

## Thermodynamic Properties of Sulfur Compounds I. Hydrogen Sulfide, Diatomic Sulfur and the Dissociation of Hydrogen Sulfide

Paul C. Cross

Citation: *J. Chem. Phys.* **3**, 168 (1935); doi: 10.1063/1.1749626

View online: <http://dx.doi.org/10.1063/1.1749626>

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It is also important to notice the results of the infrared absorption spectra of these compounds. But unfortunately, so far as we know, comparatively little work has been done with regard to the halogen alkyls. Easley, Fenner and Spence<sup>11</sup> have investigated the infrared absorption spectra of the halogen derivatives of methane. Ellis has investigated  $\text{CH}_3\text{I}$ ,  $\text{CH}_2\text{I}_2$ ,  $\text{CH}_2\text{Br}_2$ ,  $\text{CHBr}_3$  and  $\text{CHCl}_3$ . Series attributed to C—Cl, C—Br and C—I oscillations were found, starting at  $16.8\mu$ ,  $17.2\mu$  and  $17.5\mu$ , respectively. Bennett and Meyer<sup>12</sup> have investigated the methyl halides  $\text{CH}_3\text{F}$ ,  $\text{CH}_3\text{Cl}$ ,  $\text{CH}_3\text{Br}$  and  $\text{CH}_3\text{I}$ . Seven bands were found for each of the four compounds. The series converge toward the known bands of methane with a decrease in the atomic weight of the halogen in the halide. In passing from compound to compound the doublet separations increase with a decrease in the atomic weight of the halogen in the halide.

<sup>11</sup> M. A. Easley, L. Fenner and B. J. Spence, *Astrophys. J.* **67**, 185 (1928).

<sup>12</sup> W. H. Bennett and C. F. Meyer, *Phys. Rev.* **32**, 888 (1928).

It is also interesting to compare the preceding results with the fact that the larger the value of  $n$  the greater the heat of formation of the link C—X in  $\text{C}_n\text{H}_{2n+1}\text{X}$ . As examples, the values for the alkyl halides and alcohols are given in Table IV.<sup>13</sup> The rise in the heat of formation is

TABLE IV.

MOLECULES	—HEATS OF FORMATION (kcal./mole)—		
	C—O	C—Cl	C—Br
$\text{CH}_3\text{X}$	75.9	74.7	61.5
$\text{C}_2\text{H}_5\text{X}$	76.8	77.6	64.5
$n\text{-C}_3\text{H}_7\text{X}$	79.2	79.3	66.8
$n\text{-C}_4\text{H}_9\text{X}$	80.1	—	—
$iso\text{-C}_4\text{H}_9\text{X}$	81.0	81.5	—
$n\text{-C}_{11}\text{H}_{23}\text{X}$	83.1	—	—

about 1 to 2 kcal. per carbon atom added. Various explanations may be given of this, but none is offered as a final solution of the problem.

In conclusion, the author wishes to express his thanks to Professor Y. Takahashi for his helpful criticisms throughout the work, and also to "The Saito Gratitude Foundation" for defraying a part of expenses of the research.

<sup>13</sup> N. V. Sidgwick, *The Covalent Link in Chemistry* (1933), 115.

## Thermodynamic Properties of Sulfur Compounds

### I. Hydrogen Sulfide, Diatomic Sulfur and the Dissociation of Hydrogen Sulfide

PAUL C. CROSS,\* *Gates Chemical Laboratory, California Institute of Technology*

(Received December 26, 1934)

The thermodynamic properties of  $\text{H}_2\text{S}$  are calculated from the structure recently obtained by the analysis of an infrared band.  $-[(F^0 - E_0^0)/T]^*_{298.1} = 41.174$ .  $S^*_{298.1} = 49.151$ . (Not including the spin contribution.) Montgomery and Kassel's calculations for  $\text{S}_2$  are corrected in accordance with Badger's new interpretation of the data of Naudé and Christy.  $-[(F^0 - E_0^0)/T]^*_{298.1} = 47.242$ .  $S^*_{298.1} = 54.417$ . The results are applied to the reaction  $\text{H}_2\text{S} = \text{H}_2 + \frac{1}{2}\text{S}_2$ . The energy of dissociation of  $\text{H}_2\text{S}$  into normal atoms,  $E_0^0$ , is found to be 173.8 kg cal. per mole.

#### I. HYDROGEN SULFIDE

THE procedures of calculating thermodynamic properties from spectroscopic data are amply discussed in the literature.<sup>1, 2, 3</sup> The moments of inertia of the  $\text{H}_2\text{S}$  molecule, 2.667,

$3.076$ ,  $5.845 \times 10^{-40}$  g  $\text{cm}^2$ , have recently been obtained from the analysis of a vibration-rotation band in the photographic infrared.<sup>4, 5</sup> The vibrational spectrum has not been sufficiently studied to enable an exact determination of the vibrational constants. For the following calculations the values  $\nu_s = 1260 \text{ cm}^{-1}$  and  $\nu_r = \nu_e = 2620 \text{ cm}^{-1}$

\* National Research Fellow.

<sup>1</sup> W. F. Giauque, *J. Am. Chem. Soc.* **52**, 4808 (1930).

<sup>2</sup> L. S. Kassel, *J. Am. Chem. Soc.* **55**, 1351 (1933).

<sup>3</sup> A. R. Gordon and C. Barnes, *J. Chem. Phys.* **1**, 297 (1933).

<sup>4</sup> P. C. Cross, *Phys. Rev.* **46**, 536 (1934).

<sup>5</sup> P. C. Cross, *Phys. Rev.* **47**, 7 (1935).

were used. Since the calculations were not extended to extremely high temperatures, only negligible errors were introduced by using these approximate frequencies and treating the molecules as harmonic oscillators. The tables of Gordon and Barnes<sup>3</sup> greatly facilitated the determination of the vibrational contribution to the free energy, entropy, and heat capacity functions.

From the above moments of inertia, including the symmetry correction,  $R \ln 2$ , one obtains the following equation for the virtual free energy function of  $\text{H}_2\text{S}$ :<sup>6</sup>

$$[(F^0 - E_0^0)/T]^* = 4.112 - 18.300 \log_{10} T \\ + [(F^0 - E_0^0)/T]_{\text{vib.}}$$

$$[(F^0 - E_0^0)/T](\text{Absolute}) = [(F^0 - E_0^0)/T]^* \\ + [(F^0 - E_0^0)/T]_{\text{Bpin}} = [(F^0 - E_0^0)/T]^* - 2.754.$$

$$\text{Similarly, } S^* = 3.836 + 18.300 \log_{10} T + S_{\text{vib.}},$$

$$S(\text{Absolute}) = S^* + S_{\text{Bpin}} = S^* + 2.754.$$

The molar heat capacity is equal to  $4R$  plus the vibrational heat capacity for temperatures above the boiling point,  $212.77^\circ\text{K}$ .<sup>7</sup>

Calculations by direct summation at the temperature  $212.77^\circ\text{K}$  agree within the uncertainty in the constants  $R$  and  $k$  with the values from the approximate equations. The calculations were discontinued above  $1800^\circ$  because of the growing importance of the errors due to incomplete data on the vibrational terms and the lack of useful applications at those temperatures.

TABLE I. Free energy, entropy, and heat capacity of  $\text{H}_2\text{S}$ . (Not including the spin contribution.)

$T$	$-[(F^0 - E_0^0)/T]^*$	$S^*$	$C_p$	$T$	$-[(F^0 - E_0^0)/T]^*$	$S^*$	$C_p$
212.77	38.489	46.441	7.978	1000	51.24	60.25	10.85
298.1	41.174	49.151	8.121	1100	52.11	61.30	11.17
400	43.53	51.58	8.43	1200	52.92	62.29	11.46
500	45.34	53.50	8.81	1300	53.67	63.22	11.72
600	46.83	55.14	9.23	1400	54.39	64.09	11.94
700	48.13	56.60	9.67	1500	55.06	64.92	12.13
800	49.27	57.92	10.09	1600	55.70	65.71	12.30
900	50.30	59.13	10.49	1700	56.31	66.46	12.45
			1800	56.90	67.17	12.58	

<sup>6</sup>  $R = 1.9869$  (Int. Crit. Tab.).

<sup>7</sup> W. F. Giauque, private communication.

## II. DIATOMIC SULFUR

Badger's<sup>8</sup> reinterpretation of the data of Naudé and Christy<sup>9, 10</sup> on the  $\text{S}_2$  band spectrum gives the S-S separation as 1.84Å in place of the former value of 1.60Å which was in serious disagreement with all empirical methods of estimating interatomic distances.<sup>11</sup> The new values of  $-(F^0 - E_0^0)/T$  may be obtained by adding 0.55 to those given by Montgomery and Kassel.<sup>12</sup>  $-(F^0 - E_0^0)/T_{298.1} = 47.242$ .  $S_{298.1}^0 = 54.417$ .

## III. DISSOCIATION OF HYDROGEN SULFIDE

Applying the results reported here with Giauque's<sup>13</sup> calculations on hydrogen to the equilibrium measurements discussed by Lewis and Randall,<sup>14</sup> one obtains the value of  $\Delta E_0^0$  for the reaction  $\text{H}_2\text{S}(\text{g}) = \text{H}_2(\text{g}) + \frac{1}{2}\text{S}_2(\text{g})$ ,  $\Delta E_0^0 = 19.62 \pm 0.03$  kg cal. The small probable error illustrates the accuracy of the agreement between the experimental and calculated free energies. Since the energies of dissociation into normal atoms are known for  $\text{H}_2$ <sup>15</sup> and  $\text{S}_2$ <sup>10</sup>, the energy of dissociation of  $\text{H}_2\text{S}$  into normal atoms can be calculated  $E_0^0(\text{H}_2\text{S}) = E_0^0(\text{H}_2) + \frac{1}{2}E_0^0(\text{S}_2) - \Delta E_0^0 = -102.9 - 51.3 - 19.6 = -173.8$  kg cal. per mole. This corresponds to  $-86.9$  kg cal. per H-S bond.

I wish to thank Professor R. M. Badger for access to his analysis of the  $\text{S}_2$  spectrum before publication and for his interest in these results.

<sup>8</sup> R. M. Badger, Phys. Rev. **46**, 1025 (1934).

<sup>9</sup> S. M. Naudé and A. Christy, Phys. Rev. **37**, 490 (1931).

<sup>10</sup> A. Christy and S. M. Naudé, Phys. Rev. **37**, 903 (1931).

<sup>11</sup> The sum of the double bond radii gives 1.88Å (L. Pauling, Proc. Nat. Acad. Sci. **18**, 293 (1932)). The relation between the force constant and interatomic distance gives 1.90Å (R. M. Badger, J. Chem. Phys. **2**, 128 (1934)).

<sup>12</sup> C. W. Montgomery and L. S. Kassel, J. Chem. Phys. **2**, 417 (1934).

<sup>13</sup> W. F. Giauque, J. Am. Chem. Soc. **52**, 4816 (1930).

<sup>14</sup> Lewis and Randall, *Thermodynamics*, p. 541, McGraw Hill, New York, 1923.

<sup>15</sup> Jevons, *Report on Band Spectra of Diatomic Molecules*, p. 269, Cambridge, 1932.