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Note

Ideal gas state thermodynamic functions for dimethylsulfate

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Using the recently available molecular and spectroscopic data[1–3], the authors of this Note have estimated the thermodynamic functions—heat capacity, entropy, enthalpy and free energy—for dimethylsulfate in the ideal gas state at 1 atmosphere pressure. Table 1 presents the thermodynamic functions obtained by means of statistical mechanical calculations using the harmonic oscillator approximation. The internal rotational barrier contribution was treated by means of the Pitzer–Gwinn method[4] assuming that the torsional mode of the methyl group can be characterized as the motion of a symmetric rotating top. The results given in Table 1 are fitted to the correlating equation

$$A = a + bT + cT^2 \tag{1}$$

where A is any one of the calculated thermodynamic functions (Tables 1 and 2) and T is the temperature (K). The constants a, b, c in eqn (1) were evaluated using standard least-squares curve fitting methods[5] and are given in Table 2. The use of eqn (1) causes a standard deviation (Table 2) in the calculated thermodynamic function values from those as shown in Table 1. Table 3 gives the values of molecular parameters needed to calculate the presented thermodynamic functions.

Following Christe and Curtis[1], the $COSO_2OC$ molecular skeleton was considered to be nonplanar having C_{2v} symmetry. To calculate the principal moments of inertia (Table 3) the required structural data (or at least sufficiently accurate approximations) were taken from the following compounds (ref. 3) for comparison: H_2SO_4 (S=O bond distance); $NO_2 \cdot HS_2O_7$ (S–O bond length, O–S–O angle; and by comparison S–O–C angle) and $C_4H_6O_4$ (O–C bond distance). The values of the reduced moment of inertia[6,7] given in Table 3, were calculated from the equation

$$I_r = \frac{A_m A_r}{A_m + A_r} \tag{2}$$

where A_m is the moment of inertia of the rotating CH_3 group; and A_r is the moment of inertia of the rest of the molecule with respect to the same axis of rotation. The coordinates of the axis of rotation of the CH_3 group with respect to the rest of the molecule were chosen such that the rotating CH_3 group had a zero product of inertia about the axis of rotation; i.e. the rotating CH_3 group is a symmetri crotating top.

As there are no available experimental data (for instance, microwave or infrared), it was difficult to suggest with certainty any "best" value for the internal rotational barrier (Table 3). On the one hand, Christe and Curtis[1] observe that the CH_3 torsion mode for the $CH_3OSO_2OCH_3$ molecule should be below 250 cm^{-1};

TABLE 1

DIMETHYLSULFATE THERMODYNAMIC FUNCTIONS

Temperature, K	*Heat capacity C_p°, cal mole^{-1} K^{-1}*	*Entropy S°, cal mole^{-1} K^{-1}*	*Enthalpy function $(H^\circ - H_0^\circ)/T$, cal mole^{-1} K^{-1}*	*Free energy function, $-(F^\circ - H_0^\circ)/T$, cal mole^{-1} K^{-1}*
298.15	28.03	80.09	16.59	63.50
300.00	28.16	80.27	16.66	63.61
350.00	31.51	84.87	18.56	66.31
400.00	34.59	89.32	20.37	68.95
450.00	37.37	93.51	22.10	71.41
500.00	39.90	97.59	23.75	73.84
550.00	42.18	101.49	25.32	76.17
600.00	44.25	105.25	26.84	78.41
650.00	46.11	108.86	28.22	80.64
700.00	47.81	112.35	29.57	82.78
750.00	49.37	115.70	30.84	84.86
800.00	50.78	118.93	32.04	86.89
850.00	52.08	122.04	33.17	88.87
900.00	53.29	125.06	34.26	90.80
950.00	54.40	127.96	35.27	92.69
1000.00	55.42	130.78	36.26	94.52

TABLE 2

CALCULATED CONSTANTS *a*, *b* AND *c* FOR USE IN EQUATION (1)

Function	*a*	*b* × *10*^{2}	*c* × *10*^{5}	*Standard deviation*[a] *S, cal mole*$^{-1}$ *K*$^{-1}$
C_p°	6.1659	8.5000	−3.607	0.2374
$-(F^\circ - H_0^\circ)/T$	46.5977	6.08	−1.299	0.0627
S°	50.5563	10.76	−2.757	0.0937
$(H^\circ - H_0^\circ)/T$	3.9586	4.68	−1.458	0.0349

[a] Standard deviation of residuals

$$S = [\sum_{i=1}^{n} (y_{i'} - y_{i''})^2]/(n - m - 1)$$

where n is the number of observations, m is the number of independent variables, $y_{i'}$ is the observed value of y (Table 1) and $y_{i''}$ is the i-th predicted value of y (eqn (1)).

TABLE 3

SUMMARY OF MOLECULAR PARAMETERS USED

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

3050	2969	1443	1389	1165	828	556	399
3050	2969	1443	1196	1165	757	513	390
3030	1459	1443	1180	1002	590	501	253
3030	1459	1443	1180	982	568	424	

Principal moments of inertia[a], gm cm$^2 \times 10^{39}$

$I_A = 15.25794$
$I_B = 50.40475$
$I_C = 52.00085$

Reduced moment of inertia[a], gm cm$^2 \times 10^{39}$

$I_r = 0.611508$

Symmetry number[1] = 2
Internal rotational barrier[a] = 2425 cal mole^{-1}
Number of rotational barrier minima[b] = 3
Molecular weight = 126.14

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[a] Calculated, this work. [b] Considering similar substances, ref. 2, this is assumed to be a threefold barrier, hence $n = 3$.

while on the other hand, Fateley and Miller[2] present values for the CH_3 torsional frequencies for $(CH_3)_2O$ and $(CH_3)_2S$ molecules as 242 and 182 cm^{-1}, respectively. Considering the vicinal effects of the CH_3 group in dimethylsulfate, dimethylether and dimethylsulfide molecules, it was felt from molecular structural, bonding and electronic–vibrational considerations that the value of the torsional mode for dimethylsulfate should be closer to dimethylether than to the dimethylsulfide internal rotational barrier. Considering this and noting that all of these given barrier heights show an experimental uncertainty of 3.5 to 4.5%[2], it appeared reasonable to suggest that within a 5% range of uncertainty the potential barrier height for dimethylsulfate should be 2425 cal mole^{-1}. This proposed barrier for dimethylsulfate is 7.6% less than that for dimethylether, but 9.6% larger than that for dimethylsulfide. The proposed barrier height of 2425 cal mole^{-1} for dimethylsulfate as already stated is indirectly verified on the high side (should not exceed 250 cm^{-1}) by Christe and Curtis[1]. Although there are no available experimental data to verify our results, we feel, in view of our approximations and assumptions, that the uncertainty found in the calculated thermodynamic function values will be within the bounds of ±3%.

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