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Note

Thermodynamic properties of methylvinylsulphide

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Using the molecular and spectroscopic data as given by Fabian et al.[1], the authors have estimated the thermodynamic functions—heat capacity, entropy, enthalpy and free energy for methylvinylsulphide in the ideal gas state at a pressure of 1 atm. These thermodynamic functions (Table 1) were obtained by means of statistical

TABLE 1

THERMODYNAMIC FUNCTIONS OF METHYLVINYLSULPHIDE

Temperature (*K*)	*Heat capacity*, C_p° (*cal mol*$^{-1}$ *K*$^{-1}$)	*Entropy*, S° (*cal mol*$^{-1}$ *K*$^{-1}$)	*Enthalpy function*, $(H^\circ - H_0^\circ)/T$ (*cal mol*$^{-1}$ *K*$^{-1}$)	*Free energy function*, $-(F^\circ - H_0^\circ)/T$ (*cal mol*$^{-1}$ *K*$^{-1}$)
234.04	16.61	67.70	11.60	56.09
273.15	18.46	70.41	12.45	57.95
298.15	19.64	72.07	13.00	59.07
350.00	22.07	75.41	14.18	61.24
400.00	24.29	78.52	15.30	63.22
450.00	26.34	81.50	16.41	65.07
500.00	28.22	84.37	17.50	66.86
550.00	29.94	87.14	18.55	68.59
600.00	31.51	89.82	19.57	70.24
650.00	32.94	92.39	20.54	71.84
700.00	34.27	94.88	21.48	73.40
750.00	35.50	97.29	22.37	74.91
800.00	36.64	99.62	23.24	76.37
850.00	37.69	101.87	24.05	77.81
900.00	38.68	104.06	24.84	79.21
950.00	39.58	106.17	25.59	80.57

mechanical calculations considering the behaviour of the methylvinylsulphide molecule as that of a harmonic oscillator. The internal rotational barrier contribution, however, was treated by means of the method by Pitzer and Gwinn[2] assuming that

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the torsional mode of the methyl group can be characterized as the motion of a symmetric top.

Table 2 gives the values of molecular parameters needed to calculate the thermodynamic functions presented. Fabian et al.[1] have indicated that at room temperature methylvinylsulphide may have at least 2 rotational isomers: the planar

TABLE 2

SUMMARY OF MOLECULAR PARAMETERS USED

Frequencies in wave numbers[1] (cm^{-1})

3095	2994	1584	1390	1038	953	677	401
3033	2981	1442	1315	1030[a]	859	595	254
3014	2922	1432	1277	963	739	455	150[b]

Principal moments of inertia[1] ($g\ cm^2 \times 10^{40}$)

$I_A = 83$ $I_B = 156$ $I_C = 239$

Symmetry number[1] = 3

[a] According to Fabian et al.[1], ν_{11} mode of vibration overlaps ν_{12} frequency; hence since ν_{12} should be somewhat less than ν_{11} frequency[1], it is assumed in this work that $\nu_{11} = 1030\ cm^{-1}$. [b] Following the suggestion by Fabian et al.[1], we propose for torsional frequency, $\nu_{24} = 150\ cm^{-1}$. The internal rotational barrier was calculated assuming that this torsional frequency behaves as a harmonic oscillator using formula: $\nu_{torsional} = n_m/2\pi(V_0/2I_{red})^{1/2}$, where $n_m = 3$ (assumed three-fold rotational barrier); V_0 is the sought for restricted internal rotational barrier and I_{red} = reduced moment of inertia[3].

s-cis and the *s-trans* molecular structure. Of these two, the *s-cis* form is the more stable configuration with an isomer enthalpy difference[1] of 1.4 kcal mol^{-1} indicating a relatively large amount of the *s-cis* isomer molecular form present at the equilibrium state. On the other hand, for the given frequency assignments (Table 2) it can be shown by calculation that the difference between the thermodynamic properties is very small ($\leq 0.1\%$). Consequently, the thermodynamic functions presented in Table 1 and obtained by using the planar *s-cis* isomer structural data within a calculation error of 0.2% represent the thermodynamic functions for the methylvinylsulphide molecule.

Although to our knowledge there are no available experimental data to verify the results presented, we feel in view of the completeness of the experimental structural and spectroscopic data used that the thermodynamic function values calculated will be within $\pm 1.0\%$.

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