within 0.5 of 1% shows that the over-all error is somewhat reduced by compensation of component errors. The uncertainty of the extrapolation to the critical temperature accounts for the relatively large estimated limits of error in the entropy shown in Table II.

Entropy of Hydrogen at the Critical Point.—At the critical temperature a gas is indistinguishable from a liquid, and the entropies of the two phases are identical. The calorimetric entropy is evaluated in Table II.

Since the entropy is given by $\Delta S = \int C_p \mathrm{d} \ln T$, the heat capacity at constant pressure rather than the saturation heat capacity must be used to evaluate the integral. The relation between C_p and C_s is given by

$$C_s = C_p - T\left(\frac{\partial V}{\partial T}\right)_p\left(\frac{\partial P}{\partial T}\right)_s \tag{1}$$

and the corresponding entropy difference amounts to 0.499 e.u. between 20.26 and 33.24°K. C_p was computed at 12.8 atm. (the critical pressure) with the use of $P-V-T$ data, and a correction for the entropy change of the liquid in going from 1 to 12.8 atm. was applied. The entropy of mixing of the 0.21% orthohydrogen has been discussed elsewhere.[1] The entropy correction in going from a real gas to an ideal gas at 33.24°K. and 12.8 atm. was found by extrapolation from tables based on $P-V-T$ data for hydrogen.[2,9]

The entropy of a perfect gas at 33.24°K. including nuclear spin is 17.192 e.u. and the entropy of mixing is 0.016 e.u. The statistical entropy is thus 17.208 e.u. which is in satisfactory agreement with our experimental value of 17.2 e.u.

Acknowledgments.—We wish to thank Mr. Howard Altman and Mr. W. D. Wood, who helped with the runs and with calculations.

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(9) H. W. Wooley, R. S. Scott and F. G. Brickwedde, *J. Research Natl. Bur. Standards*, **41**, 379 (1948), RP 1932.

Columbus, Ohio

[Contribution No. 42 from the Thermodynamics Laboratory, Petroleum Experiment Station, Bureau of Mines]

Thermodynamic Functions and Heat of Formation of S_8(Gas)[1]

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The thermodynamic functions $(F^0 - H_0^\circ)/T$, $(H^\circ - H_0^\circ)/T$, $H^\circ - H_0^\circ$, S°, and C_p°, for S_8(gas) at selected temperatures to 1000°K. were calculated from spectroscopic and molecular structure data. Values of the heat of formation of S_8(gas) from rhombic sulfur were computed from published experimental data. The value $\Delta H_{f0}^\circ = 25.23 \pm 0.05$ kcal. mole^{-1} was selected as the most probable. The heat, free energy and equilibrium constant at selected temperatures were calculated for the reaction $4S_2(\text{gas}) = S_8(\text{gas})$. A vibrational assignment previously proposed for S_8 was found to be inconsistent with the vapor pressure and thermal data for rhombic sulfur and was revised to remove the inconsistency. Consideration of tautomers of the cyclic S_8 molecule other than the one of D_{4d} symmetry made it seem unlikely that these make significant contributions to the thermodynamic properties at temperatures below 1000°K.

In order to utilize fully the thermodynamic data that are being obtained for organic sulfur compounds in this Laboratory and elsewhere, it is necessary to have thermodynamic data of equal quality for elemental sulfur. Because elemental sulfur occurs in some petroleum crudes and refinery processes, accurate values of its thermodynamic properties are pertinent to petroleum technology. Only two comprehensive correlations of the thermodynamic properties of elemental sulfur have been published. The earlier one, that of Lewis and Randall,[2] antedates their book published in 1923. The more recent one, published by Kelley[3] in 1937, took advantage of newer data that had been obtained since the time of Lewis and Randall's work.

Additional and more accurate data that have become available for elemental sulfur since 1937 make an up-to-date correlation of its thermodynamic properties desirable, and such a correlation has been undertaken in this Laboratory. This paper presents values of the chemical thermodynamic properties of S_8(gas) that were computed from spectroscopic, molecular structure, vapor pressure and other data as a part of the over-all correlation. Values of the chemical thermodynamic properties of two simpler sulfur species, S_2(gas) and S(gas), are already available from the recent work of Evans and Wagman.[4]

Vibrational Assignment and Thermodynamic Functions

Vibrational Assignment.—Calculation of thermodynamic functions for S_8 required a complete assignment of the fundamental vibrational frequencies of the molecule. Bernstein and Powling[5] recently reviewed and added to the available spectroscopic data for S_8 and proposed a vibrational assignment that is essentially an extension of the earlier incomplete assignment of Bhagavantam and Venkatarayudu.[6] When thermodynamic functions computed from Bernstein and Powling's assignment were used with vapor pressure data for rhombic sulfur to compute ΔH_0° for the reaction 8S(rhombic) =

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[1] This investigation was part of American Petroleum Institute Research Project 48A on "The Production, Isolation and Purification of Sulfur Compounds and Measurement of their Properties," which the Bureau of Mines conducts at Bartlesville, Okla., and Laramie, Wyo.

[2] G. N. Lewis and M. Randall, (a) This Journal, **33**, 476 (1911); (b) *ibid.*, **36**, 2468 (1914); (c) "Thermodynamics and the Free Energy of Chemical Substances," McGraw-Hill Book Co., Inc., New York, N. Y., 1923, pp. 534–535.

[3] K. K. Kelley, "Contributions to the Data on Theoretical Metallurgy. VII. The Thermodynamic Properties of Sulfur and its Inorganic Compounds," Bureau of Mines Bulletin 406, U. S. Govt. Printing Office, Washington, D. C., 1937, pp. 2–11.

[4] W. H. Evans and D. D. Wagman, *J. Research Natl. Bur. Standards*, **49**, 141 (1952).

[5] H. J. Bernstein and J. Powling, *J. Chem. Phys.*, **18**, 1018 (1950); *ibid.*, **19**, 139 (1951).

[6] S. Bhagavantam and T. Venkatarayudu, *Proc. Indian Acad. Sci.*, **8A**, 115 (1938).

S_8(gas), the values of ΔH_0° showed a marked trend with the temperatures of the vapor pressure measurements. This result prompted critical examination of Bernstein and Powling's assignment. It was observed that these investigators had not assigned one of the strongest Raman lines and two of the strongest infrared bands as fundamental frequencies. Therefore, a new assignment was proposed, which included these three strong observed frequencies as fundamentals.

This assignment is discussed best by reference to Table I, which gives the symmetry classes and selection rules for D_{4d} point-group symmetry, the classification of the vibrations into S–S–S bending and S–S stretching modes, and the frequency assigned to each vibration. The Raman-active classes will be considered first. The two strong polarized lines observed in the Raman spectrum (216 and 470 cm.$^{-1}$) may be assigned at once to the two A_1 frequencies. The five remaining Raman-active frequencies of the E_2 and E_3 classes should appear as depolarized lines. Three of these are S–S–S bending frequencies, which are probably lower than 300 cm.$^{-1}$, and two are S–S stretching frequencies, which are probably between 400 and 575 cm.$^{-1}$. The strong depolarized lines at 86, 152 and 435 cm.$^{-1}$ can confidently be assigned to two of the bending and one of the stretching frequencies. For the remaining bending frequency, it is necessary to choose between the weak depolarized lines at 185 and 243 cm.$^{-1}$. The former is assigned as the fundamental frequency because it cannot be explained as an overtone or combination, whereas the 243 cm.$^{-1}$ frequency can be so explained. The only unassigned Raman line in the region where the remaining stretching frequency is expected is the very weak one at 520 cm.$^{-1}$. These frequencies may be assigned to the E_2 and E_3 classes by comparison with the results of the force constant calculations of Bhagavantam and Venkatarayudu. The frequencies calculated by these authors increase in the order: 122, E_2; 211, E_3; 243, E_2; 456, E_2; and 542, E_3. The analogous order of the observed frequencies is: 86, E_2; 152, E_3; 185, E_2; 435, E_2; and 520, E_3. The infrared-active fundamentals will be considered next. There are three of these (one in the B_2 class and two in the E_1 class) and three strong infrared bands (150, 225 and 465 cm.$^{-1}$) to be assigned to them. The second infrared band was observed as a region of strong absorption between 200 and 250 cm.$^{-1}$. Bhagavantam and Venkatarayudu's calculated values for the infrared-active frequencies are: 181, E_1; 255, B_2; and 481, E_1, by analogy with which the observed frequencies may be assigned as: 150, E_1; 225, B_2; and 465, E_1. One frequency remains in the inactive B_1 class. Following Bernstein and Powling, a value of 532 cm.$^{-1}$ is obtained for this frequency by interpreting the weak infrared band at 1052 cm.$^{-1}$ as the combination 520 (E_3) + 532 (B_1) = 1052 (E_1).

TABLE I

VIBRATIONAL ASSIGNMENT FOR S_8

Symmetry class and selection rules	Type of vibration	Frequency, cm.$^{-1}$
A_1	S-S-S bend.	216
Raman, p	S-S str.	470
B_1	S-S str.	532
Inactive		
B_2	S-S-S bend.	225
Infrared		
E_1	S-S-S bend.	150
Infrared	S-S str.	465
E_2	S-S-S bend.	86
Raman, d	S-S-S bend.	185
	S-S str.	435
E_3	S-S-S bend.	152
Raman, d	S-S str.	520

Figure 1 shows that the marked trend with temperature in the values of ΔH_0° for the reaction 8S(rhombic) = S_8(gas), calculated from vapor pressure data by use of Bernstein and Powling's vibrational assignment, is removed when the vibrational assignment of Table I is used instead. The calculation of the values of ΔH_0° from vapor pressure data is treated in a subsequent section.

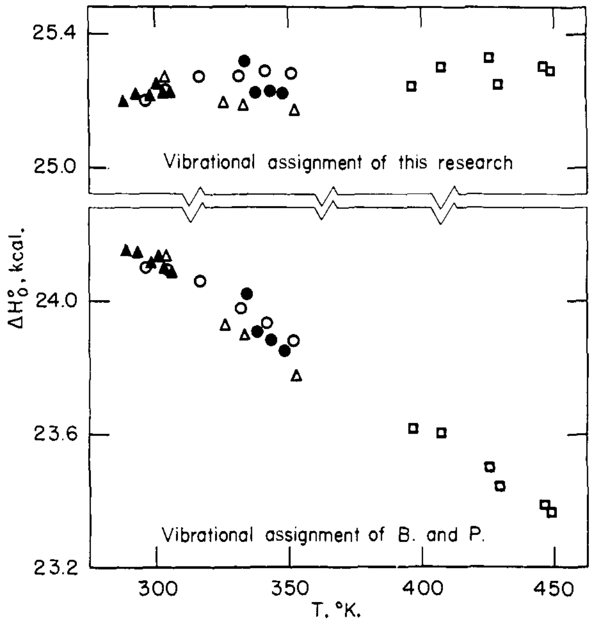

Fig. 1.—Values of ΔH_0° for the reaction, 8 S(rhombic) = S_8(gas), calculated by use of the vibrational assignments for S_8 of this research and of Bernstein and Powling, from the vapor pressure data of West and Menzies, □; Bradley, ▲; Fouretier, ○; Taillade, △; and Neumann, ●.

Thermodynamic Functions.—The rigid rotator, harmonic oscillator approximation was used to compute thermodynamic functions for S_8. Translational and rotational contributions were calculated from the equations of Wagman, *et al.*[7] The moments of inertia calculated for a model with D_{4d} symmetry, S–S bond distances of 2.08 Å., S–S–S angles of 105°[8] and atomic masses based on the 1951 atomic weight of sulfur are: $I_x = I_y = 1.2808$ and $I_z = 2.3197 \times 10^{-37}$ g. cm.^{2}; $I_xI_yI_z = 3.805 \times 10^{-111}$ g.^{3} cm.^{6}. The vibrational contribu-

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(7) D. D. Wagman, J. E. Kilpatrick, W. J. Taylor, K. S. Pitzer and F. D. Rossini, *J. Research Natl. Bur. Standards*, **34**, 143 (1945).

(8) L. Pauling, *Proc. Natl. Acad. Sci.*, **35**, 495 (1949).

tions were calculated from the foregoing vibrational assignment. The calculated values of the thermodynamic functions are listed in Table II. Contributions from tautomers of the S_8 molecule other than the one of D_{4d} symmetry are not included in the tabulated values. These contributions cannot be calculated at the present time because the needed values of the energies of tautomerism are not known. However, the contributions are certainly insignificant for temperatures below 450°K., and their omission from the thermodynamic functions used to calculate ΔH_{f0}° in the next section of this paper introduces no uncertainty into the value obtained for that quantity. The contributions may become significant at temperatures near 1000°K. Whenever the needed values of the energies of tautomerism become available, it will be possible to compute the contributions and apply them as corrections to the values tabulated in Table II. The tautomers of the S_8 molecule and their possible contributions to the thermodynamic functions are discussed more fully in the appendix at the end of this paper.

TABLE II

MOLAL THERMODYNAMIC FUNCTIONS OF S_8(GAS)

T, °K.	$-(F^\circ - H_0^\circ)/T$, cal. deg.$^{-1}$	$(H^\circ - H_0^\circ)/T$ cal. deg.$^{-1}$	$H^\circ - H_0^\circ$, cal.	S°, cal. deg.$^{-1}$	C_p°, cal. deg.$^{-1}$
273.16	75.27	24.27	6629	99.54	36.23
298.16	77.44	25.31	7547	102.76	37.17
300	77.60	25.38	7615	102.99	37.25
400	85.39	28.70	11480	114.08	39.73
500	92.06	31.05	15530	123.13	41.05
600	97.88	32.78	19670	130.66	41.82
700	103.03	34.12	23880	137.15	42.30
800	107.67	35.16	28130	142.82	42.62
900	111.85	36.00	32400	147.85	42.84
1000	115.68	36.69	36690	152.38	43.01

ΔH_0° for the Formation of S_8(Gas)

Values of ΔH_0° for the formation of S_8(gas) from rhombic sulfur (the standard reference state) were computed from values of the partial pressure of S_8 over sulfur at various temperatures. For this purpose it was necessary (a) to make a critical selection of the published vapor-pressure data for rhombic and liquid sulfur, (b) to have values of the thermodynamic functions of rhombic and liquid sulfur in addition to those for S_8(gas) and (c) to consider the composition of the vapor over rhombic or liquid sulfur with reference to the partial pressure of S_8 in the vapor.

The reported measurements of the vapor pressure of rhombic sulfur are widely divergent. Only five recent sets of measurements, which fall into two groups differing by about 35%, were considered. In the high group are the measurements of Fouretier,[9] who determined the pressure exerted on a "piston," and those of Taillade,[10] who used the gas-entrainment method. In the low group are the measurements of Neumann,[11] of Bradley[12] and of Rideal and Wiggins,[13] all of whom used the Knudson effusion method. The reported measurements of the vapor pressure of liquid sulfur are also divergent. The data of West and Menzies[14] were selected because they cover the range 120–540° smoothly and are in good agreement with the careful measurements made by Mueller and Burgess[15] in a study of the sulfur point. The results of other workers cover shorter ranges and do not join smoothly.

Thermodynamic functions for rhombic sulfur were based on the accurate calorimetric data of Eastman and McGavock.[16] Thermodynamic functions for equilibrium liquid sulfur were based on the rather limited calorimetric data of Lewis and Randall.[2a] Although the reliability of Lewis and Randall's measurements and their interpretation have been questioned,[17] these are the only available thermal data for liquid sulfur that are suitable for calculation of the needed thermodynamic functions. Lewis and Randall's treatment appears to be valid below 175°, but the thermodynamic functions based on such scanty data are necessarily less accurate than those for rhombic sulfur.

The nature of sulfur vapor between 350 and 850° has not yet been definitely established. Preuner and Schupp[18] were able to correlate their vapor density data by assuming that only S_2, S_6 and S_8 were present. Recently, Klemm and Kilian[19] and Braune, Peter and Neveling[20] showed that some of Preuner and Schupp's measurements were in error by as much as 10%. Braune, *et al.*, found that they could not correlate their data without including an additional specie (S_4) among the species in the vapor. In the lower temperature range of interest in the present work, 15–175°, S_8 and S_6 are the only important species in the vapor. The partial pressures of S_8 in the equilibrium vapor were calculated from an extrapolation of the equilibrium constants given by Braune, *et al.*, for the reaction $3S_8(\text{gas}) = 4S_6(\text{gas})$. Although the interpretation of the vapor density data of Braune, *et al.*, may be open to some question, any errors in the reported equilibrium constants are probably no greater than any errors introduced by the extrapolation outside the range of the experimental measurements.

Rhombic sulfur consists entirely of S_8 molecules. The most likely mechanism for the sublimation of rhombic sulfur is that the molecules leave the crystal as S_8, and then, in the vapor state, part of them dissociate to molecules of S_6 (and other species in insignificant amounts) to form the equilibrium vapor. If the rate of dissociation is much slower than the rate at which S_8 molecules leave the crystal, the pressure observed in a fast experiment will be

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(9) G. Fouretier, *Compt. rend.*, **218**, 194 (1944).

(10) M. Taillade, *ibid.*, **218**, 836 (1944).

(11) K. Neumann, *Z. physik. Chem.*, **A171**, 399, 416 (1934).

(12) R. S. Bradley, *Proc. Royal Soc. (London)*, **A205**, 553 (1951).

(13) E. Rideal and P. M. Wiggins, *ibid.*, **A210**, 291 (1952).

(14) W. A. West and A. W. Menzies, *J. Phys. Chem.*, **33**, 1880 (1929).

(15) E. F. Mueller and H. A. Burgess, *Natl. Bur. Standards, Sci. Papers*, **15**, 163 (1919).

(16) E. D. Eastman and W. C. McGavock, THIS JOURNAL, **59**, 145 (1937).

(17) G. P. Ford and V. K. LaMer, *ibid.*, **72**, 1959 (1950).

(18) G. Preuner and W. Schupp, *Z. physik. Chem.*, **68**, 129 (1909).

(19) W. Klemm and H. Kilian, *ibid.*, **B49**, 279 (1941).

(20) H. Braune, S. Peter and V. Neveling, *Z. Naturforsch.*, **6a**, 32 (1951).

only that of S_8 over rhombic sulfur. As the dissociation proceeds in a slower experiment, the partial pressure of S_8 will remain constant but the total pressure will increase and finally approach the equilibrium value.

Values for ΔH_0° for the reaction 8S(rhombic) = S_8(gas) were calculated from each vapor pressure datum for rhombic sulfur by two alternative assumptions: (a) no dissociation of S_8 and (b) complete equilibration between S_8 and S_6. Since liquid sulfur is an equilibrium mixture of species, the vapor over liquid sulfur must necessarily also be an equilibrium mixture; and, therefore, each vapor pressure datum for the liquid was treated only on the basis of complete equilibration. All of the calculated values of ΔH_0° are presented in Table III.

TABLE III

VAPOR PRESSURE DATA FOR RHOMBIC AND LIQUID SULFUR AND CALCULATED VALUES OF ΔH_0°, IN KCAL., FOR THE REACTION 8S(RHOMBIC) = S_8(GAS)

Investigators	T, °K.	p(total),[a] mm.	ΔH_0° calcd. for no dissociation	ΔH_0° calcd. for complete equilibration
West and Menzies (liquid)	396.5	4.0×10^{-2}		*25.245*
	407.6	7.6×10^{-2}		*25.300*
	425.5	21.8×10^{-2}		*25.330*
	429.3	28.0×10^{-2}		*25.251*
	446.1	63.0×10^{-2}		*25.303*
	448.8	72.0×10^{-2}		*25.290*
Fouretier (rhombic)	296.2	1.7×10^{-6}	25.014	*25.201*
	304.1	4.65×10^{-6}	25.046	*25.234*
	316.9	22×10^{-6}	25.079	*25.273*
	331.6	119×10^{-6}	25.082	*25.275*
	341.5	338×10^{-6}	25.090	*25.288*
	351.5	920×10^{-6}	25.086	*25.287*
	351.6	940×10^{-6}	25.080	*25.276*
Taillade (rhombic)	303.8	3.96×10^{-6}	25.121	*25.270*
	325.8	65.4×10^{-6}	25.051	*25.194*
	333.0	147×10^{-6}	25.045	*25.185*
	333.3	151×10^{-6}	25.047	*25.187*
	352.5	1110×10^{-6}	25.024	*25.172*
Neumann (rhombic)	334.0	1.08×10^{-4}	*25.320*	25.474
	338.1	1.94×10^{-4}	*25.226*	25.374
	343.2	3.28×10^{-4}	*25.229*	25.380
	348.1	5.44×10^{-4}	*25.223*	25.373
Bradley (rhombic)	288.26	0.40×10^{-6}	*25.197*	25.341
	292.96	0.76×10^{-6}	*25.218*	25.364
	298.23	1.59×10^{-6}	*25.215*	25.361
	300.66	2.11×10^{-6}	*25.246*	25.394
	303.16	3.06×10^{-6}	*25.223*	25.368
	305.66	4.28×10^{-6}	*25.223*	25.370

[a] The values of Fouretier and West and Menzies are directly measured pressures. The values of the other investigators are actually values of $\overline{N}p/8$, where $\overline{N}$ is the average number of sulfur atoms per molecule in the vapor.

Inspection of Table III shows, first, that the high group of vapor pressure measurements for rhombic sulfur, those of Fouretier and of Taillade, gives values of ΔH_0° consistent with those obtained from data for the liquid when they are interpreted on the basis of complete equilibrium. Fouretier's measurements by a static method probably allowed enough time for equilibrium to be established. In Taillade's gas entrainment method, the carrier gases may have accelerated the rate of equilibration. Inspection of Table III shows, second, that the low group of vapor pressure measurements for rhombic sulfur, those of Neumann and of Bradley, when interpreted on the basis of only S_8 present in the vapor, gives values of ΔH_0° consistent with those obtained from data for the liquid. Both Neumann and Bradley used dynamic methods in the absence of other gases, and the time available for dissociation of S_8 into other species was probably so short that a negligible amount of dissociation occurred. Support for this argument is found in Neumann's measurements, which were made both with an effusion cell and with a torsion balance. The average molecular formula calculated by comparison of the two sets of measurements was $S_{7.9-8.0}$, a formula much closer to that of pure S_8 vapor than that of the equilibrium vapor, $S_{7.5}$. It is seen that a consistent set of values of ΔH_0° is obtained if the vapor pressure data of Fouretier and of Taillade for rhombic sulfur and those of West and Menzies for liquid sulfur are interpreted on the basis of complete equilibrium in the vapor and if the vapor pressure data of Neumann and of Bradley for rhombic sulfur are interpreted on the basis of only S_8 in the vapor. Such interpretations are reasonable in view of the experimental methods used by the different investigators. The values of ΔH_0° so obtained all lie in the range 25.20 to 25.33 kcal. mole^{-1}. These are the values that are italicized in Table III and are plotted in Fig. 1.

A most probable value for ΔH_0° was selected by the appropriate averaging of the individual values. Before averaging, certain of the individual values were rejected as being less reliable than the rest, namely, those based on Fouretier's measurements at the two lowest temperatures, which are probably low because of residual gas; those based on Taillade's measurements in which the carrier gas was water vapor which may not have been inert; and one value based on a datum of Neumann that is obviously out of line with his other data. Consideration was given to the uncertainties involved in the interpretation of the different kinds of vapor pressure data, and the individual values of ΔH_0° were weighted accordingly. The values from the data of Neumann and of Bradley were given the most weight, because the only uncertainty in the interpretation of these data lies in the assumption that the vapor was solely S_8. The values from the data of Fouretier and of Taillade were given less weight because their interpretation involves not only uncertainty in the assumption of complete equilibrium, but also uncertainty in the equilibrium concentration of S_8 in the vapor. The values from the data of West and Menzies for the liquid were given still less weight because their interpretation involves not only uncertainty in the equilibrium concentration of S_8 in the vapor, but also uncertainty in the thermodynamic functions of liquid sulfur. The most probable value of ΔH_0° that was obtained by this averaging procedure was 25.23 ± 0.05 kcal. mole^{-1}.

Heat, Free Energy and Equilibrium Constant for the Formation of S_8(Gas)

The value of 25.23 kcal. mole^{-1} for ΔH°_0 of the reaction 8S(rhombic) = S_8(gas) was used to calculate the heat, free energy and common logarithm of the equilibrium constant for the formation of S_8(gas) from rhombic sulfur at several temperatures. In order to extend the useful range of the data on the reactions of formation, these were also calculated on the basis of S_2(gas) as the reference state for sulfur. The value of ΔH°_0 for the reaction 2S(rhombic) = S_2(gas) was taken from the paper of Evans and Wagman.[4] The calculated values of the several chemical thermodynamic properties are listed in Table IV.

TABLE IV

HEAT, FREE ENERGY AND EQUILIBRIUM CONSTANT FOR THE FORMATION OF S_8(GAS)

T, °K.	ΔH°_f, kcal. mole^{-1}	ΔF°_f, kcal. mole^{-1}	$\log_{10} Kf$
	$8S(\text{rhombic}) \rightarrow S_8(\text{gas})$		
0	25.230	25.23	$-\infty$
273.16	24.50	12.91	−10.329
298.16	24.35	11.89	− 8.715
368.6	23.88	8.96	− 5.312
	$4S_2(\text{gas}) \rightarrow S_8(\text{gas})$		
0	−97.97	−97.97	∞
273.16	−99.14	−67.50	+54.00
298.16	−98.99	−64.61	+47.36
300	−98.97	−64.41	+46.92
400	−98.30	−52.97	+28.94
500	−97.56	−41.74	+18.24
600	−96.80	−30.65	+11.16
700	−96.04	−19.68	+ 6.14
800	−95.28	− 8.81	+ 2.41
900	−94.52	+ 1.95	− 0.47
1000	−93.72	+12.63	− 2.76

Equilibrium constants for the reaction $4S_2$(gas) = S_8(gas) have been calculated from the observed density of sulfur vapor as a function of pressure and temperature. Some values obtained from the interpretation of vapor density data are compared in Table V with those calculated in this research. The comparison is unsatisfactory. Attempts to resolve the inconsistency have not been successful. In particular, it was found that the inconsistency was not the result of neglect of contributions from tautomers other than the one of D_{4d} symmetry to the thermodynamic functions of S_8(gas). An attempt to fit the equilibrium constants of Braune, *et al.*, by the empirical inclusion of such contributions to the thermodynamic functions led to the absurd result that the calculated partial pressure of S_8(gas) over liquid sulfur above 250° was greater than the total observed pressure. It seems most likely that the inconsistency arises in the treatment of the vapor density data. The presence of species intermediate between S_2 and S_6 in sulfur vapor seems indisputable.[21] However, the absence of species other than S_2, S_4, S_6 and S_8 has not been demonstrated. The nature of the inconsistency suggests that other species will be found.

TABLE V

$\text{Log}_{10}\ K_f$, $4S_2$(gas) = S_8(gas)

T, °K.	Preuner & Schupp[18]	Braune, *et al.*[20]	This research
600	+11.37[a]	+11.50	+11.16
800	+ 2.33[a]	+ 3.10	+ 2.41
1000	− 3.16[a]	− 1.95	− 2.76

[a] Calculated from the smoothed equation of Kelley[3] based on Preuner and Schupp's data.

Appendix

Tautomerism of S_8.—In crystals of rhombic and monoclinic sulfur, the S_8 molecules are in the "crown" configuration of D_{4d} symmetry. However, in the gas phase, S_8 may exhibit tautomerism among several molecular configurations somewhat analogous both to the well-known chair-boat tautomerism of cyclohexane and to the *trans-skew* tautomerism of *n*-butane. The tautomerism of S_8 was considered from the standpoint of what contributions it might make to the thermodynamic functions.

The model that was selected for examination was one with equal bond distances and 105° bond angles, and with potential energy barriers to internal rotation about the S–S bonds of the form $(^1/_2)V_0(1 + \cos 2\phi)$, where V_0 is the barrier height and ϕ is the dihedral angle between two adjacent S–S–S planes measured from the *cis* configuration. There are 18 internal degrees of freedom in the S_8 molecule, *i.e.*, 18 parameters are required to specify its configuration. If 16 of these are assigned to the 8 bond distances and 8 bond angles, the remaining 2 determine the 8 dihedral angles about S–S bonds. Unfortunately, it is not possible to express the 8 dihedral angles explicitly in terms of two parameters and thereby calculate the potential energy as a function of those parameters. This difficulty was avoided by use of an accurately machined molecular model on which it was possible to measure the dihedral angles. Dihedral angles were measured and the potential energy was calculated for enough different configurations to explore thoroughly the range of possible configurations. Three different kinds of configuration were found to give minima on the potential energy surface: (a) the "crown" form of D_{4d} symmetry with a symmetry number of 8; (b) the "cradle" form of D_{2d} symmetry with a symmetry number of 4; (c) a form of C_1 symmetry with a symmetry number of 1. This form can have *d*- and *l*-isomers. This configuration of lowest symmetry is very "floppy" in the sense that the minimum on the potential energy surface is in a trough and not a hole.

The D_{4d} tautomer is the most stable. The other two forms were found to be about equally stable, and the energy difference between either of them and the D_{4d} tautomer was found to be about 1.2 V_0. The value of 1.2 V_0 is an approximation for two reasons. The angle of the minimum in the assumed potential energy barrier for rotation about the S–S bonds is $\phi = 90°$. If other values had been selected in the probable range of 85 to 100°, somewhat different results would have been obtained for the energy difference. Also the assumption of rigid bonds and bond angles leads to a somewhat high value for the energy difference, because in the actual molecule a part of the torsional strain will be relieved by distortions of bond distances and angles from their normal values. For purposes of the present discussion it is only necessary to select a lower limit to the energy difference. A reasonable value is V_0.

The value of V_0, the height of the barrier to internal rotation about an S–S bond in S_8, is not known, but its magnitude may be estimated from the values in structurally related molecules. Spectroscopically observed torsional frequencies of the disulfide linkage have led to the following estimates of the barrier height to internal rotation about an S–S bond: 9.5 kcal. mole^{-1} in 2,3-dithiabutane,[22] 13.2 kcal. mole^{-1} in 3,4-dithiahexane[23] and 14.2 kcal. mole^{-1} in S_2Cl_2.[24] The value of V_0 for S_8 is estimated to be in the range of values observed for these disulfides, *i.e.*, between 9 and 15 kcal. mole^{-1}. Pauling[8] has calculated a lower value of 4.9 kcal. mole^{-1} for V_0 from the energy difference between S_8 and S_6, but his method of calculation is quite sensitive to the as-

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[22] D. W. Scott, H. L. Finke, M. E. Gross, G. B. Guthrie and H. M. Huffman, THIS JOURNAL, **72**, 2424 (1950).

[23] D. W. Scott, H. L. Finke, J. P. McCullough, M. E. Gross, R. E. Pennington and Guy Waddington, *ibid.*, **74**, 2478 (1952).

[24] Unpublished calculations.

sumed value of ϕ for minimum potential energy. Only a small and quite reasonable change in that parameter is required to bring the calculated value of V_0 for S_8 up into the range of the more directly determined values for the disulfides.

The contribution of tautomerism to the thermodynamic functions can be obtained from the partition function

$$Q = 1 + \exp\left[-\Delta F(\mathrm{D_{2d}})/RT\right] + \exp\left[-\Delta F(\mathrm{C_1})/RT\right]$$

in which ΔF(tautomer) is the free-energy change for the reaction $S_8(\mathrm{D_{4d}}) = S_8$(tautomer). If the energy of the $\mathrm{D_{2d}}$ form and of the $\mathrm{C_1}$ form are taken to be equal to each other and to V_0, one may write

$$Q \cong 1 + A\exp(-V_0/RT)$$

in which $A = \exp[\Delta S(\mathrm{D_{2d}})/R] + \exp[\Delta S(\mathrm{C_1})/R]$, with ΔS (tautomer) defined as the entropy change for the reaction $S_8(\mathrm{D_{4d}}) = S_8$(tautomer). If the values of ΔS(tautomer) are determined solely by differences in symmetry number and the existence of *d*- and *l*-isomers of the $\mathrm{C_1}$ form, then $A = 2 + 2(8) = 18$. Differences in moments of inertia and vibrational frequencies of the tautomers will make A differ somewhat from 18, but that value is a good enough estimate for purposes of the present discussion.

The contributions of tautomerism to the function $-(F^\circ - H_0^\circ)/T$, in cal. deg.$^{-1}$ mole^{-1} at 450 and 1000°K. were calculated for V_0 equal to 5, 9 and 15 kcal. mole^{-1} with the results shown below.

	V_0 = 5 kcal. mole^{-1}	V_0 = 9 kcal. mole^{-1}	V_0 = 15 kcal. mole^{-1}
450°K.	0.14	0.002	0.000003
1000°K.	1.80	.36	.02

These values are essentially upper limits of the contributions, because V_0 is the probable lower limit of the energy difference between the tautomers. It is seen that if V_0 is in the expected range of 9 to 15 kcal. mole^{-1}, the contributions of tautomerism, even at 1000°K., are of just borderline significance. Only if V_0 has an improbably low value of 5 kcal. mole^{-1} are the contributions large at temperatures near 1000°K. In either case, the contributions are small at 450°K.

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cis- and *trans-*Dichloroethylenes. The Infrared Spectra from 130–400 Cm.$^{-1}$ and the Thermodynamic Properties[1]

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The infrared spectrum of *trans*-dichloroethylene shows a strong Q branch at 227 cm.$^{-1}$ and a shoulder of medium strength near 250 cm.$^{-1}$ which are interpreted as the heretofore unobserved $\mathrm{A_u}$ and $\mathrm{B_u}$ fundamentals, respectively. The spectrum of the *cis* isomer merely confirms bands known from the Raman spectrum. The force constants for out-of-plane motions are calculated. Thermodynamic functions are calculated from the completed molecular data for each isomer and are used to interpret the *cis–trans* equilibrium data. The *cis* isomer is found to be 445 ± 20 cal./mole lower in energy at 0°K., and the cause of this energy difference is discussed.

In the case of the 2-butenes the *trans* isomer is known to be the one of lower energy and this is believed to be the usual case. The dichloroethylenes are an exception in that the *cis* isomer has the lower energy. Thus a careful study of *cis-* and *trans*-dichloroethylenes is of considerable interest.

The vibrational spectra of *cis-* and *trans*-dichloroethylene and the statistical thermodynamics of the equilibrium between them have been the subject of an extensive series of investigations. Recent studies of a general nature are those of Bernstein and Ramsay[2] and of Wood and Stevenson,[3] who give references to earlier work. In spite of extensive studies, the absence of infrared spectra for the *trans* isomer below about 400 cm.$^{-1}$ has prevented a satisfactory completion of this work. Since the *trans* molecule has a center of symmetry, the Raman spectrum does not yield the frequencies of the antisymmetric modes as fundamentals and there are two modes in the heretofore unobserved range. Attempts have been made to infer these frequencies indirectly, but we shall see that these have not yielded valid results.

Experimental.—The grating spectrometer employed in this investigation was described recently.[4] The samples were from the Matheson Co. The sample of the *cis* isomer melted at −80.4° which is within 0.1° of the accepted melting point and its infrared spectrum (3–15 μ) showed no bands of the *trans* isomer or of other likely impurities. Consequently, this sample was used without further purification. Initially the sample of the *trans* isomer showed considerable impurity of *cis*. This was largely removed by distillation with an efficient column so that, in the sample used, the infrared spectrum showed only traces of the stronger bands of the *cis* isomer.

The spectrum of *trans*-dichloroethylene in the range 130–400 cm.$^{-1}$ is shown in Fig. 1. The accuracy of the percentage transmission becomes gradually poorer with decreasing frequency. While there is no doubt about the strong absorption near 230 cm.$^{-1}$, the weak peak near 150 cm.$^{-1}$ must be regarded as doubtful at present. The corresponding spectrum was taken for the *cis* isomer, but it showed no marked features beyond the expected band at 173 cm.$^{-1}$ which was weak. Thus this spectrum was not investigated further.

Spectral Interpretation.—We accept the assignments of Bernstein and Ramsay[2] for *cis*-dichloroethylene and for all fundamentals except $\mu_7(\mathrm{A_u})$ and $\mu_{12}(\mathrm{B_u})$ of *trans*-dichloroethylene. For the latter these authors suggested 192 and 265 cm.$^{-1}$, respectively, but it is apparent from Fig. 1 that these are not correct. Also we must note that the "reststrahlen" spectrometer results presented re-

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[1] This work was assisted by the American Petroleum Institute through Research Project 50.

[2] H. J. Bernstein and D. A. Ramsay, *J. Chem. Phys.*, **17**, 556 (1949).

[3] R. E. Wood and D. P. Stevenson, THIS JOURNAL, **63**, 1650 (1941).

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