

### The Entropy of Dimethyl Sulfide from Low Temperature Calorimetric Measurements. Restricted Rotation of the Methyl Groups

In order to arrive at a satisfactory theory for the potential restricting the rotation of methyl groups in many molecules, it is desirable to determine how the magnitude of the barrier depends on the kind of atom to which the methyl groups are bonded. Recently we have obtained an estimate of the barriers in dimethyl sulfide by comparing the entropy obtained from calorimetric measurements extending to low temperatures with that computed from molecular data.

The heat capacities of dimethyl sulfide in the temperature range 13.4 to 291°K, heat of fusion, and heat of vaporization at 291°K were accurately determined in an adiabatic calorimeter equipped with a calibrated platinum resistance thermometer. In addition, precise measurements of the vapor pressure were made from 250 to 293°K. The size of the sample in the calorimeter was 1.4432 moles, with an estimated impurity of 0.007 mole percent. Complete details will be published later.

In Table I are given the entropy changes calculated from our calorimetric data. The final temperature and pressure are those for the directly measured heat of vaporization, 6696 cal./mole, which may be compared with 6690 cal./mole calculated from the Clapeyron relation, assuming that the gas follows the Berthelot equation of state, with critical temperature 503°K and critical pressure 54.6 atmos.<sup>1</sup> This same assumption was made in the correction for gas imperfection.

The calculation of the entropy from molecular data is summarized in Table II. The translational entropy comes from the familiar Sackur-Tetrode equation. The following frequencies and multiplicities,<sup>2</sup> as well as the usual approximation of harmonic oscillation, were used to obtain the vibrational entropy: 284, 695, 742, 1030 (2), 1262 (2), 1323 (2), 1445 (4), and 2900 (6) cm<sup>-1</sup>. The calculation of the rotational entropy was made by means of the formulas of Crawford,<sup>3</sup> in the derivation of which it is assumed that the potential energy of each methyl group has the form

TABLE I. Molal entropy of dimethyl sulfide from calorimetric data.

0-15°K, Debye extrapolation, $h\nu/k=110.4$	0.369
15-174.855°K, graphical	21.156
Fusion, 1908.4/174.855	10.914
174.855-291.06°K, graphical	13.821
Vaporization, 6696/291.06	23.006
Entropy of actual gas, 291.06°K, 365.5 mm	69.27 ± 0.1
Correction for gas imperfection	0.08
Entropy of ideal gas, 291.06°K, 365.5 mm	69.35 cal./deg. mole

TABLE II. Molal entropy of gaseous dimethyl sulfide from molecular data at 291.06°K and 365.5 mm.

$S_{trans}$	39.63
$S_{vib}$ (Harmonic)	2.31
$S_{rot}$ ( $V=2015$ cal./mole)	27.41
Total entropy ( $V=2015$ )	69.35 cal./deg. mole
( $V=1800$ )	69.60
( $V=0$ )	71.03
( $V=\infty$ )	64.08

$(V/2)(1 - \cos 3\alpha)$ , where  $\alpha$  is the angular displacement of the methyl group from its equilibrium position. The bond angles and interatomic distances taken were  $\angle C-S-C = 102^\circ$ ,  $C-S = 1.82\text{A}$ ,<sup>4</sup>  $C-H = 1.09\text{A}$ , and tetrahedral angles for the methyl groups. These values lead to principal moments of inertia of 45.49, 116.1, and  $151.0 \times 10^{-40}$  g cm<sup>2</sup> and to a moment of inertia  $5.303 \times 10^{-40}$  and reduced moment of inertia  $4.818 \times 10^{-40}$  for each methyl group. Since the ratio of these last two is nearly unity, use of Pitzer's tables<sup>5</sup> does not cause great error at the temperature of interest. Thus the entropy for  $V=2015$  cal./mole calculated with the aid of Pitzer's tables is 69.28 cal./deg. mole rather than 69.35 cal./deg. mole by the more accurate method of Crawford.

It is seen that if the values assumed for the structural parameters and for the vibrational frequencies are sufficiently accurate, a potential barrier of about 2000 cal./mole for each methyl group is required for dimethyl sulfide. The fact that the barriers in ethane<sup>6</sup> and in the methyl amines<sup>7</sup> are of about this same magnitude, while that in dimethyl acetylene<sup>8</sup> is negligible, suggests that the restriction is mainly due to the proximity of the methyl groups rather than to the kind of atom to which the methyl groups are attached.

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