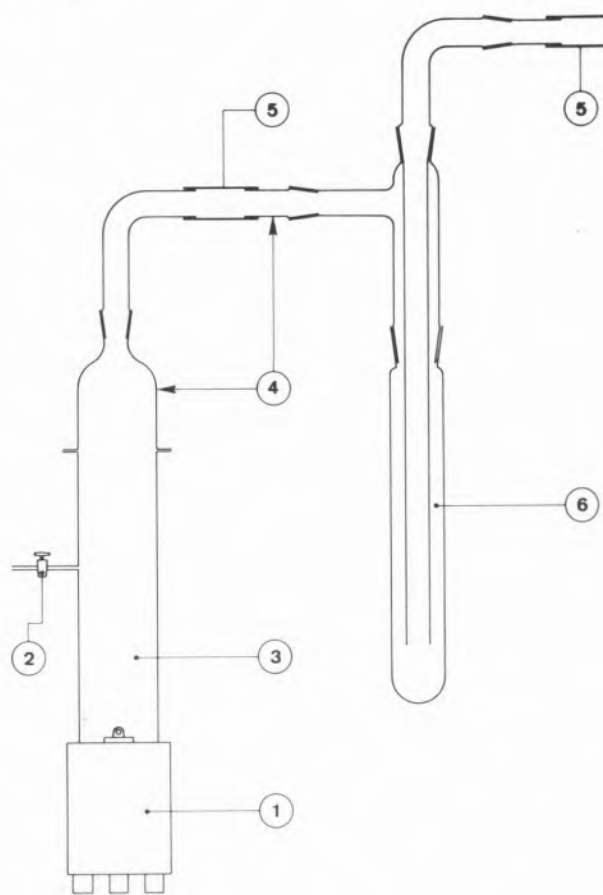


Fig. 2

Vacuum chamber and vacuum line: Brass block (1), nitrogen inlet (2), vacuum chamber (3), moveable connection with the vacuum line (4), neoprene tubing (5) and liquid nitrogen trap (6)

The time required for each experiment depended upon the substance under investigation, the bath temperature and the area of the effusion hole. Each run had to be long enough to assure a considerable mass of evaporated compound.

COMPOUNDS— $[\text{Fe}(\eta\text{-C}_5\text{H}_5)_2]$  was prepared by the reported method [4] and purified by resublimation in vacuum ( $\approx 1.3$  Pa) at  $70^\circ\text{C}$ .

$[\text{Mo}(\eta\text{-C}_5\text{H}_5)_2(\text{CH}_3)_2]$  was synthesized as described by BENFIELD and GREEN [5] and resublimed in vacuum ( $\approx 1.3$  Pa) at  $100^\circ\text{C}$ .

### 3 — RESULTS AND DISCUSSION

#### $[\text{Fe}(\eta\text{-C}_5\text{H}_5)_2]$

The vapour pressures of ferrocene, evaluated from the results obtained with the two cells each with a different effusion hole mentioned above, are presented in Tables 1 and 2. In those calculations, the equation [3, 6]

$$p = \frac{m}{At} \left( \frac{2\pi RT}{M} \right)^{1/2} \left( \frac{3l+8r}{8r} \right) \left( \frac{1}{1+K_2 r/2\lambda} \right) \quad (1)$$

Table 1  
Vapour pressures of  $[\text{Fe}(\eta\text{-C}_5\text{H}_5)_2, c]$   
Hole dimensions:  $A = 6.55 \times 10^{-3} \text{ cm}^2$ ,  
 $r = 4.566 \times 10^{-2} \text{ cm}$  and  $l = 11.5 \times 10^{-3} \text{ cm}$

T/K	t/s	m/g	p/Pa
299.65	39828	0.09245	1.055
300.95	31874	0.08295	1.177
302.15	31904	0.09544	1.343
303.05	27789	0.09074	1.459
300.55	33466	0.08470	1.146
298.95	33145	0.07150	0.983
296.95	34683	0.06070	0.803
297.55	32440	0.06052	0.854

Table 2  
Vapour pressures of  $[\text{Fe}(\eta\text{-C}_5\text{H}_5)_2, c]$   
Hole dimensions:  $A = 4.09 \times 10^{-3} \text{ cm}^2$ ,  
 $r = 3.608 \times 10^{-2} \text{ cm}$ , and  $l = 8.9 \times 10^{-3} \text{ cm}$

T/K	t/s	m/g	p/Pa
297.35	42175	0.04780	0.839
297.75	38123	0.04509	0.875
298.35	43754	0.05469	0.923
298.95	31948	0.04244	0.980
299.65	32813	0.04655	1.044
299.99	31070	0.04619	1.093
300.67	33803	0.05331	1.157
301.14	29653	0.04912	1.213

was used.  $m/g$  is the weight loss of compound during the time  $t/s$ ,  $A/\text{cm}^2$  is the area of the effusion hole, and  $M$  is the molecular weight of gaseous species. The correction term  $(3l+8r)/8r$  accounts for the fact that  $r/\text{cm}$ , the hole radius, is not infinitely larger than  $l/\text{cm}$ , the thickness of the foil where the hole was drilled. The second correction factor appears because  $\lambda/\text{cm}$ , the mean free path of the gaseous species, is not infinitely larger than  $r$ ;  $K_2$  is a constant equal to 0.48 when  $l \ll r$ .

The calculation of the mean free path from the equation

$$\lambda = \frac{kT}{\sqrt{2} \pi \sigma^2 p} \quad (2),$$

where  $k$  is Boltzmann constant, implied an estimation of the collision diameter  $\sigma/\text{cm}$  and a previous knowledge of the vapour pressure at temperature  $T$ . It was assumed  $\sigma = 736 \text{ pm}$  [3], the arithmetic mean of the two principal axis of ferrocene. An error of 10% in this value causes only 1% error in the vapour pressure. An initial  $\lambda_1$  was calculated after obtaining a first  $p_1$  by the expression

$$p_1 = \frac{m}{At} \left( \frac{2\pi RT}{M} \right)^{1/2} \left( \frac{3l+8r}{8r} \right) \quad (3).$$

$\lambda_1$  was then used to evaluate  $p_2$  by equation (1) which in turn was used to obtain  $\lambda_2$ . A third value for the vapour pressure,  $p_3$ , was finally derived.  $p_3$  differs from  $p_4$  by less of 0.03%.

$(p, T)$  values of Tables 1 and 2 were adjusted to Clausius-Clapeyron equation

$$\ln p = - \frac{B}{T} + C \quad (4)$$

by the least squares method. Two straight lines with correlation factors of 0.9997 and 0.9996 were obtained:

$$\ln p = (29.30 \pm 0.75) - (8765 \pm 224)/T \quad (5)$$

$$\ln p = (29.08 \pm 0.79) - (8699 \pm 237)/T \quad (6)$$

$(\ln p, 1/T)$  values of both Tables are represented in fig. 3.

The average of the slopes of equations (5) and (6) leads to a mean value for the enthalpy of sublima-

tion of ferrocene in the temperature range 297–303 K, which is assumed to be equal to  $\Delta H_{\text{S}}^{\circ}$ :

$$\Delta H_{\text{S}}^{\circ}[\text{Fe}(\eta\text{-C}_5\text{H}_5)_2] = 72.60 \pm 1.36 \text{ kJ mol}^{-1}$$

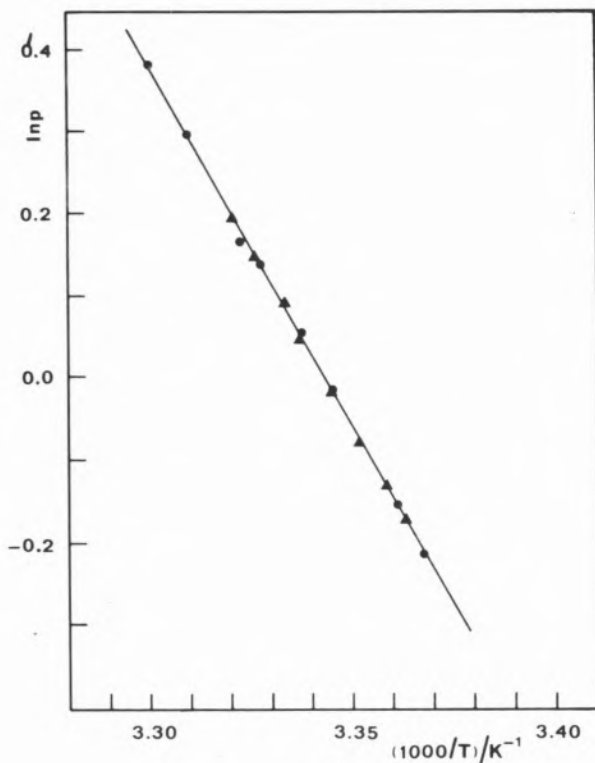


Fig. 3  
Vapour pressures of  $[\text{Fe}(\eta\text{-C}_5\text{H}_5)_2, \text{c}]$   
Circles — Values from Table 1  
Triangles — Values from Table 2

All the uncertainty intervals presented include Student's factor for 95% confidence level. However it is a common procedure in these kind of studies to consider only the mean standard deviation. Therefore, for comparison purposes the uncertainty of  $\Delta H_{\text{S}}^{\circ}[\text{Fe}(\eta\text{-C}_5\text{H}_5)_2]$  is reduced to  $\pm 0.56 \text{ kJ mol}^{-1}$ . Other literature values for the heat of sublimation of ferrocene are collected in Table 3. It can be seen

Table 3  
 $\Delta H_{\text{S}}^{\circ}[\text{Fe}(\eta\text{-C}_5\text{H}_5)_2]$  at 298.15 K

Method	$\Delta H_{\text{S}}^{\circ}/\text{kJ mol}^{-1}$	Year	Reference
Bourdon gauge	74.98	1952	[8]
Thermistor gauge	$72.38 \pm 1.26$	1962	[3]
Knudsen cell	$73.35 \pm 0.42$	1962	[3]
Knudsen cell	$72.73 \pm 0.54$	1969	[7]
Knudsen cell	$72.60 \pm 0.56$	1979	This work

that our value agrees well with previous results, particularly with the most recent ones.



The agreement between the vapour pressures of ferrocene obtained with the two different effusion holes demonstrated that self-cooling effect did not occur. As the vapour pressures of  $[\text{Mo}(\eta\text{-C}_5\text{H}_5)_2(\text{CH}_3)_2]$  are about 30 times smaller (Table 4), self-

Table 4  
Vapour pressures of  $[\text{Mo}(\eta\text{-C}_5\text{H}_5)_2(\text{CH}_3)_2, \text{c}]$

T/K	t/s	m/g	p/Pa
301.25	79675	0.00796	0.0412
303.20	82987	0.00974	0.0485
310.95	85380	0.02037	0.0993
313.55	72858	0.02174	0.1243
312.15	76838	0.01953	0.1059
312.15	74935	0.01984	0.1102
309.95	78765	0.01657	0.0875
308.95	75159	0.01436	0.0794
308.40	91450	0.01633	0.0742

-cooling effect was assumed to be inexistent in this case. Thus only one series of experiments was performed, using the largest effusion hole.

The experimental results are presented in Table 4. The vapour pressures were calculated by the method already described. A value  $1000 (\pm 100) \text{ pm}$  was assumed for the collision diameter. In the present case an error of 10% in  $\sigma$  causes only 0.1% error in the final value of  $p$ .

The least squares analysis of  $\ln p$  vs.  $1/T$  (fig. 4) led to

$$\ln p = (24.90 \pm 1.62) - (8469 \pm 501)/T \quad (7)$$

with a correlation factor of 0.998. From the slope of equation (7) a mean enthalpy of sublimation in the temperature range 301–314 K can be derived. This value is considered equal to  $\Delta H_{\text{S}}^{\circ}$ :

$$\Delta H_{\text{S}}^{\circ}[\text{Mo}(\eta\text{-C}_5\text{H}_5)_2(\text{CH}_3)_2] = 70.4 \pm 4.2 \text{ kJ mol}^{-1}$$

All the uncertainty intervals presented include Student's factor.

The differences between enthalpies of sublimation of analogous tungsten and molybdenum com-



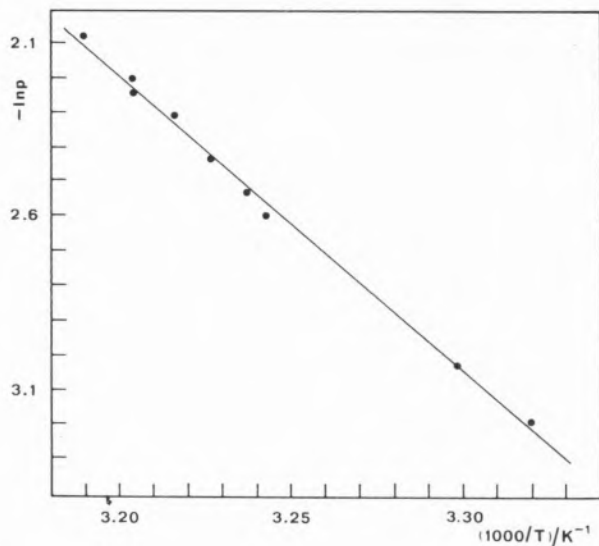


Fig. 4  
Vapour pressures of  $[Mo(\eta-C_5H_5)_2(CH_3)_2]c$

pounds are usually about  $4.2 \text{ kJ mol}^{-1}$  [9-13]. This evidence based the estimation of  $\Delta H_S^0$  for the tungsten complex. This is shown in Table 5, together with  $\Delta H_f^0(c)$  values derived in previous studies [2], and the obtained  $\Delta H_f^0(g)$  values.

Table 5  
Thermochemical data for  $[M(\eta-C_5H_5)_2(CH_3)_2]$  complexes ( $M = Mo, W$ ). Values in  $\text{kJ mol}^{-1}$ .

$[M(\eta-C_5H_5)_2(CH_3)_2]$	$\Delta H_f^0(c)$	$\Delta H_S^0$	$\Delta H_f^0(g)$
M = Mo	$283.8 \pm 4.0$	$70.4 \pm 4.2$	$354.2 \pm 5.8$
M = W	$284.8^* \pm 3.5$	$(74.6 \pm 4.2)$	$359.4 \pm 5.5$

\* — The value presented in ref. [2] is affected by a small calculation error.

The bond enthalpy contributions  $\bar{D}(M-CH_3)$  ( $M = Mo, W$ ) were finally recalculated as described in [2] from the new values of  $\Delta H_S^0$  and auxiliary literature data [2, 12, 14-16], including a recent value for  $\Delta H^0[CH_3, g]$  [17]:

$$\begin{aligned}\bar{D}(Mo-CH_3) &= 154.5 & \text{kJ mol}^{-1} \\ \bar{D}(W-CH_3) &= 209.9 & \text{kJ mol}^{-1}\end{aligned}$$

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## RESUMO

Entalpia de sublimação padrão do complexo



Redeterminação das energias de ligação  $Mo-CH_3$  e  $W-CH_3$ .

Usando resultados termoquímicos previamente publicados e  $\Delta H_S^0[Mo(\eta-C_5H_5)_2(CH_3)_2] = 70.4 \pm 4.2 \text{ kJ mol}^{-1}$ , valor obtido neste trabalho, chegou-se às energias de ligação  $D(Mo-CH_3) = 154.5 \text{ kJ mol}^{-1}$  e  $D(W-CH_3) = 209.9 \text{ kJ mol}^{-1}$  nos complexos  $[M(\eta-C_5H_5)_2(CH_3)_2]$  ( $M = Mo, W$ ). A entalpia de sublimação referida foi calculada através de medidas de pressão-temperatura, feitas usando uma célula de Knudsen. Esta célula, que é também descrita, foi testada comparando o valor determinado para  $\Delta H^0[Fe(\eta-C_5H_5)_2] = 72.60 \text{ kJ mol}^{-1}$  com outros resultados da literatura.