Journal of Organometallic Chemistry
Elsevier Sequoia S.A., Lausanne
Printed in The Netherlands

NOTE

VAPOR PRESSURE AND THIRD-LAW ENTROPY OF FERROCENE

JOHN T. S. ANDREWS AND EDGAR F. WESTRUM, JR.
Department of Chemistry, University of Michigan, Ann Arbor, Michigan 48104 (U.S.A.)

(Received January 31st, 1969)

Subsequent to Edwards and Kington's[1] use of a third-law entropy check to show that the rings in the ferrocene (dicyclopentadienyliron) molecule rotate essentially freely about the ring-to-metal bond, new data relevant to the statistical calculation of the entropy have appeared and imply the desirability of performing the entropy check anew. The frequency assignments of Lippincott and Nelson[2] used in evaluating the vibrational entropy of the molecule have been superceded by the assignment of Stammreich (reported by Fritz[3]), and the structural parameters affecting rotational entropies are now available from the electron-diffraction study of Bohn and Haaland[4]

TABLE 1

FREQUENCY ASSIGNMENTS FOR FERROCENE[a]

Symmetry species[b]	Frequency number	Frequencies		Symmetry species[b]	Frequency number	Frequencies	
		Ref. 3	Ref. 2			Ref. 3	Ref. 2
A_{1g}	1	3110	3099	A_{2u}	8	3086	3085
	3	1390	1105		10	1408	1108
	4	306	303		11	478	478
A_{2u}	9	1104	811	A_{1g}	2	1105	804
A_{2g}	7	(1249)	1200	A_{1u}	5	(1253)	1200
					6	Torsion	
E_{1g}	14	818	800	E_{1u}	19	814	834
	16	390	388		21	490	492
					22	(170)	150
E_{1u}	17	3086	3075	E_{1g}	12	3089	3085
	18	1004	1002		13	998	1010
	20	1408	1411		15	1412	1408
E_{2g}	23	3045	3085	E_{2u}	29	(3035)	3100
	24	1361	1178		30	(1351)	1170
	26	1527	1590		32	[1527]	1550
	27	1054	900		33	(1054)	900
E_{2u}	31	(1188)	1050	E_{2g}	25	1184	1050
	34	(567)	500		28	591	500

[a] Units: cm^{-1}. [b] The frequencies of the E species are doubly degenerate.

rather than from the X-ray study of Eiland and Pepinsky[5] (used by Edwards and Kington). The electron diffraction determination also provides an independent estimate of the energy barrier to internal rotation.

Both sets of vibrational frequency assignments for ferrocene are listed in Table 1 ; those of Stammreich are employed for the computation of the entropy contributions ($S_{\text{trans}}+S_{\text{rot}}+S_{\text{vib}}+S_{\text{ir}}=S_{\text{tot}}$) listed for several temperatures in Table 2. Comparison of the spectroscopic S_{tot} with S° gas as evaluated using the vapor pressure data of Edwards and Kington leads to an entropy discrepancy of about 1.6 cal · mole^{-1}·°K^{-1} in the sense opposite to that explicable by the use of the Third Law. The concern is accented by Turnbull's[6] use of these new data together with empirical relationships regarding the entropy of sublimation of dicyclopentadienyl metal compounds to obtain an "entropy discrepancy" of 1.2 cal · mole^{-1}·°K^{-1} which he attributed to vibrational anharmonicity, etc.

TABLE 2

STANDARD SPECTROSCOPIC ENTROPY OF FERROCENE[a]

T	S°_{trans}	S_{rot}	S_{vib}	S_{ir}	$S^\circ(\text{g})^b$ (spectro)	$\Delta S_{\text{rr}}{}^c$
270	41.08	24.38	12.04	5.37	82.87	−0.31
273.15	41.13	24.41	12.29	5.38	83.21	−0.30
280	41.26	24.49	12.84	5.40	83.99	−0.29
290	41.43	24.59	13.66	5.44	85.12	−0.27
298.15	41.57	24.67	14.34	5.46	86.04	−0.26
300	41.60	24.69	14.50	5.47	86.26	−0.25
					±0.3	±0.15[d]

[a] Units: cal, mole, °K. [b] For the freely rotating system. [c] ΔS_{rr} is the entropy decrement from the free to the restricted rotator. [d] At 298.15°K, based on Haaland's uncertainty in the barrier height.

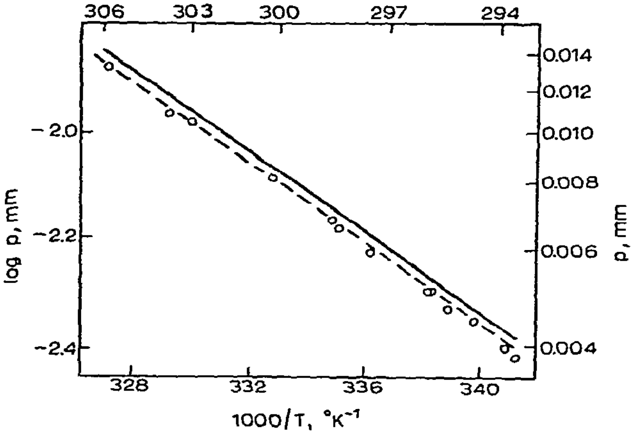

Fig. 1. The vapor pressure of ferrocene as a function of temperature. The ○ represent the experimental determinations of this research. The dashed line represents the least squares fit to these values, and the solid line is the curve reported by Edwards and Kington[1].

We, therefore, redetermined the vapor (or sublimation) pressure of ferrocene using a Knudsen effusion apparatus similar to that described by Edwards and Kington. The resultant pressures computed according to the formulations described elsewhere[7], are compared in Fig. 1 with those previously reported[1] and may be represented by the relationship (p in mm, T in °K):

$$\log_{10} p = A + B/T + C \cdot \log_{10} T$$

in which $A = 28.17 \pm 0.10$, $B = -4581 \pm 29$ °K and $C = -6.04$. The values of A and B were determined by a least squares analysis of the data; that of C was constrained to accord with the difference between the measured heat capacity of the crystal phase and the calculated heat capacity of the vapor phase. The enthalpy and entropy of vaporization may then be expressed as:

$$\Delta H_{vap} = 20.96 \pm 0.13 - 0.012\ T\ (\text{kcal} \cdot \text{mole}^{-1})$$
$$\Delta S_{vap} = (20960 \pm 130)/T - 12\ (\text{cal} \cdot \text{mole}^{-1} \cdot {}^{\circ}\text{K}^{-1})$$

Haaland and Nilsson[8] evaluated the energy barrier to internal rotation in ferrocene as 900±300 cal·mole^{-1}. This value with the partition function for the free rotor enables us to calculate the entropy decrement between the free and the restricted rotor (*cf.* Pitzer and Brewer[9]). The calculation shows the entropy of the restricted rotor to be about 0.3 cal·mole^{-1}·°K^{-1} lower than that of the free rotor. As shown in Table 3, the total statistico-mechanical entropy based on the new spectral and structural data accords (within experimental error, 0.7±0.6 cal·mole^{-1}·°K^{-1}) with the third-law entropy calculated in part from the sublimation pressure data reported herein. Inclusion of the term from Table 2 calculated for the rotational barrier of Haaland worsens the agreement by 0.3±0.2 cal·mole^{-1}·°K^{-1}. The presence of a small barrier to the rotation of the cyclopentadienyl rings about the main symmetry axis cannot certainly be excluded if allowance is made for neglect of vibrational anharmonicity and possible rotation–vibration coupling.

TABLE 3

ENTROPY COMPARISON FOR FERROCENE[a]

T	$S^{\circ}(c)$[b]	ΔS_{vap}[c]	ΔS_{comp}[d]	S° (g) (3rd Law)	S'° (g) (spectro)	$S^{\circ} - S'^{\circ}$
270	47.29	65.64	−29.35	83.58	82.87	0.71
273.15	47.78	64.74	−28.59	83.93	83.21	0.72
280	48.84	62.87	−27.01	84.70	83.99	0.71
290	50.40	60.29	−24.85	85.84	85.12	0.72
298.15	51.68	58.31	−23.21	86.78	86.04	0.74
300	51.97	57.88	−22.85	87.00	86.26	0.74
	±0.1	±0.4	±0.3	±0.5	±0.3	±0.6

[a] Units: cal, mole, °K. [b] Standard entropy of crystal, from ref. 1. [c] ΔS_{vap}, entropy of vaporization (sublimation) at T. [d] ΔS_{comp}, entropy of compression from saturation pressure to one atm.

Standard deviations have been used for precision indices throughout.

ACKNOWLEDGEMENT

The generous support of this research by the U.S. Atomic Energy Commission is acknowledged with gratitude.

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