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Citation: [The Journal of Chemical Physics](#) **18**, 77 (1950); doi: 10.1063/1.1747462

View online: <http://dx.doi.org/10.1063/1.1747462>

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# The Thermodynamic Functions of Methyl Mercaptan and Dimethyl Sulfide

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(Received May 23, 1949)

The entropies, free energies, heat capacities and heat contents of methyl mercaptan and dimethyl sulfide have been calculated from 298.16°K to 1500°K at 100°K intervals. The free energies of formation of these compounds have also been calculated for this temperature range based both on sulfur gas and rhombic sulfur as the standard states of sulfur.

## I. INTRODUCTION

THE entropy of methyl mercaptan and dimethyl sulfide at the boiling point has been measured by Russell, Osborne, and Yost,<sup>1</sup> and by Osborne, Doescher, and Yost,<sup>2</sup> respectively. From these values and values calculated using spectroscopic data they determined the hindered rotation potential of the methyl groups. Their value for dimethyl sulfide agrees with the potential calculated by Thompson<sup>3</sup> who obtained the infra-red spectrum of this compound. In view of the growing commercial importance of these compounds it seemed desirable to complete the thermodynamic calculations and tabulate them in much the same way as has been done by the National Bureau of Standards and the American Petroleum Institute for hydrocarbons.

## II. CALCULATIONS

### Entropy, Free Energy, Heat Capacity, Heat Content

The entropy, free energy, heat capacity and heat content of methyl mercaptan and dimethyl sulfide

were computed, at 100°K intervals, from 298.16°K to 1500°K by calculating the translational, classical rotational, vibrational and hindered rotational contributions at each temperature and summing. The equations and tables used were those given in Taylor's and Glasstone's *Treatise on Physical Chemistry*.<sup>4</sup>

In calculating the restricted rotation contribution a potential of 1460 cal. was used for methyl mercaptan and 1900 cal., rather than 2000 cal., given by Osborne, Doescher, and Yost,<sup>2</sup> for dimethyl sulfide, because with our graphs this gave a more exact fit with the measured entropy. The difference, 100 cal., can scarcely be regarded as significant.

Since the equations and tables used were based on the old value of the gas constant  $R$ , the values obtained for the entropy, free energy, heat capacity, and heat content were corrected to the new value by multiplying by 1.00014. This was done only for the total entropy, free energy, heat capacity, and heat content, not for the individual contributions of translation, rotation, etc. The results of the calculations are given in Tables I and II. The entropy values were adjusted, where necessary,

TABLE I. Summary of thermodynamic functions of methyl mercaptan.

$T^{\circ}\text{K}$	298.16	300	400	500	600	700	800	900	1000	1100	1200	1300	1400	1500
$S^{\circ}$	60.86	60.94	64.66	68.08	71.13	73.96	76.59	79.06	81.38	83.58	85.64	87.60	89.47	91.25
$-\left(\frac{F^{\circ}-H_0^{\circ}}{T}\right)$	51.16	51.23	54.09	56.60	58.76	60.73	62.55	64.25	65.85	67.37	68.80	70.17	71.49	72.75
$C_p^{\circ}$	12.12	12.15	14.11	15.96	17.62	19.08	20.38	21.53	22.54	23.43	24.21	24.89	25.49	26.00
$\left(\frac{H^{\circ}-H_0^{\circ}}{T}\right)$	9.70	9.71	10.57	11.48	12.37	13.23	14.04	14.81	15.53	16.21	16.84	17.43	17.98	18.50
$H^{\circ}-H_0^{\circ}$	2892	2913	4228	5740	7422	9261	11232	13329	15530	17831	20208	22659	25172	27750

TABLE II. Summary of thermodynamic functions of dimethyl sulfide.

$T^{\circ}\text{K}$	298.16	300	400	500	600	700	800	900	1000	1100	1200	1300	1400	1500
$S^{\circ}$	68.25	68.36	73.75	78.55	82.99	87.18	91.15	94.91	98.47	101.84	105.03	108.02	110.88	113.61
$-\left(\frac{F^{\circ}-H_0^{\circ}}{T}\right)$	55.69	55.77	59.64	62.92	65.90	68.65	71.23	73.69	76.01	78.23	80.34	82.33	84.28	86.13
$C_p^{\circ}$	17.00	17.15	20.25	23.27	26.07	28.56	30.76	32.68	34.35	35.82	37.10	38.22	39.17	40.01
$\left(\frac{H^{\circ}-H_0^{\circ}}{T}\right)$	12.56	12.59	14.11	15.63	17.09	18.53	19.92	21.22	22.46	23.61	24.69	25.69	26.60	27.48
$H^{\circ}-H_0^{\circ}$	3745	3777	5644	7815	10254	12971	15936	19098	22460	25971	29628	33397	37240	41220

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<sup>1</sup> Russell, Osborne, and Yost, *J. Am. Chem. Soc.* **64**, 165 (1942).<sup>2</sup> Osborne, Doescher, and Yost, *J. Am. Chem. Soc.* **64**, 169 (1942).<sup>3</sup> H. W. Thompson, *Trans. Faraday Soc.* **37**, 38 (1941).<sup>4</sup> H. S. Taylor and S. Glasstone, *Treatise on Physical Chemistry I. Atomistics and Thermodynamics* (D. Van Nostrand Company, Inc., New York, 1942).

TABLE III. Free energies of formation.

T°K	CH <sub>3</sub> SH		CH <sub>3</sub> SCH <sub>3</sub>	
	$\Delta F_f^\circ$ S <sub>2</sub> (gas)	$\Delta F_f^\circ$ S(rh)	$\Delta F_f^\circ$ S <sub>2</sub> (gas)	$\Delta F_f^\circ$ S(rh)
298.16	-8919	+760	-5344	+4335
300	-8865	778	-5244	4399
400	-5723	1989	+ 448	8160
500	-2442	3391	6431	12264
600	+ 973	4978	12589	16594
700	4469	6701	18861	21091
800	8010	8519	25212	25721
900	11599	10441	31603	30495
1000	15207	12437	38038	35268
1100	18833	14506	44489	40162
1200	22471	16642	50959	45130
1300	26100	18825	57463	50191
1400	29717	21052	63913	55248
1500	33345	23345	71780	61780

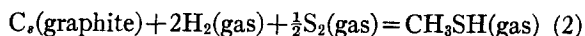
to satisfy the equality  $S^\circ = (H^\circ - H_0^\circ/T) - (F^\circ - H_0^\circ/T)$ . This adjustment amounted to 0.06 in two cases but in general it was 0.00 or  $\pm 0.01$ .

### Free Energy of Formation

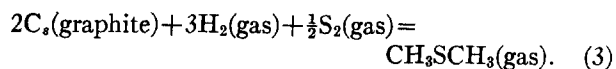
With the free energy tables given here and those given in "Selected values of chemical thermodynamic properties"<sup>5</sup> it was most convenient to calculate the free energy of formation of methyl mercaptan and of dimethyl sulfide, as a function of temperature, by using the relation

$$F^\circ = H_0^\circ + (F^\circ - H_0^\circ/T)T. \quad (1)$$

This involves determining  $\Delta H_0^\circ$  for the reactions of the formation of the compounds in their standard states from the elements in their standard states. Since the free energy functions were not available for rhombic sulfur, which is generally taken to be the standard state of sulfur,<sup>6</sup> and since they were for diatomic sulfur gas, the free energies were calculated for the reactions



and



<sup>5</sup> "Selected values of chemical thermodynamic properties," Nat. Bur. Stand. (1947).

<sup>6</sup> G. N. Lewis and M. Randall, *Thermodynamics and Free Energy of Chemical Substances* (McGraw-Hill Book Company, Inc., New York, 1923).

These were converted to rhombic sulfur using the free energy data given by Kelley<sup>7</sup> for the reaction



The quantity  $\Delta H_0^\circ$  was found for reactions (2) and (3) by determining the free energy change at 298.16°K using the relation

$$\Delta F^\circ = \Delta H^\circ - T\Delta S^\circ \quad (5)$$

and also evaluating  $\Delta(F^\circ - H_0^\circ/T)$  at 298.16°K.  $\Delta H_{298.16}^\circ$  was obtained, for each reaction, by using heat content values given in reference 5 for  $CH_3SH$ ,  $\Delta H_f^\circ = -2.97$  kcal./mole;<sup>8</sup>  $CH_3SCH_3$ ,  $\Delta H_f^\circ = -6.90$  kcal./mole;<sup>9</sup>  $S_2(g)$ ,  $\Delta H_f^\circ = +29.86$  kcal./mole.<sup>10</sup> For reaction (2)  $\Delta H^\circ = -17.90$  kcal./mole and for reaction (3)  $\Delta H^\circ = -21.830$  kcal./mole. From the same source and the entropies given here  $\Delta S^\circ = -30.128$  e.u. for reaction (2) and  $\Delta S^\circ = -55.278$  e.u. for reaction (3), using 54.41 e.u. for the entropy of  $S_2(g)$ .<sup>7</sup> Therefore  $\Delta F_{298.16}^\circ = -8914$  cal. for reaction (2) and  $\Delta F_{298.16}^\circ = -5339$  for reaction (3). From values of  $(F^\circ - H_0^\circ)/T$  given here, in the tables of reference 5 and by Kelley<sup>7</sup>  $\Delta(F^\circ - H_0^\circ)_{298.16} = 6506$  cal. for reaction (2) and  $\Delta(F^\circ - H_0^\circ)_{298.16} = 12596$  cal. for reaction (3). Combining the  $\Delta F^\circ$  and  $\Delta(F^\circ - H_0^\circ)$  values  $\Delta H_0^\circ = -15423$  cal. for reaction (2) and  $\Delta H_0^\circ = -17935$  cal. for reaction (3).

With these values of  $\Delta H_0^\circ$  the free energy changes at several temperatures were calculated for reactions (2) and (3) and the results are given in Table III. The free energies of formation based on rhombic sulfur as the standard state are also given. It will be noted that there is some change in these values from those given in the previous note on this subject.<sup>11</sup> This is due to the different values for the heats of formations of  $CH_3SH$  and  $CH_3SCH_3$  used here.

### ACKNOWLEDGMENT

It is a pleasure to acknowledge my indebtedness to Doctors F. D. Rossini and D. D. Wagman of the Bureau of Standards and Professors Gibson and Brewer of the University of California for their suggestions regarding this work.

<sup>7</sup> K. K. Kelley, "Thermodynamic properties of sulfur and its inorganic compounds," Bureau of Mines Bulletin 406, 1937.

<sup>8</sup> Selected values of chemical thermodynamic properties, Nat. Bur. Stand., Series I, table 23-12 (1947).

<sup>9</sup> See reference 8, table 23-42.

<sup>10</sup> See reference 8, table 14-2.

<sup>11</sup> J. Chem. Phys., 17, 499 (1949).