Internal Rotation and Third Law Entropy of Ferrocene

ARNE HAALAND

Department of Chemistry, University of Oslo, Blindern, Oslo 3, Norway

The third law entropy of gaseous ferrocene at 298.15°K and 1 atm. was first reported by Edwards and Kington.[1] Recently Andrews and Westrum [2] have redetermined the vapor pressure of the compound as a function of temperature and have obtained pressures that are slightly lower than those reported by Edwards and Kington.[3] After correction for this discrepancy the third law entropy is 86.78 ± 0.50 cal.mole^{-1}deg.$^{-1}$.[2]

Andrews and Westrum [2] have also calculated the spectroscopic entropy under the assumption of nonhindered rotation of the cyclopentadienyl rings. Their results are listed in Table 1. The spectroscopic entropy is found to be 0.74 ± 0.60 cal mole^{-1} deg.$^{-1}$ less than the third law entropy. Haaland and Nilsson have determined the barrier to internal rotation in ferrocene by means of gas phase electron diffraction;[4] $V_0 = 900 \pm 300$ cal. mole^{-1}. When this is taken into account, the spectroscopic entropy is decreased by 0.26 ± 0.15 cal. mole^{-1} deg.$^{-1}$,[2] and the fit becomes worse.

The assignment of vibrational frequencies on which Andrews and Westrum base their calculations [5] have, however, been found to be incorrect.[6,7] We have therefore repeated the calculation of the spectroscopic entropy and have obtained a value which after inclusion of the effect of the restricting potential is in satisfactory agreement with the third law entropy.

The calculations have been based on the molecular parameters of Haaland and Nilsson,[4] since those of Bohn and Haaland [8] have been found to be flawed by a minor scale error.[4] This leads to insignificant changes in $S_{rot.}$ and $S_{int.rot.}$. The assignment of vibrational frequencies used is listed in Table 2. For IR and Raman active lines the assignment is that of Hartley and Ware [7] who have studied the spectrum of crystalline ferrocene. These workers do not assign ν_{27}, so this frequency was taken from Long and Huege.[6] The inactive frequencies have been taken from the crystal spectra reported by Winter, Curnutte and Whitcomb [9] but the assignment of ν_{32} is changed to 1351 cm^{-1} in order to make it roughly equal to ν_{26}. Winter *et al.*[9] interpreted this line as $\nu_{22}+\nu_{30}$. ν_7 which is not assigned in any of these studies was taken from Fritz.[5]

The spectroscopic entropy for molecules with a restricting barrier of 900 cal. mole^{-1} is found to be 86.38 cal. mole^{-1} deg.$^{-1}$ in satisfactory agreement with the third law entropy of 86.78 ± 0.50 cal. mole^{-1} deg.$^{-1}$. It should be noted that about one third of the vibrational entropy is associated with the doubly degenerate ring-metal-ring deformation frequency at $\nu_{22} = 179$ cm^{-1}. Fritz [10] gives the position of this line in the crystal spectrum as 166.3 ± 0.5 cm^{-1}. If this value is used, the spectroscopic entropy becomes 86.78 cal. mole^{-1} deg.$^{-1}$ in perfect agreement with the third law value.

The uncertainties involved in the present calculation (the use of crystal spectra, the neglect of anharmonicity) are so large that it should not be taken as a confirmation of the existence of a restricting barrier of the magnitude found by Haaland and Nilsson. It merely demonstrates that a satisfactory agreement between third law

Table 1. Spectroscopic entropy of ferrocene gas at 298.15°K and 1 atm. in units of cal. mole^{-1} deg^{-1}.

	$S^\circ_{trans.}$	$S_{rot.}$	$S_{vib.}$	$S_{int.rot.}$	$\Delta S_{rest.rot.}$	S°_{total}
Ref. 2	41.57	24.67	14.34	5.46		86.04 ± 0.3
This work	41.57	24.70	14.90	5.47	−0.26	86.38

Third law entropy $S^\circ = 86.78 \pm 0.5$.

Table 2. Fundamental frequencies of ferrocene.

Number, species and activity		ν (cm^{-1})	Ref.
a_{1g}	1	3112	7
R	2	815	7
	3	1106	7
	4	311	7
a_{1u}	5	1257	9
	6	Ring torsion	
a_{2g}	7	1249	5
a_{2u}	8	3098	7
IR	9	818	7
	10	1107	7
	11	477	7
e_{1g}	12	3089	7
R	13	1001	7
	14	815	7
	15	1414	7
	16	393	7
e_{1u}	17	3098	7
IR	18	1006	7
	19	840	7
	20	1414	7
	21	490	7
	22	179	7
e_{2g}	23	3103	7
R	24	1197	7
	25	1062	7
	26	1358	7
	27	892	6
	28	600	7
e_{2u}	29	3159	9
	30	1189	9
	31	1056	9
	32	1351	9
	33	885	9
	34	569	9

and spectroscopic entropies can be obtained with such a barrier as well as without one.

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On the Molecular Structure of Perfluorobicyclo(2.2.0) hexa-2,5-diene (Perfluoro-Dewar-benzene)

BIRGIT ANDERSEN and H. M. SEIP

Department of Chemistry, University of Oslo, Oslo 3, Norway

and

B. BEAGLEY

Department of Chemistry, The University of Manchester Institute of Science and Technology, Manchester

We wish in this note to report some preliminary results of an electron-diffraction investigation of gaseous perfluoro-Dewar-benzene (Fig. 1). The compound was kindly supplied by the organic section of the Chemistry Department at the University of Manchester Institute of Science and Technology. The intensity data were recorded with a Balzer diffraction instrument in the same department. The results presented here are based on intensity data from only one nozzle-to-plate distance, *i.e.* about 50 cm. Because of the very limited s-range (1.5–16.0 Å^{-1}) a precision determination of all the molecular parameters could not be carried out.