

Ideal Gas Thermodynamic Functions of the Isotopic Hydrogen Sulfides¹

Lester Haar,² Joe C. Bradley, and Abraham S. Friedman

The ideal gas thermodynamic functions for H₂S, D₂S, T₂S, HDS, HTS, and DTS were calculated from molecular data. The recent spectroscopic data for H₂S and D₂S by Allen [1]³ were employed. The zero-order frequencies for the other isotopes were obtained by a normal coordinate treatment. The partition functions are obtained in closed form. The calculations include high-temperature corrections for vibrational anharmonicity, rotation-vibration coupling, centrifugal stretching, and a low-temperature correction for nonclassical rotation. The statistical calculations were performed on the Bureau's digital computer. Tables of C_p°/R , $(H^\circ - E_0^\circ)/RT$, $-(F^\circ - E_0^\circ)/RT$, and S°/R have been calculated at close temperature intervals from 50° to 5,000° K.

1. Introduction

Procedures were developed in earlier papers [2, 3] for the National Bureau of Standards Eastern Automatic Computer—SEAC, to calculate the ideal gas thermodynamic functions for a variety of molecules. A closed form analytical expression for the partition function is used, which includes terms for anharmonicity, rotation-vibration interaction, centrifugal stretching, and nonclassical rotation. The internal partition function used in the calculations is

$$Q = \frac{1}{S} \left[\prod_i (1 - e^{-u_i})^{-1} \right] \left[\frac{\pi}{\sigma_A \sigma_B \sigma_C} \right]^{1/2} \left[1 + \frac{\theta_1}{T} + \frac{\theta_2}{T^2} \right] \times \\ [1 + \rho T] \left[\prod_{i \leq j} (1 + f_{ij}) \right] \left[\prod_i \left(1 + 1/2 \frac{\delta_i}{(e^{u_i} - 1)} \right) \right]$$

The rotational partition function for an asymmetric top was derived by Stripp and Kirkwood [4] and Woolley [5].

This expression is

$$Q_{\text{rot}} = \left[\frac{\pi}{\sigma_A \sigma_B \sigma_C} \right]^{1/2} f(\sigma_A, \sigma_B, \sigma_C) \text{ where } \sigma = \frac{h^2}{8\pi^2 k T I}$$

The function $f(\sigma_A, \sigma_B, \sigma_C)$ has the form

$$f(\sigma_A, \sigma_B, \sigma_C) = 1 + \frac{\theta_1}{T} + \frac{\theta_2}{T^2} + \dots$$

where the θ_i are constants. Woolley [5] also calculated ortho-para effects, not included in this expression.

The other internal contributions considered in the partition function are

$$Q_{\text{centrifugal stretching}} = 1 + \rho T$$

$$Q_{\text{anharmonicity}} = \prod_{i \leq j} (1 + f_{ij}),$$

$$Q_{\text{rotation-vibration coupling}} = \prod_i \left(1 + 1/2 \frac{\delta_i}{(e^{u_i} - 1)} \right),$$

and S is the symmetry number. In these expressions ρ represents the centrifugal stretching constant, and δ_i are the rotation-vibration coupling constants;

$$f_{ij} = \frac{X_{ij} \frac{hc}{kT}}{(e^{u_i} - 1)(e^{u_j} - 1)}$$

where the X_{ij} are the observed vibrational anharmonicity coefficients, and

$$u_i = \nu_i \frac{hc}{kT}$$

where ν_i are the observed fundamentals.

Details of the method of computation are found in [2].

The thermodynamic functions can be expressed in terms of $\ln Q$ or the derivatives of Q .

$$\frac{F^\circ - E_0^\circ}{RT} = -\ln Q$$

$$\frac{H^\circ - E_0^\circ}{RT} = -\frac{Q'}{QT}$$

$$\frac{S^\circ}{R} = \frac{Q'}{QT} + \ln Q$$

$$\frac{C_p^\circ}{R} = \frac{Q''}{QT^2} - \frac{Q'^2}{Q^2 T}$$

$$\text{where } Q' = \frac{dQ}{d\left(\frac{1}{T}\right)} \text{ and } Q'' = \frac{d^2 Q}{d\left(\frac{1}{T}\right)^2}$$

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² Present address: Johns Hopkins University Applied Physics Laboratory.

³ Figures in brackets indicate the literature references at the end of this paper.

2. Molecular Constants

The molecular constants used are based primarily on data for H₂S and D₂S, reported by Allen [1]. A normal coordinate analysis yielded zero order vibrational frequencies for HDS, HTS and T₂S. The values for the centrifugal stretching constants calculated by Allen are $\rho_{\text{H}_2\text{S}}=1.68 \times 10^{-5}(\text{°K})^{-1}$ and $\rho_{\text{D}_2\text{S}}=1.78 \times 10^{-5}(\text{°K})^{-1}$. For the calculation of the thermodynamic functions of the six isotopic hydrogen sulfide molecules, $1.7 \times 10^{-5}(\text{°K})^{-1}$ was used for this constant.

The anharmonicity and rotation-vibration interaction constants for T₂S, HDS, HTS, and DTS were calculated from the relations

$$X'_{ij} = X_{ij} \left(\frac{\omega'_i \omega'_j}{\omega_i \omega_j} \right)$$

and

$$\delta'_i = \delta_i \left(\frac{\omega'_i}{\omega_i} \right)$$

respectively, where the prime quantities refer to the reference molecule.

This procedure for estimating anharmonicity and rotation-vibration coupling constants is applicable only to molecules of the same symmetry class as the

TABLE 1. Comparison of observed and calculated anharmonic constants of H₂S and D₂S

| | H ₂ S | | D ₂ S | |
|-----------------|------------------|------------|------------------|------------|
| | Allen | Calculated | Allen | Calculated |
| X ₁₁ | 25 | 22 | 13 | 11 |
| X ₂₂ | 5.5 | 9.1 | 3.0 | 4.7 |
| X ₃₃ | 24 | 23 | 12 | 12 |
| X ₁₂ | 24 | 8.0 | 12 | 4.3 |
| X ₁₃ | 94 | 81 | 50 | 42 |
| X ₂₃ | 19 | 10 | 10 | 5.4 |

X_{ij} in cm⁻¹

reference molecule. H₂S was used as the reference molecule for T₂S. In order to obtain estimates of these constants for the three X-Y-Z type molecules, HDS, HTS, and DTS, the reference molecule HDO was employed in the above expressions. This extension of the isotope relations was tested by comparing the experimental values for H₂S and D₂S [1] with those calculated using H₂O as a reference molecule. The comparison is given in table 1.

The chemical atomic weight of sulfur used in the calculations of the translational entropies was obtained from the values listed by Wichers [6]. The isotopic masses used in the zero-point frequency and equilibrium moment of inertia calculations are the values listed by Mattauch and Fluegge [7].

The molecular constants used in the calculations are listed in table 2.

3. Thermal Properties

The heat capacity, enthalpy, free energy, and entropy for H₂S, HDS, D₂S, HTS, DTS, and T₂S are tabulated in dimensionless units in tables 3 through 8. The very small changes in the constants of table 2, obtained by using the other isotopes of sulfur in the compound formulas, together with the very large relative abundance of S³², result in a completely negligible difference between the properties of XYS³² tabulated here and the naturally occurring mixture of XYS³², XYS³³, XYS³⁴, and XYS³⁶. The contributions of nuclear spin and isotopic mixing have been omitted; the contribution of excited electronic states, only significant near the highest temperatures, have been omitted. The values computed by Woolley [5] of the ortho-para effect for H₂S at 50° and 100° K are 0.024 and 0.00001 respectively for (C_v^o/R) symmetric - (C_v^o/R) antisymmetric. These are not included in the values tabulated in table 3. For D₂S and T₂S the effects are appreciably smaller and have been likewise omitted from the tables. Tables 3 through 8 also include the first differences for the tabulated thermodynamic functions.

TABLE 2. Molecular constants

| | Units | H ₂ S | HDS | D ₂ S | HTS | DTS | T ₂ S |
|-----------------------------|--|------------------|--------|------------------|--------|---------|------------------|
| p ₁ | cm ⁻¹ ----- | 2616 | 1910 | 1895 | 1556 | 1594 | 1585 |
| p ₂ | cm ⁻¹ ----- | 1183 | 1039 | 856.0 | 983.0 | 791.0 | 713.8 |
| p ₃ | cm ⁻¹ ----- | 2625 | 2636 | 1906 | 2636 | 1921 | 1594 |
| X ₁₁ | cm ⁻¹ ----- | 25 | 21 | 13 | 14 | 6.8 | 7.6 |
| X ₁₂ | cm ⁻¹ ----- | 5.5 | 5.5 | 3.0 | 4.9 | 3.1 | 3.2 |
| X ₃₃ | cm ⁻¹ ----- | 24 | 41 | 12 | 41 | 21 | 8.1 |
| X ₁₂ | cm ⁻¹ ----- | 22 | 4.3 | 12 | 3.4 | 2.7 | 3.0 |
| X ₁₃ | cm ⁻¹ ----- | 94 | 6.3 | 50 | 5.2 | 3.7 | 29 |
| X ₂₃ | cm ⁻¹ ----- | 19 | 11 | 10 | 10 | 5.9 | 3.7 |
| δ ₁ | dimensionless---- | 0.051 | 0.033 | 0.037 | 0.027 | 0.028 | 0.031 |
| δ ₂ | dimensionless---- | -.039 | -.061 | -.028 | -.058 | -.046 | -.024 |
| δ ₃ | dimensionless---- | .036 | .044 | .026 | .045 | .033 | .022 |
| I _a ^A | g cm ² ×10 ⁻⁴⁰ ----- | 2.694 | 2.863 | 5.083 | 2.967 | 5.448 | 7.210 |
| I _a ^B | g cm ² ×10 ⁻⁴⁰ ----- | 3.103 | 5.667 | 6.201 | 8.133 | 8.429 | 9.286 |
| I _a ^C | g cm ² ×10 ⁻⁴⁰ ----- | 5.797 | 8.530 | 11.28 | 11.10 | 13.88 | 16.50 |
| θ ₁ | °K----- | 2.4306 | 1.5732 | 1.1897 | 1.2089 | 0.96680 | 0.81330 |
| θ ₂ | (°K) ² ----- | 4.8078 | 2.2275 | 1.5140 | 1.3155 | .84065 | .59567 |
| ρ | (°K) ⁻¹ ×10 ⁻⁵ ----- | 1.7 | 1.7 | 1.7 | 1.7 | 1.7 | 1.7 |

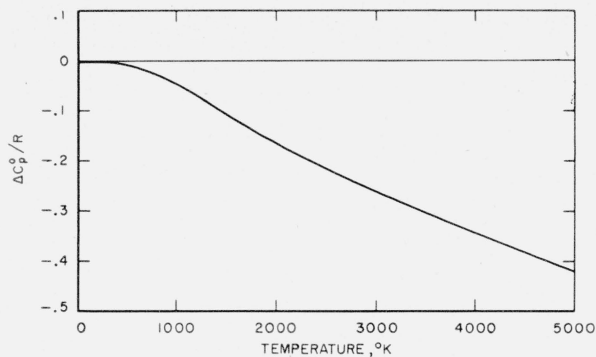


FIGURE 1. Comparison of ideal gas heat capacity functions for H_2S .

The SEAC values lie on the base line. The curve represents the difference between the rigid-rotator, harmonic-oscillator calculations, and the SEAC calculations.

The uncertainty in the calculated anharmonicity and rotation-vibration coupling constants for HDS , HTS , and DTS depends on the validity of using HDO as a reference molecule in the isotope expressions for X_{ij} and δ_i . The uncertainty in these constants for T_2S , estimated from the differences between experimental and calculated values for analogous molecules, is probably below 20 percent. The resulting uncertainty in the fundamentals for T_2S are approximately 1 percent, assuming negligible uncertainty in the calculated zero order frequencies. At temperatures below $1,000^\circ K$ this results in an uncertainty in the third place to the right of the decimal for the tabulated thermodynamic functions of T_2S . The uncertainty in the tabulated results for H_2S and D_2S would not exceed that for T_2S . At higher temperatures the uncertainty in the thermodynamic functions is larger, due to neglected higher order terms in the energy level expressions, and the omission of the effect of rotational cut-off.

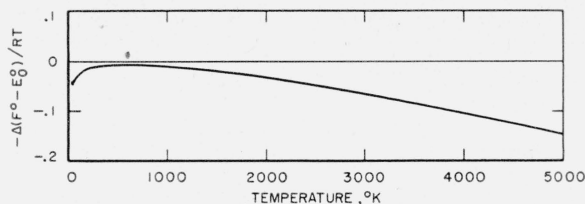


FIGURE 2. Comparison of ideal gas free energy functions for H_2S .

The SEAC values lie on the base line. The curve represents the difference between the rigid-rotator, harmonic-oscillator calculations, and the SEAC calculations.

Two sets of calculations of thermodynamic functions were made on the SEAC: one set for only harmonic oscillator, rigid rotator contributions; and the tabulated set, which includes these plus first order effects for centrifugal stretching, vibrational anharmonicity, rotation-vibration coupling and low temperature nonclassical rotation terms. A comparison of the two different sets of calculations of C_p/R and $-(F^\circ - E_0^\circ)/RT$ for H_2S is given in figures 1 and 2 from 50° to $5,000^\circ K$.

4. References

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