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VAPOUR PRESSURES AND ENTHALPIES OF SUBLIMATION OF FERROCENE, COBALTOCENE AND NICKELOCENE

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ABSTRACT

The vapour pressure measurements for three metallocenes were made using the Knudsen effusion method. With the Clausius–Clapeyron equation the enthalpies of sublimation were calculated as ferrocene, $\Delta_{\text{sub}}H_{\text{m}}^{0}$ (293.6 K) = 72.07 ± 0.36 kJ mol^{-1}; cobaltocene, $\Delta_{\text{sub}}H_{\text{m}}^{0}$ (310.5 K) = 72.09 ± 0.11 kJ mol^{-1}; nickelocene, $\Delta_{\text{sub}}H_{\text{m}}^{0}$ (294.5 K) = 71.47 ± 0.63 kJ mol^{-1}.

INTRODUCTION

Metallocenes and their derivatives have a wide chemical and thermochemical importance since they are representatives of a family of compounds whose symmetry permits the calculation of the bond energy terms. For this calculation, however, the precise enthalpies of sublimation are necessary.

While for ferrocene several pertinent works have been reported [1–6] and nickelocene has been studied by Turnbull [7], the experimental vapour presure and enthalpy of sublimation for cobaltocene are not available. In our laboratory a systematic work on the thermochemistry of organometallic compounds has been initiated and we have considered that more vapour pressure measurements on these three compounds would be convenient.

EXPERIMENTAL

The substances employed in this work were ferrocene (Fluka) purified by sublimation and naphthalene (Merck) purified by zone melting; purities were determined by DSC as 99.90 and 99.98 mol%, respectively. Cobaltocene (sublimed, Strem Chem.) and nickelocene (sublimed, Fluka) were used from ampoules opened just before the experiments; purity determination by DSC for the two last compounds was not possible.

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The vapour pressure determinations were made by the Knudsen method using a stainless steel cylindrical cell ($h = 23$ mm, $d = 13.4$ mm). The effusion hole was made on platinum foil (thickness 0.044 mm) which was soldered on the brass cover. The seal between the body and cover of the cell was a teflon gasket (thickness 0.7 mm), and several assays were made for testing the quality of the seal. The hole area was measured by optical microscopy and was determined as 0.256 mm^2.

The total mass loss rate was measured with an electrobalance (Cahn R-100) coupled to the vacuum system. A digital multimeter (HP-3478A) was connected to the analogical output of the balance, and data were taken automatically with a microcomputer (HP-85B). Full scale and linearity of the balance were tested before and after each experiment with known masses.

The temperature was maintained constant within 0.005 K with a solid state thermistor controller and measured with a platinum resistance thermometer (Guildline-9535) calibrated against one calibrated to N.B.S. Thermocouples inside the cylindrical glass tubes of the balance were placed near the sides and bottom of the Knudsen cell and showed no temperature differences with the one placed in the bath. The precision of the temperature measurements was estimated as 0.05 K or better.

The system was tested with naphthalene, since this was recommended as reference substance for vapour pressure measurements [8]. The test was satisfactory and agreed with the vapour pressures and enthalpies of sublimation reported by De Kruif and Van Ginkel [9] and Colomina et al. [10] using the Knudsen effusion method.

RESULTS

The vapour pressures were calculated with the Knudsen equation

$$P_{\mathrm{v}} = \frac{\Delta m}{\Delta t}\frac{1}{A}\sqrt{\left(\frac{2\pi RT}{M}\right)}\frac{1}{F} \tag{1}$$

where $\Delta m/\Delta t$ is the mass loss rate, A is the effusion hole area, R is the gas constant, T is the absolute temperature, M is the molar mass and F is the Clausing factor [11]. The results are summarized in Tables 1, 2 and 3. We have used a non-weighted least-squares fit of the data to eqn. (2)

$$R \ln P = A + B/T \tag{2}$$

The third and fourth columns in Tables 1–3 show the experimental and calculated values of pressure and the fifth and sixth columns the difference of pressures and $100\Delta \ln P$ values.

The negative of the values of coefficient B are identified as the enthalpy of sublimation $\Delta_{\mathrm{sub}}H_{\mathrm{m}}^{0}(T)$ at the mean temperature at which the vapour

TABLE 1

Vapour pressures of ferrocene

T (K)	$(\Delta m/\Delta t)\times 10^7$ (g s^{-1})	P_{exp} (Pa)	P_{cal} (Pa)	ΔP (Pa)	$100\Delta \ln P$
278.15	1.11	0.13	0.13	0.00	0.80
281.15	1.52	0.18	0.18	0.00	0.08
286.15	2.52	0.30	0.31	−0.01	−2.71
288.61	3.34	0.41	0.40	0.01	2.70
293.85	5.63	0.67	0.68	−0.01	−1.75
297.93	8.39	1.03	1.02	0.01	0.86
299.67	9.93	1.21	1.21	0.00	0.07
302.18	12.43	1.53	1.54	−0.01	−0.50
305.54	17.05	2.10	2.11	−0.01	−0.38
309.00	23.58	2.92	2.90	0.02	0.82

$A = 242.09 \pm 1.23$ J K^{-1} mol^{-1}; $B = -72073 \pm 362$ J mol^{-1}.

pressure measurements were made. The enthalpies of sublimation are presented in Table 4 and the standard deviation is the same as that of the slope B of eqn. (2) and it was calculated as indicated in ref. 12.

DISCUSSION

Table 5 collects the values of enthalpy of sublimation for ferrocene in order to show the reliability of our measurements. There is very good agreement with the most recent values reported in the literature [3–6]

TABLE 2

Vapour pressures of cobaltocene

T (K)	$(\Delta m/\Delta t)\times 10^7$ (g s^{-1})	P_{exp} (Pa)	P_{cal} (Pa)	ΔP (Pa)	$100\Delta \ln P$
296.53	3.49	0.42	0.42	0.00	−0.43
298.86	4.39	0.53	0.53	0.00	0.04
300.38	5.04	0.61	0.61	0.00	−0.59
302.35	6.09	0.74	0.74	0.00	−0.08
304.72	7.62	0.93	0.93	0.00	0.47
306.50	8.99	1.10	1.09	0.01	0.73
308.15	10.35	1.27	1.27	0.00	−0.05
310.45	12.75	1.57	1.57	0.00	0.31
312.30	14.98	1.85	1.85	0.00	0.17
317.17	22.74	2.83	2.83	0.00	0.05
320.08	28.96	3.62	3.63	−0.01	−0.19
324.54	41.64	5.24	5.26	−0.02	−0.44

$A = 235.95 \pm 0.36$ J K^{-1} mol^{-1}; $B = -72095 \pm 111$ J mol^{-1}.

TABLE 3

Vapour pressures of nickelocene

T (K)	$(\Delta m/\Delta t)\times 10^7$ (g s^{-1})	P_{exp} (Pa)	P_{cal} (Pa)	ΔP (Pa)	100Δ ln P
283.40	1.95	0.23	0.22	0.01	5.39
285.55	2.28	0.27	0.27	0.00	−1.41
287.75	2.87	0.34	0.34	0.00	−1.37
289.18	3.28	0.39	0.40	−0.01	−2.43
291.25	4.11	0.49	0.49	−0.00	−0.73
293.33	5.01	0.60	0.61	−0.01	−1.40
295.78	6.40	0.77	0.78	−0.01	−0.73
297.85	7.87	0.95	0.95	0.00	0.08
299.57	9.26	1.12	1.12	0.00	−0.03
301.46	11.12	1.35	1.34	0.01	0.66
303.29	13.22	1.61	1.59	0.02	1.06
305.70	16.44	2.01	1.99	0.02	0.91

$A = 239.51 \pm 2.14$ J K^{-1} mol^{-1}; $B = -71468 \pm 630$ J mol^{-1}.

TABLE 4

Enthalpies of sublimation of metallocenes

Substance	T (K)	$\Delta_{sub} H_m^0 (T)$ (kJ mol^{-1})
Ferrocene	293.6	72.07 ± 0.36
Cobaltocene	310.5	72.09 ± 0.11
Nickelocene	294.5	71.47 ± 0.63

TABLE 5

Enthalpies of sublimation of ferrocene

Reference	T (K)	Method	$\Delta_{sub} H_m^0 (T)$ (kJ mol^{-1})
1	357–454	Bourdon gauge	70.46
2	323–367	Knudsen effusion	83.26
3	295–303	Knudsen effusion	76.56 ± 0.13
3	295–303	Knudsen effusion with Hiby and Pahl factor	73.35 ± 0.42
3	295–303	Static-thermistor gauge	72.38 ± 1.26
4	293–306	Knudson effusion	72.72 ± 0.54
5	288–353	Torsion–effusion	72.85 ± 0.88 [a]
6	277–297	Torsion–effusion	75.90 ± 0.69
6	277–297	Knudsen effusion	73.39 ± 0.12
6	329–360	Static diaphragm gauge	70.45 ± 0.23
This work	278–309	Knudsen effusion	72.07 ± 0.13

[a] Calculated from the vapour pressure–temperature equation of ref. 5.

considering the temperature range of the study and the experimental errors.

Turnbull [7] has reported the only value of enthalpy of sublimation for nickelocene (72.4 ± 1.2 kJ mol^{-1}), in good agreement with our value (71.47 ± 0.20 kJ mol^{-1}).

For cobaltocene no experimental data of vapour pressure have been reported, therefore no comparison is possible.

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