

Thermodynamics of Some Simple Sulfur-Containing Molecules

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The thermodynamic functions $(F^\circ - H_0^\circ)/T$, $(H^\circ - H_0^\circ)/T$, S° ($H^\circ - H_0^\circ$), and C_p° are calculated to high temperatures for gaseous sulfur (monatomic and diatomic), sulfur monoxide, sulfur dioxide, sulfur trioxide, and hydrogen sulfide from molecular and spectroscopic data. Values of the heats of formation of the various atomic and molecular species are selected from published experimental data, and certain industrially important equilibria are calculated.

1. Introduction

The calculation of the thermodynamic properties of a number of simple gaseous sulfur-containing molecules has been carried out as a part of the Bureau's program on the compilation of tables of Selected Values of Chemical Thermodynamic Properties. The data on a large number of inorganic sulfur compounds had been critically evaluated by K. K. Kelley in 1936 [1].¹ Since that date, sufficient new information has been reported in the literature to warrant a reevaluation and recalculation of the properties of gaseous monatomic and diatomic sulfur, sulfur monoxide, sulfur dioxide, sulfur trioxide, and hydrogen sulfide.²

The calculations are divided into two parts: (a) Calculation of the thermodynamic functions, $(F^\circ - H_0^\circ)/T$, $(H^\circ - H_0^\circ)/T$, S° , $(H^\circ - H_0^\circ)$, and C_p° , for the various molecules in the ideal gaseous state; and (b) selection of "best" values for the heats of formation of the various compounds.

2. Units

The calorie used in these calculations is the thermochemical calorie, defined as 4.1840 abs j. The gas constant R is taken as 1.98719 cal/mole °K. The atomic weights used are H, 1.0080; O, 16.0000; S, 32.066 [2]. The standard states chosen for the elements are O₂ (g), H₂ (g), both in the ideal gas state at 1-atm pressure, and S (c, rhombic). As is customary, nuclear spin and isotopic mixing contributions to the entropy and free-energy functions have been omitted.

3. Calculation of the Thermodynamic Functions

The translational contributions to the free-energy function, $(F^\circ - H_0^\circ)/T$; the heat-content function, $(H^\circ - H_0^\circ)/T$; entropy, S° ; and heat capacity, C_p° , were calculated for all the molecules, using the equations given by Wagman et al. [3].

¹ Figures in brackets indicate the literature references given at the end of this paper.

² The higher polymeric forms of sulfur, S₄, S₆, and S₈, are not included in this report. The necessary molecular data on S₄ and S₆ are not available; indeed the existence of S₄, which has been assumed in the interpretation of the most recent gas density measurements [3], is still unproved. Dr. George Guthrie of the U. S. Bureau of Mines, Bartlesville, Okla., has recently completed calculations of the thermodynamic functions of gaseous S₄ [5].

For monatomic sulfur gas the only other contribution is from the electronic excitation. The electronic functions were calculated by direct summation of the energy levels, using term values and multiplicities (table 1) from Moore [4] and the conversion factor 1 cm⁻¹ = 2.85851 cal/mole. Only the five lowest levels are significant below 5,000°K.

TABLE 1. Spectroscopic energy levels for S (g)

Term designation	Energy	Multiplicity
	cm ⁻¹	
³ P ₂	0.0	5
³ P ₁	396.8	3
³ P ₀	573.6	1
¹ D ₂	9239.0	5
¹ S ₀	22181.4	1

For diatomic sulfur gas the rotational and vibrational constants selected by Herzberg [5] for the isotopic S₃₂ molecule were corrected to the naturally occurring isotopic mixture, using the relations given by Herzberg [6]:

$$\sqrt{\frac{\mu}{\mu_1}} = \rho = \frac{\omega_{e1}}{\omega_e} \quad \text{and} \quad x_{e1}\omega_{e1} = \rho^2 x_e \omega_e,$$

where ω_e is the fundamental equilibrium vibrational frequency, x_e the anharmonicity constant, and μ the reduced mass. These corrected values, $\omega_e = 724.62$ cm⁻¹ and $x_e \omega_e = 2.844$ cm⁻¹, were used to calculate approximate thermodynamic functions, assuming a rigid rotator of symmetry number 2 and an independent harmonic oscillator of frequency $\omega_e - 2x_e \omega_e$. In the rigid rotator calculation the equations given by Wagman et al. [3] were used. The harmonic oscillator calculations were carried out, using the tables of the Planck-Einstein functions calculated by Johnston, Savedoff, and Belzer [7]. The triplet electronic ground state required the addition of $R \ln 3$ to the entropy and $-R \ln 3$ to the free-energy function.

Corrections for rotational stretching, vibrational anharmonicity, and rotational-vibrational interaction were calculated by using the second-order expansions given by Mayer and Mayer [8] at 300, 500, 1,000, 1,500, and 2,000°K; values at intermediate temperatures were obtained by graphical interpolation. At

1,500°K these corrections amounted to -0.03 cal/mole °K for the free-energy function, 0.04 for the heat-content function, and 0.09 for the heat capacity.

For sulfur monoxide gas the rotational and vibrational constants taken from Herzberg [5] were corrected for isotopic composition to give the constants $\omega_e=1123.09\text{ cm}^{-1}$ and $x_e\omega_e=6.109\text{ cm}^{-1}$, which were used in the rigid rotator-harmonic oscillator calculation. The triplet ground state required the addition of $R \ln 3$ to the entropy and $-R \ln 3$ to the free-energy function. Anharmonicity and stretching corrections were evaluated as for diatomic sulfur gas. At 1,500° K these corrections were -0.02, 0.02, and 0.05 cal/mole °K for the free-energy function, heat-content function, and heat capacity, respectively.

For sulfur dioxide gas, the product of the moments of inertia was taken as the average of the microwave measurements of Dailey, Golden, and Wilson [9], who obtained $106.403 \times 10^{-117}\text{ g}^3\text{cm}^6$, Sirvetz [10], $107.007 \times 10^{-117}\text{ g}^3\text{cm}^6$, and Crable and Smith [11], $106.996 \times 10^{-117}\text{ g}^3\text{cm}^6$. This product of the moments of inertia, $106.80 \times 10^{-117}\text{ g}^3\text{cm}^6$, and the vibrational frequencies given by Herzberg [12] were used in a rigid rotator-harmonic oscillator calculation. As the available data do not permit the calculation of the anharmonicities, these were estimated from the relation, based on the data for sulfur monoxide, $X_{ij}=0.003(v_i+v_j)$, where X_{ij} is the anharmonicity arising from the interaction of the two fundamental frequencies ν_i and ν_j [13]. These were used to correct the rigid rotator-harmonic oscillator calculation by the method developed by Stockmayer, Kavanagh, and Mickley [13]. In this treatment the vibrational levels of a molecule with nondegenerate fundamental frequencies are taken as

$$\frac{E_v - E_0}{hc} = \sum v_i \nu_i - \sum_i X_{ii}(v_i - 1) - \sum_{i < j} X_{ij} v_i v_j,$$

where ν_i are the observed fundamentals, in cm^{-1} , v_i are quantum numbers, and X_{ii} are the anharmonicities, in cm^{-1} , as calculated above. If the anharmonicities are considered to be small, their contribution to the Boltzmann factor can be expanded and the vibrational partition function Q_v readily summed:

$$Q_v = \prod_i [1 - e^{-u_i}]^{-1} \left[1 + \sum_{i < j} f_{ij} + \dots \right],$$

where

$$u_i = hc\nu_i/kT$$

$$f_{ii} = 2X_{ii}hc[kT(e^{u_i} - 1)]^{-2}$$

$$f_{ij} = X_{ij}hc[kT(e^{u_i} - 1)(e^{u_j} - 1)]^{-1}.$$

This expression is equivalent to $Q'_v Q_c$, where Q'_v is the partition function for a harmonic oscillator with frequencies ν_i , and Q_c is the partition function containing the anharmonicities. Q_c may then be written as

$$Q_c = 1 + \sum_{i < j} f_{ij}.$$

From this the correction to the free-energy function is given by $-F_c/T = R \ln Q_c$. Differentiation with respect to T gives the corrections to the heat-content function, $H_c/T = RT(d \ln Q_c/dT)$, and the heat capacity, $C_c = R d(T^2 d \ln Q_c/dT)/dT$. In this way corrections to the free energy function, heat content function, and heat capacity (amounting to -0.05, 0.10, and 0.23 cal/mole °K at 1,500°K, respectively,) were calculated at 300°, 500°, 1,000°, and 1,500°K; intermediate values were interpolated graphically.

The value 59.29 cal/mole °K for the entropy at 298.16 °K may be compared with 59.24 ± 0.10 [14] obtained from the low-temperature calorimetric data of Giauque and Stephenson [15].

In the case of sulfur trioxide gas, the recent calculations of Stockmayer, Kavanagh, and Mickley [13] were checked and converted to the values of the fundamental constants used in this paper.

For hydrogen sulfide gas, the rigid rotator-harmonic oscillator calculations and corrections, made in the same way as for sulfur dioxide, were based upon the recent complete vibrational analysis of Allen, Cross, and King [16], which gives the anharmonicity terms. Moments of inertia were taken from the work of Allen, Cross, and Wilson [17], Grady, Cross, and King [18], and Hainer and King [19] and corrected to approximate equilibrium values by comparison with water vapor. These gave a product $I_x I_y I_z$ equal to $49.25 \times 10^{-120}\text{ g}^3\text{cm}^6$. A stretching correction, insignificant in the case of the other polyatomic molecules, was applied by using the method of Wilson [20]. The corrections to the rigid rotator-harmonic oscillator at 1,500 °K were -0.06, 0.08, and 0.22 cal/mole °K for the free-energy function, heat-content function, and heat capacity.

The calculated value of the entropy at 298.16 °K, 49.17 cal/mole °K, may be compared with the value [14] 49.11 ± 0.10 obtained from the low-temperature calorimetric data of Clusius and Frank [21] and Giauque and Blue [22].

To correct values of ΔH_f° and ΔF_f° between 0 °K and 298.16 °K, it was necessary to know the thermodynamic functions at the latter temperature for crystalline rhombic sulfur. These were obtained by graphical integration of the heat-capacity data of Eastman and McGavock [23] as follows:

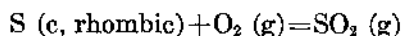
TABLE 2. Thermodynamic functions for S (c, rhombic)

	298.16° K	300° K
	cal/mole °K	cal/mole °K
$(F^\circ - H_0^\circ)/T$	-4.086	-4.097
$(H^\circ - H_0^\circ)/T$	3.532	3.544
C_p°	5.401	5.412

4. Selection of the "Best" Values for the Heats of Formation

The heat of formation of sulfur dioxide gas is based upon the combustion measurements of Eckman and Rossini [24], who burned excess sulfur in

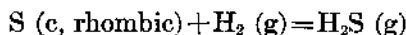
oxygen under conditions precluding the formation of sulfur trioxide. Their data, when corrected for the atomic weight of sulfur, give for the selected value:



$$\Delta H_{298.16}^{\circ} = -70.947 \pm 0.050 \text{ kcal/mole.}^3$$

The earlier combustion measurements at constant pressure of Thomsen [26], which yield $\Delta H_{298.16}^{\circ} = -71.04 \pm 0.50$ kcal/mole, confirm this value. Berthelot [27, 28], in two sets of combustions at constant volume using two different analytical techniques, obtained $\Delta H_{298.16}^{\circ} = -69.46 \pm 1.00$ kcal/mole. The data of Giran [29], who obtained heats of combustion at various high oxygen pressures, give $\Delta H_{298.16}^{\circ} = -70.5 \pm 0.8$ kcal/mole.

The value for the heat of formation of hydrogen sulfide gas is based upon: (a) the heat of combustion of hydrogen sulfide gas obtained by Zeumer and Roth [30] and by Thomsen [26], together with the value for the heat of formation of $\text{SO}_2 (\text{g})$ selected above and that for water given by Rossini et al. [25]; (b) the heat of reaction of $\text{H}_2\text{S} (\text{g})$ with a solution of iodine in aqueous hydriodic acid [26], combined with the appropriate values of the heats of formation given in Rossini et al.; and (c), the heat of reaction derived from the equilibrium measurements of Pollitzer [31] on the reaction of $\text{H}_2\text{S} (\text{g})$ with crystalline iodine to give hydrogen iodide gas and rhombic sulfur, together with the heat of formation of $\text{HI} (\text{g})$ given by Rossini et al. These results, as summarized in table 3, lead to



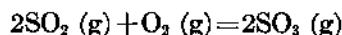
$$\Delta H_{298.16}^{\circ} = -4.82 \pm 0.10 \text{ kcal/mole.}$$

TABLE 3. Heat of formation of $\text{H}_2\text{S} (\text{g})$

Observer	Method	$\Delta H_{298.16}^{\circ}$
Thomsen [26].....	Combustion of H_2S	<i>kcal/mole</i> -2.61 \pm 0.50
Thomsen [26].....	Reaction with HI-I_2 (aqueous).....	-4.82 \pm 0.20
Pollitzer [31].....	Reaction with $\text{I}_2 (\text{c})$	-4.81 \pm 0.20
Zeumer and Roth [30].....	Combustion of H_2S	-4.82 \pm 0.14

* Omitted in obtaining "best" value.

For sulfur trioxide several sets of high-temperature measurements of the equilibrium between sulfur dioxide, sulfur trioxide, and oxygen are available. These were combined with the appropriate free-energy functions [32] and the heat of formation of sulfur dioxide to calculate the values of $\Delta H_{298.16}^{\circ}$ for the reaction



and $\Delta H_{298.16}^{\circ}$ for sulfur trioxide gas given in table 4.

A value of -94.35 ± 0.12 kcal/mole for the heat of formation of sulfur trioxide gas was obtained from

³ The uncertainties in ΔH given in this section of the paper represent the present writers' best estimates of the overall uncertainties in the values.

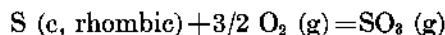
TABLE 4. Heats of dissociation of $\text{SO}_2 (\text{g})$ *

Observer	Number of measurements	$\Delta H_{298.16}^{\circ}$	$\Delta H_{298.16}^{\circ} \text{ SO}_2 (\text{g})$
Bodländer and Koppen [33].....	6	<i>kcal</i> -46.28 \pm 0.36	<i>kcal</i> -94.37 \pm 0.60
Knietzsch [34].....	11	-44.23 \pm 0.50	-93.84 \pm 0.80
Lunge and Reinhardt [35].....	39	-45.25 \pm 0.26	-94.36 \pm 0.20
Bodenstein and Pohl [36].....	49	-45.57 \pm 0.04	-94.52 \pm 0.04
Lucas [37].....	7	-49.33 \pm 0.65	-96.40 \pm 1.40
Taylor and Lenher [40].....	4	-45.45 \pm 0.10	-94.46 \pm 0.12
Kapustinskiĭ and Shamovskii [38, 39].....	11	-45.57 \pm 0.08	-94.52 \pm 0.07

* The uncertainties given for ΔH represent the probable error of the mean of the measurements. Those given for $\Delta H_{298.16}^{\circ}$, as elsewhere in this paper, are the estimated over-all uncertainties.

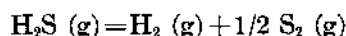
calorimetric measurements of Roth and coworkers [41-43] through a series of reactions involving the heat of solution of liquid sulfur trioxide in water [42], the heat of solution of gaseous sulfur dioxide in aqueous hydrogen peroxide [41], the heat of decomposition of hydrogen peroxide [41], the heat of dilution of sulfuric acid [25, 42], and the heat of vaporization of sulfur trioxide [25].

As the best value a weighted average was taken to give



$$\Delta H_{298.16}^{\circ} = -94.47 \pm 0.07 \text{ kcal.}$$

Because of the complex polymerization in sulfur vapor below 1,000°K [1, 53], the best value for the heat of formation of diatomic sulfur gas is obtained from measurements of dissociation of hydrogen sulfide at high temperatures, where sulfur exists primarily as S_2 . Three series of such measurements are available [44, 45, 46]. All were carried out by determining the pressure of the hydrogen formed by the dissociation of hydrogen sulfide, using a platinum membrane. In addition, Preuner and Schupp [45] measured the increase in total pressure of a small sample of H_2S when heated in a sealed bulb; these results give a $\Delta H_{298.16}^{\circ}$ differing less than 0.02 kcal from the over-all average. Combination of the equilibrium constants calculated from these measurements with the appropriate free-energy functions [32] gives the values for the heat of dissociation



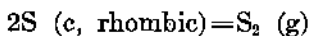
tabulated in table 5.

TABLE 5. Heat of dissociation of H_2S

Observer	Number of measurements	$\Delta H_{298.16}^{\circ}$ *
Preuner [44].....	5	<i>kcal</i> 19.506 \pm 0.040
Preuner and Schupp [45].....	20	19.528 \pm 0.031
Randall and Bichowsky [46].....	4	19.557 \pm 0.044

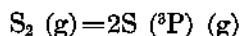
* The uncertainties given for $\Delta H_{298.16}^{\circ}$ represent the probable error of the mean of the measurements.

The weighted average 19.53 ± 0.02 kcal, the heat of formation of hydrogen sulfide selected previously, and the appropriate heat-content functions [32] give the heat of formation of diatomic sulfur gas:



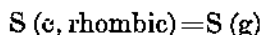
$$\Delta H_{298.15}^\circ = 30.84 \pm 0.15 \text{ kcal.}$$

The best value for the heat of formation of monatomic sulfur gas appears to be that derived from spectroscopic studies. From a study of predissociation, Olsson [47] selected a value of 3.6 electron volts (ev) as an upper limit for the dissociation energy of diatomic sulfur gas into normal ^3P sulfur atoms.⁴ Considering all such data and by comparison with molecules of similar structure Goldfinger, Juenehomme and Rosen [48] selected 4.41 ev for the dissociation into one normal ^3P atom and one excited ^1D atom. Herzberg [5] favored a value of 3.6 ev or lower for the dissociation into normal atoms, and Gaydon [49], after summarizing the evidence, assumed that the value of 4.41 ev from predissociation measurements corresponds to the true dissociation energy. If the value 4.41 ev is selected as dissociation into one normal atom and one excited ^1D atom, as favored by Herzberg, then the dissociation energy is



$$\Delta H_0^\circ = 75.3 \pm 0.5 \text{ kcal.}^5$$

Partial confirmation of this lower value is furnished by high-temperature gas-density measurements. Nernst [50], using the Victor-Meyer method at 1,900 to 2,300 °K, obtained 71 ± 8 kcal for ΔH_0° ; von Wartenberg [51] in the same way obtained 75 ± 10 kcal. Using the spectroscopic value of ΔH_0° and the value for diatomic sulfur gas,



$$\Delta H_{298.15}^\circ = 53.54 \pm 0.50 \text{ kcal.}$$

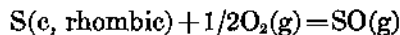
Additional confirmation is afforded by measurements of Bjerrum [52] on the heat of dissociation of hydrogen sulfide gas at 2,900 to 3,200 °K. For the dissociation to monatomic sulfur and diatomic hydrogen gases he found $\Delta H_0^\circ = 51 \pm 15$ kcal, which leads to a value of $\Delta H_{298.15}^\circ$ for S (g) of 56 ± 15 kcal.

The spectroscopic data on sulfur monoxide gas do not lead to a definite value for the dissociation of the molecule because of the uncertainty in the energy states of the dissociation products. Herzberg [5] favors dissociation into $\text{S}(^1\text{D}) + \text{O}(^3\text{P})$, which leads to a dissociation energy of 4.001 ev. Gaydon [49] assumes dissociation to $\text{S}(^3\text{P}) + \text{O}(^1\text{P})$, with a dissociation energy greater by the difference $\text{S}(^1\text{D}) - \text{S}(^3\text{P})$, or 5.146 ev. (Dissociation into the third simple combination of products, $\text{S}(^3\text{P}) + \text{O}(^1\text{D})$, appears unlikely because of the greater energy differences in-

⁴ 1 ev/molecule = 23060.5 cal/mole.

⁵ Since this report was written measurements of the heat of formation of HS (g) by Franklin and Lumpkin [55] and of the dissociation energy D_0 for HS by Porter [56] indicate that the higher value of 4.41 ev for D_0 of S_2 is probably the correct value. If this value is accepted, the values of ΔH_0° and ΔF_0° for S (g) will be increased by 13.2 kcal, with corresponding changes in $\log_{10} K_f$.

involved.) The lower value was selected because the dissociation is apparently of the same type as that of S_2 and O_2 . Combining this value with the values for gaseous atomic sulfur and oxygen [25], the heat of formation of sulfur monoxide is calculated



$$\Delta H_{298.15}^\circ = 19.30 \pm 0.50 \text{ kcal.}^6$$

In order to extend the useful range of the data on the reactions of formation, the values of ΔH_f° selected above were converted to values based on $\text{S}_2(\text{g})$ as the standard reference state for sulfur. The values of the heat of formation, ΔH_f° ; free energy of formation, ΔF_f° ; and logarithm of the equilibrium constant of formation, $\log_{10} K_f$, were then calculated at temperatures up to 1,500° K by the relations

$$\Delta H_{f_T}^\circ = \Delta H_f^\circ + \Delta(H_T^\circ - H_0^\circ)$$

$$\Delta F_{f_T}^\circ = \Delta H_f^\circ + T\Delta[(F^\circ - H_0^\circ)/T]$$

$$\log_{10} K_f = -(\Delta F_{f_T}^\circ / 4.57567 T).$$

The values calculated in this manner, as well as the thermodynamic functions for the six gaseous molecules considered, are given in tables 6 to 12.

As examples of the applications of these tables, three industrially important reactions were considered. Figure 1 shows the equilibrium composition obtained when gaseous hydrogen sulfide decomposes

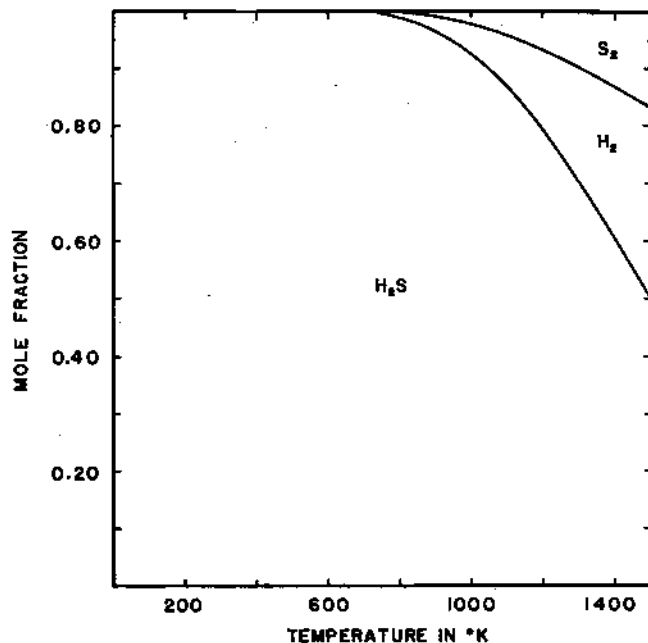
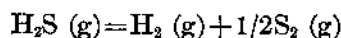


FIGURE 1. Equilibrium composition for a $2\text{H}_2\text{S}:\text{S}_2$ mixture at 1-atmosphere pressure as a function of temperature.

The vertical width of a band represents the mole fraction of the component present.

⁶ As indicated in footnote 5, the best value of D_0 (S_2) appears to be 4.41 ev. By reasoning as above, the higher value of 5.146 ev appears more likely for D_0 of SO. If this value is accepted, as well as 4.41 ev for D_0 of S_2 , the values of ΔH_f° and ΔF_f° for SO (g) will become more negative by 13.2 kcal, with corresponding changes in $\log_{10} K_f$.

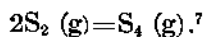
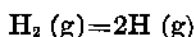
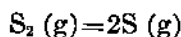
under a total pressure of 1 atm. The ordinate gives the mole fraction of each component; the abscissa the absolute temperature. The equilibrium composition was obtained by first calculating the equilibrium constant for the reaction



at various temperatures, using the relation

$$-4.57567 \log_{10} K = \Delta F_T^\circ / T$$

and the values of the free energies of formation given in the present paper and in Rossini et al. [32]. The values of K were then used to obtain the equilibrium composition in the usual way. The side reactions



were also considered. After the values for H_2 and S_2 were obtained, they were used to calculate the concentrations of the other possible products; in no case were the side reactions significant.

Figure 2 shows the equilibrium composition obtained in the gaseous decomposition of sulfur trioxide

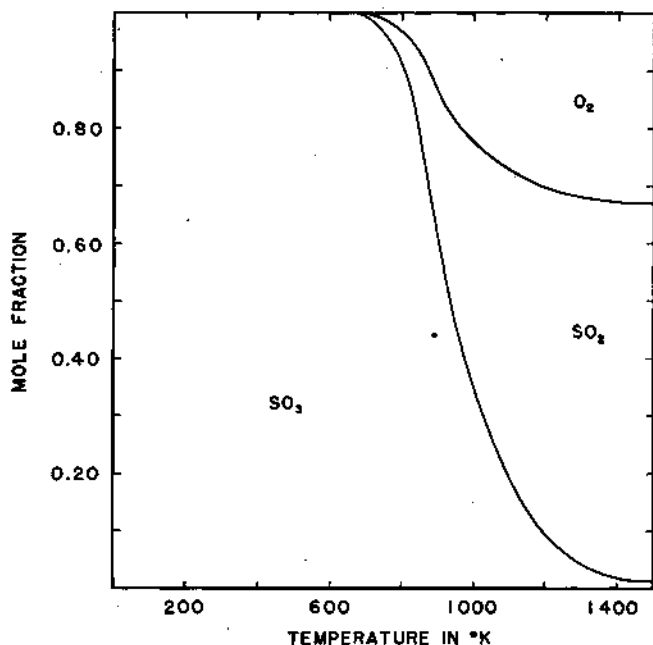
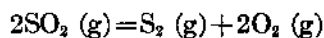
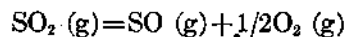


FIGURE 2. Equilibrium composition for a $3\text{O}_2:\text{S}_2$ mixture at 1-atmosphere pressure as a function of temperature.

The vertical width of a band represents the mole fraction of the component present.

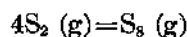
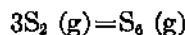
⁷ For the calculation of the equilibrium compositions of the various sulfur species the data of Braune, Peter, and Neveling [53] were used.

at a total pressure of 1 atm. Possible side reactions considered were



all were unimportant.

Figure 3 shows the equilibrium composition of the vapor obtained from mixing two molecular volumes of hydrogen sulfide and one of sulfur dioxide at a total final pressure of 1 atm. At temperatures below about 500° K liquid sulfur separates [1] with a corresponding increase in the concentration of the water vapor. Side reactions considered, in addition to those listed above, were



Of these, only the sulfur polymerization was significant; for this, the results of Braune, Peter, and Neveling [53] were used, although their data are not completely satisfactory. These results indicate that recovery of sulfur from hydrogen sulfide gas by partial oxidation should be feasible.

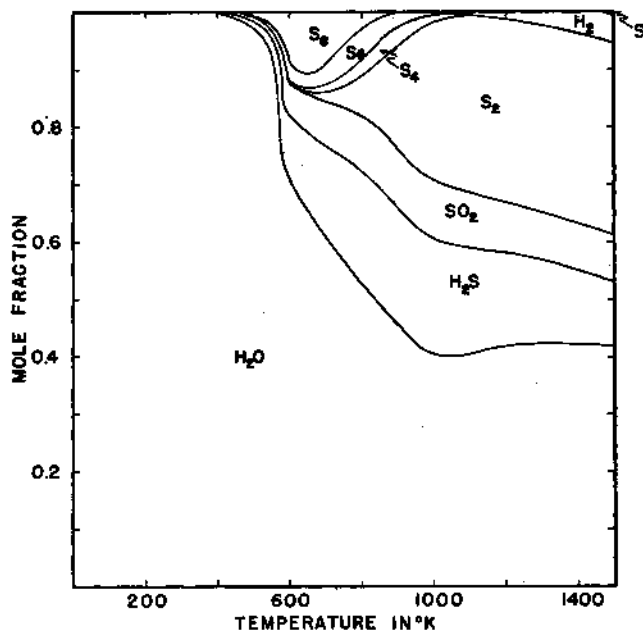


FIGURE 3. Equilibrium composition for a $2\text{H}_2\text{S}:\text{SO}_2$ mixture at 1-atmosphere pressure as a function of temperature.

The vertical width of a band represents the mole fraction of the component present.

TABLE 6. Heat, free energy, and equilibrium constant of formation, free-energy function, heat-content function, entropy, heat content (or enthalpy), and heat capacity for S (g)

Reference states for elements, used for calculating ΔH_f° , ΔF_f° , and $\log K_f$: S₂ (g).

Property	Units	Temperature in °K														
		0	298.16	300	400	500	600	700	800	900	1,000	1,100	1,200	1,300	1,400	1,500
ΔH_f°	kcal/mole	37.6	38.12	38.12	38.29	38.42	38.54	38.64	38.72	38.80	38.88	38.95	39.02	39.09	39.14	39.20
ΔF_f°	kcal/mole	37.6	34.29	34.27	32.96	31.61	30.24	28.85	27.45	26.03	24.61	23.17	21.74	20.21	18.85	17.40
$\log_e K_f$			-25.134	-24.965	-18.003	-13.817	-11.015	-9.007	-7.499	-6.321	-5.378	-4.603	-3.959	-3.598	-2.943	-2.535
$(F^\circ - H^\circ)/T$	cal/deg mole	0	-34.7499	-34.7828	-36.3295	-37.5384	-38.5271	-39.3603	-40.0307	-40.7132	-41.2764	-41.7844	-42.2466	-42.6703	-43.0613	-43.4244
$(F^\circ - H^\circ)/T$	cal/deg mole	0	5.3364	5.3384	5.4033	5.4237	5.4177	5.4009	5.3803	5.3590	5.3353	5.3185	5.3007	5.2841	5.2591	5.2558
$H^\circ - H^\circ$	cal/deg mole	0	40.0363	40.1212	41.7358	42.9621	43.9445	44.7617	45.4610	46.0722	46.6147	47.1032	47.5473	47.9544	48.3304	48.6800
$H^\circ - H^\circ$	cal/mole	0	1591.1	1601.5	2162.5	2711.8	3250.6	3780.6	4304.2	4823.1	5338.3	5850.7	6360.8	6869.3	7376.7	7883.4
C_p°	cal/deg mole	0	5.6585	5.6574	5.5634	5.4358	5.3393	5.2661	5.2107	5.1685	5.1363	5.1116	5.0928	5.0789	5.0693	5.0337

TABLE 7. Free-energy function, heat-content function, entropy, heat content (or enthalpy), and heat capacity for S (g)

Property	Units	Temperature in °K									
		1,600	1,700	1,800	1,900	2,000	2,100	2,200	2,300	2,400	2,500
$(F^\circ - H^\circ)/T$	cal/deg mole	-43.7631	-44.0806	-44.3795	-44.6617	-44.9290	-45.1830	-45.4249	-45.6560	-45.8770	-46.0889
$(H^\circ - H^\circ)/T$	cal/deg mole	5.2435	5.2328	5.2235	5.2155	5.2087	5.2031	5.1985	5.1951	5.1927	5.1911
S°	cal/deg mole	49.0066	49.3134	49.6030	49.8772	50.1377	50.3861	50.6235	50.8511	51.0697	51.2800
$H^\circ - H^\circ$	cal/mole	8389.6	8895.8	9402.3	9903.4	10417.4	10936.5	11458.9	11984.7	12462.5	12977.8
C_p°	cal/deg mole	5.0618	5.0632	5.0678	5.0752	5.0852	5.0974	5.1115	5.1272	5.1442	5.1623

Property	Units	Temperature in °K									
		2,750	3,000	3,250	3,500	3,750	4,000	4,250	4,500	4,750	5,000
$(F^\circ - H^\circ)/T$	cal/deg mole	-46.5837	-47.0354	-47.4514	-47.8371	-48.1970	-48.5343	-48.8518	-49.1518	-49.4363	-49.7058
$(H^\circ - H^\circ)/T$	cal/deg mole	5.1906	5.1943	5.2010	5.2099	5.2204	5.2318	5.2436	5.2555	5.2673	5.2787
S°	cal/deg mole	51.7743	52.2297	52.6524	53.0470	53.4174	53.7661	54.0954	54.4073	54.7036	54.9855
$H^\circ - H^\circ$	cal/mole	14274.2	15682.9	16903.2	18034.6	19076.5	20027.2	20885.3	21649.8	22319.7	22893.5
C_p°	cal/deg mole	5.2098	5.2581	5.3045	5.3472	5.3854	5.4185	5.4464	5.4694	5.4878	5.5021

TABLE 8. Heat, free energy, and equilibrium constant of formation, free-energy function, heat-content function, entropy, heat content (or enthalpy), and heat capacity for S₂ (g)

Reference states for elements, used for calculating ΔH_f° , ΔF_f° , and $\log K_f$: S₂ (g).

Property	Units	Temperature in °K														
		0	298.16	300	400	500	600	700	800	900	1,000	1,100	1,200	1,300	1,400	1,500
ΔH_f°	kcal/mole	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
ΔF_f°	kcal/mole	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
$\log_e K_f$		0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
$(F^\circ - H^\circ)/T$	cal/deg mole	0	-47.33	-47.37	-49.47	-51.13	-52.52	-53.72	-54.78	-55.72	-56.57	-57.34	-58.06	-58.72	-59.34	-59.92
$(H^\circ - H^\circ)/T$	cal/deg mole	0	7.18	7.18	7.38	7.56	7.71	7.94	8.15	8.34	8.51	8.68	8.84	8.99	9.14	9.28
S°	cal/deg mole	0	54.51	54.55	56.85	58.69	60.23	61.56	62.73	63.76	64.68	65.52	66.30	67.01	67.68	68.30
$H^\circ - H^\circ$	cal/mole	0	2141	2154	2952	3780	4626	5488	6360	7236	8110	8988	9868	10777	11676	12570
C_p°	cal/deg mole	0	7.76	7.77	8.14	8.39	8.64	8.85	9.03	9.19	9.34	9.48	9.61	9.73	9.84	9.94

TABLE 9. Heat, free energy, and equilibrium constant of formation, free-energy function, heat-content function, entropy, heat content (or enthalpy), and heat capacity for SO (g)
Reference states for elements, used for calculating ΔH_f° , ΔF_f° , and $\log K_f$: O₂ (g); S₂ (g).

Property	Units	Temperature in °K														
		0	298.16	300	400	500	600	700	800	900	1,000	1,100	1,200	1,300	1,400	1,500
ΔH_f°	kcal/mole	3.9	3.88	3.88	3.87	3.86	3.86	3.86	3.87	3.87	3.87	3.87	3.87	3.87	3.87	3.86
ΔF_f°	kcal/mole	3.9	3.49	3.49	3.36	3.24	3.11	2.99	2.87	2.74	2.61	2.48	2.35	2.23	2.11	1.99
$\log_{10} K_f$			-2.558	-2.542	-1.836	-1.416	-1.133	-0.934	-0.784	-0.665	-0.570	-0.488	-0.428	-0.375	-0.329	-0.290
$(F^\circ - H^\circ)/T$	cal/deg mole	0	-46.07	-48.10	-48.13	-49.73	-51.05	-52.20	-53.20	-54.10	-54.92	-55.67	-56.36	-56.99	-57.55	-58.14
$(H^\circ - H^\circ)/T$	cal/deg mole	0	7.01	7.01	7.11	7.23	7.36	7.48	7.59	7.77	7.85	7.85	7.92	7.98	8.01	8.00
S°	cal/deg mole	0	53.03	53.11	55.24	55.96	58.42	59.68	60.79	61.79	62.69	63.52	64.28	64.97	65.62	66.23
$H^\circ - H^\circ$	cal/mole	0	2090	2103	2844	3615	4416	5236	6072	6921	7770	8635	9504	10374	11256	12135
C_p°	cal/deg mole	0	7.23	7.24	7.57	7.87	8.11	8.29	8.42	8.52	8.60	8.66	8.71	8.75	8.79	8.82

TABLE 10. Heat, free energy, and equilibrium constant of formation, free-energy function, heat-content function, entropy, heat content (or enthalpy), and heat capacity for SO₂ (g)
Reference states for elements, used for calculating ΔH_f° , ΔF_f° , and $\log K_f$: O₂ (g); S₂ (g).

Property	Units	Temperature in °K														
		0	298.16	300	400	500	600	700	800	900	1,000	1,100	1,200	1,300	1,400	1,500
ΔH_f°	kcal/mole	-85.746	-86.367	-86.387	-86.48	-86.55	-86.58	-86.59	-86.59	-86.57	-86.55	-86.51	-86.48	-86.43	-86.39	-86.35
ΔF_f°	kcal/mole	-85.746	-87.678	-87.592	-88.38	-89.24	-90.17	-91.15	-92.18	-93.27	-94.41	-95.60	-96.82	-98.09	-99.37	-100.71
$\log_{10} K_f$			64.1935	63.8100	48.288	39.006	32.844	28.458	25.182	22.649	20.633	18.994	17.633	16.490	15.512	14.673
$(F^\circ - H^\circ)/T$	cal/deg mole	0	-50.84	-50.89	-53.38	-55.40	-57.11	-58.61	-59.96	-61.18	-62.30	-63.34	-64.30	-65.20	-66.04	-66.84
$(H^\circ - H^\circ)/T$	cal/deg mole	0	8.45	8.46	8.84	9.22	9.60	9.94	10.24	10.51	10.75	10.97	11.16	11.34	11.50	11.64
S°	cal/deg mole	0	59.29	59.25	62.22	64.62	66.71	68.55	70.20	71.69	73.05	74.31	75.46	76.54	77.54	78.48
$H^\circ - H^\circ$	cal/mole	0	2519	2538	3536	4610	5760	6968	8192	9459	10750	12067	13392	14742	16100	17480
C_p°	cal/deg mole	0	9.53	9.54	10.39	11.12	11.71	12.17	12.53	12.82	13.03	13.20	13.35	13.47	13.57	13.65

TABLE 11. Heat, free energy, and equilibrium constant of formation, free-energy function, heat-content function, entropy, heat content (or enthalpy), and heat capacity for SO₃ (g)
Reference states for elements, used for calculating ΔH_f° , ΔF_f° , and $\log K_f$: O₂ (g); S₂ (g).

Property	Units	Temperature in °K														
		0	298.16	300	400	500	600	700	800	900	1,000	1,100	1,200	1,300	1,400	1,500
ΔH_f°	kcal/mole	-108.49	-109.89	-109.89	-110.05	-110.08	-110.00	-109.86	-109.67	-109.44	-109.16	-108.86	-108.54	-108.19	-107.82	-107.43
ΔF_f°	kcal/mole	-108.49	-95.09	-98.02	-94.03	-90.02	-86.02	-82.04	-78.08	-74.15	-70.24	-66.37	-62.51	-58.68	-54.87	-51.08
$\log_{10} K_f$			71.899	71.407	61.375	53.347	47.332	42.614	38.330	34.306	30.551	27.116	23.944	21.000	18.355	16.000
$(F^\circ - H^\circ)/T$	cal/deg mole	0	-61.89	-61.95	-64.76	-67.14	-69.26	-71.18	-72.94	-74.57	-76.08	-77.48	-78.78	-80.00	-81.14	-82.20
$(H^\circ - H^\circ)/T$	cal/deg mole	0	9.30	9.32	10.25	11.18	12.04	12.80	13.48	14.08	14.63	15.12	15.56	15.96	16.33	16.67
S°	cal/deg mole	0	61.19	61.27	65.01	68.32	71.30	73.98	76.42	78.65	80.71	82.62	84.39	86.05	87.61	89.07
$H^\circ - H^\circ$	cal/mole	0	2773	2795	4100	5590	7224	8960	10784	12672	14630	16632	18672	20748	22852	25000
C_p°	cal/deg mole	0	12.10	12.13	14.06	15.66	16.90	17.86	18.61	19.23	19.76	20.21	20.61	20.96	21.28	21.58

TABLE 12. Heat, free energy, and equilibrium constant of formation, free-energy function, heat-content function, entropy, heat content (or enthalpy), and heat capacity for H₂S (g)
Reference states for elements, used for calculating ΔH_f° , ΔF_f° , and $\log K_f$: H₂ (g); S₂ (g).

Property	Units	Temperature in °K														
		0	298.16	300	400	500	600	700	800	900	1,000	1,100	1,200	1,300	1,400	1,500
ΔH_f°	kcal/mole	-19.53	-20.24	-20.24	-20.50	-20.74	-20.95	-21.13	-21.27	-21.38	-21.45	-21.50	-21.54	-21.55	-21.55	-21.54
ΔF_f°	kcal/mole	-19.53	-17.47	-17.45	-16.48	-15.44	-14.36	-13.25	-12.11	-10.97	-9.80	-8.64	-7.47	-6.29	-5.11	-3.94
$\log_{10} K_f$			12.805	12.712	9.004	6.749	5.231	4.137	3.308	2.664	2.142	1.717	1.360	1.027	0.798	0.574
$(F^\circ - H^\circ)/T$	cal/deg mole	0	-41.17	-41.21	-43.52	-45.34	-46.85	-48.15	-49.31	-50.35	-51.29	-52.17	-52.99	-53.75	-54.47	-55.16
$(H^\circ - H^\circ)/T$	cal/deg mole	0	8.00	8.00	8.09	8.21	8.37	8.54	8.72	8.91	9.10	9.29	9.47	9.65	9.82	9.98
S°	cal/deg mole	0	49.17	49.21	51.61	53.55	55.22	56.69	58.03	59.26	60.39	61.46	62.46	63.40	64.29	65.14
$H^\circ - H^\circ$	cal/mole	0	2385	2400	3235	4105	5022	5978	6976	8019	9100	10219	11364	12545	13748	14970
C_p°	cal/deg mole	0	8.19	8.20	8.53	8.83	9.35	9.78	10.21	10.62	11.00	11.34	11.64	11.92	12.16	12.37

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