From the definition of F

$$1 - F = \frac{S_\infty - S_A}{S_\infty - S_{A_0}} = \frac{S_\infty - S_B}{S_\infty - S_{B_0}} \quad (6)$$

$$(S_\infty - S_A) = (1 - F)(S_\infty - S_{A_0}) \quad (7)$$

$$(S_\infty - S_B\,) = (1 - F)(S_\infty - S_{B_0}) \quad (8)$$

Substitution of equations 7 and 8 in 5 gives

$$\frac{S_\infty - S}{S_\infty - S_0} = \frac{(1 - F)[a(S_\infty - S_{A_0}) + b(S_\infty - S_{B_0})]}{a(S_\infty - S_{A_0}) + b(S_\infty - S_{B_0})} = 1 - F \quad (9)$$

Therefore

$$F = 1 - \frac{S_\infty - S}{S_\infty - S_0} = \frac{S - S_0}{S_\infty - S_0} \quad (10)$$

Alternatively from the definitions of F' and F'_0

$$1 - F' = \frac{S_\infty - S}{S_\infty - S_{A_0}} \quad (11)$$

$$1 - F'_0 = \frac{S_\infty - S_0}{S_\infty - S_{A_0}} \quad (12)$$

$$\frac{1 - F'}{1 - F'_0} = \frac{S_\infty - S}{S_\infty - S_0} = 1 - F \quad (13)$$

$$F = 1 - \frac{1 - F'}{1 - F'_0} = \frac{F' - F'_0}{1 - F'_0} \quad (14)$$

Summary

1. In aqueous perchloric acid solution a slow exchange between Tl(I) and Tl(III) has been observed. The exchange rate in aqueous solutions 0.8 to 3.5 f. $HClO_4$, 0.0 to 0.4 f. $NaNO_3$, 10–25 mf. $TlClO_4$, 5–25 mf. $Tl(ClO_4)_3$, 10 to 50°, and μ adjusted to 3.68 with $NaClO_4$ is well represented by

$$R = [\mathrm{Tl(I)}][\mathrm{Tl(III)}]\left\{k + \frac{k'}{[\mathrm{H}^+]} + k''\,[\mathrm{NO_3}^+]\right\}$$

where

$$k = 3.8 \times 10^8\, e^{-17{,}600/RT}\ \mathrm{mole}^{-1}\cdot\mathrm{liter}\cdot\mathrm{sec.}^{-1}$$

$$k' = 7.9 \times 10^2\, e^{-10.300/RT}\ \mathrm{sec.}^{-1}$$

$$k'' = 2.5 \times 10^8\, c^{-16.000/RT}\ \mathrm{mole}^{-2}\cdot\mathrm{liter}^2\cdot\mathrm{sec.}^{-1}$$

2. The presence of platinum black in the exchange solution caused a marked increase in the exchange rate; the presence of finely divided silica gel caused no measurable change in the rate.

3. Four precipitation methods for the separation of Tl(I) and Tl(III) were studied. All caused measurable and reproducible apparent zero-time exchanges due to coprecipitation or separation-induced exchange or both. It was found that separation-induced exchange was the predominant effect for at least two of the methods studied.

4. The following expression is derived which relates F, the fraction exchange that occurs in solution in time t, to F', the observed fraction exchange at time t, and F'_0, the observed fraction exchange at time zero (apparent zero-time exchange).

$$F = (F' - F'_0)/(1 - F'_0)$$

This expression is valid as long as the separation-induced exchange and the degree of separation are reproducible in a given exchange run. The expression has been checked experimentally.

ST. LOUIS 5, MISSOURI RECEIVED NOVEMBER 26, 1948

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, OREGON STATE COLLEGE]

A Magnetic Study of Sulfur Vapor[1,2]

BY ALLEN B. SCOTT

By comparison with O_2, it has long been assumed that diatomic sulfur molecules are in the $^3\Sigma$ state and are thus paramagnetic. Neel[3] has measured the susceptibility of sulfur vapor at several temperatures, and, basing his calculation of the concentration of S_2 upon the vapor density measurements of Preuner and Schupp,[4] showed that this assumption was approximately correct, though his value for $\chi_M T$ was about 40% different from the theoretical value, and varied considerably with temperature. He was unable to conclude whether the disagreement was due to error in his magnetic data, error in the vapor equilibrium data, or was really an indication that S_2 was not truly in the triplet state.

An attempt has been made in this Laboratory to reinvestigate the susceptibility of sulfur vapor as a step in elucidating the complex equilibrium among the aggregates in sulfur vapor. If it can be established that S_2 has the theoretical moment of the triplet state, the measurement of susceptibility will then suffice to determine the concentration of S_2 in the presence of higher aggregates. In this paper are reported the results of a determination of the susceptibility of sulfur vapor at several temperatures between 550 and 850° which indicate that S_2 has the correct moment for the triplet state.

Experimental

The method was essentially that used in the measurement of the susceptibility of thermally dissociated iodine vapor.[5] A method for detecting the amount of displacement of the balance beam, consisting of a micro-

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(2) Presented before the Division of Physical and Inorganic Chemistry at the San Francisco Meeting of the American Chemical Society, March 28, 1949.

(3) Neel, *Compt. rend.*, **194**, 2035 (1932).

(4) Preuner and Schupp, *Z. physik. Chem.*, **68**, 129 (1909).

(5) Scott and Cromwell, THIS JOURNAL, **70**, 3981 (1948).

metrically adjustable scale in place of the photographic recording device, was found time-saving and gave more consistent results. By means of a micrometer, the scale could be positioned so that the oscillations of the slit image were symmetrical about the scale index, as viewed through a telescope; after applying the field or lifting the calibrating weight, the scale was again positioned and the difference between micrometer readings was proportional to the displacing force.

In practice, it was found that small changes in the location of the bulb in the field caused a significant change in the force of the field upon the bulb. In the previous work with iodine errors due to slight positional changes were overcome by taking a large number of measurements over an extended period of time. In order to save time and eliminate constructively the source of these errors, the height of the bulb was adjusted by always bringing the balance beam to the same initial position by means of a small solenoid acting upon a fine iron wire at the end of the beam opposite the bulb suspension. The current through the solenoid was adjusted manually to bring the slit image to a constant initial scale position; the current was maintained while the field was applied, and the new scale position obtained.

The furnace was made of somewhat larger (19 mm. o.d.) quartz tubing, which necessitated less lagging in order that it could be placed between the magnet poles. The variation in temperature throughout the length of the bulb was 33°. The average temperature was obtained from several measurements along the length of the bulb and was correct within about 5°. The thermocouples used were chromel-alumel, calibrated at the freezing points of C. P. $K_2Cr_2O_7$, KCl, and NaCl.

C. P. sulfur was recrystallized twice from redistilled carbon disulfide and then twice distilled in a stream of nitrogen. At each distillation approximately one-fourth of the original amount was rejected. On the second distillation, the vapor was condensed in the Vycor tube, of 10 mm. i. d., to be used in the magnetic measurements, and the tube was evacuated and sealed. The mass of sulfur contained was determined after the experiments by evaporating all sulfur out of the tip of the bulb, breaking the tip, weighing before and after driving the sulfur out at 500° in the muffle furnace. Two samples were used in the measurement, one of volume 9.90 cc. containing 57.0 mg. S, and the other 9.85 cc. containing 46.7 mg.

The field strength was 8080 oersteds.

The force due to the magnetic field upon the bulb alone was taken as the force on the bulb and contents at room temperature, since the force upon small amounts of solid sulfur condensed in the tips of the bulb in regions of approximately constant field strength is negligible. The temperature independence of susceptibility of the Vycor tubing used was verified by measurements at room temperature and 850° upon an empty bulb. The force upon the empty bulb was, within the average deviation, the same at both temperatures.

Results and Discussion

At 850° and vapor density 5.76 mg./cc., the force of the field upon the sulfur vapor, after correcting for the force due to the bulb, was 1.69 mg. in the direction of paramagnetism. The cross-sectional area of the bulb was 0.785 sq. cm. The calculated volume susceptibility was 6.47×10^{-8} c. g. s. unit. The volume susceptibility due to the diamagnetism of sulfur may be calculated from the mass susceptibility which was assumed to be -0.49×10^{-6} c. g. s. unit; this leads to a diamagnetic volume susceptibility at this density of -2.8×10^{-9} c. g. s. unit. Thus the paramagnetic volume susceptibility, κ, was 6.75×10^{-8} unit.

In the same manner were calculated the susceptibilities at other temperatures and those for the sample of density 4.74 mg./cc. The cross-sectional area of the second bulb was 0.810 sq. cm. These data are tabulated in Table I.

In order to compute the molar susceptibility of S_2, it is necessary to evaluate its partial pressure in the mixed vapor. Preuner and Schupp[2] have determined the equilibrium constants for the reactions

$$S_8 = 4S_2 \qquad (1)$$

$$S_6 = 3S_2 \qquad (2)$$

at several temperatures, including 550, 650 and 850°, and these constants were used directly. A plot of log κ against $1/T$ from 450 to 850° is very nearly linear in both cases, and the constants at 750°, obtained from the plot, were: (1) $K_{\text{mm.}} = 1.5 \times 10^{12}$ and (2) $K_{\text{mm.}} = 5.1 \times 10^7$. These direct constants differ somewhat from those calculated from the standard free energy equations of Kelley,[6] since his equations are based on the average data in a lower temperature range; however the difference is not of great significance in view of the relatively large probable error in the magnetic measurements.

It must be noted also that the above data were obtained at pressures generally below 1000 mm., while the present work necessitated pressures up to six times as high to obtain sufficient force on the sample. In the absence of thermodynamic data for the vapor species present it is impossible to evaluate what error is introduced by making this extrapolation; however, since the temperatures are high, it is unlikely that the error is of serious consequence. Similarly, it was necessary to assume ideal behavior for the computation of total pressures.

For the case of density 5.76 mg./cc., at 850°, the equilibrium data give the proportion of S_2 in the vapor as 90.2 weight per cent. This leads to a molar paramagnetic susceptibility of 8.3×10^{-4} c. g. s. unit and a Curie constant, $\chi_M T$, of 0.93. Similar results for the other cases are tabulated in Table I. The susceptibilities given are the paramagnetic part only, as in each case the observed volume susceptibility was corrected for the diamagnetism of the entire mass of sulfur present.

TABLE I

PARAMAGNETIC SUSCEPTIBILITY OF S VAPOR

t	Force of field, mg.	$\kappa \times 10^8$	$\chi_M \times 10^4$	$\chi_M \times 10^4$ (theoret.)	$\chi_M T$
		Density, 5.76 mg./cc.			
850	1.69	6.75	8.3	8.83	0.93
750	1.18	4.80	9.3	9.70	0.95
650	0.42	1.9	9.8	10.8	0.91
550	0.11	0.71	14	12.1	
		Density, 4.74 mg./cc.			
850	1.73	6.65	9.6	8.83	1.08
750	0.92	3.63	7.7	9.70	0.79
650	0.35	1.6	8.8	10.8	0.81
550	0.19	0.94	19	12.1	

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[6] Kelley, *U. S. Bur. Mines, Bull. No.* **406** (1937).

In Fig. 1 is shown the observed variation of combined paramagnetic and diamagnetic volume susceptibility with temperature, compared to that calculated by the use of the Van Vleck equation, the diamagnetism of sulfur, and the equilibrium constants of Preuner and Schupp.

The relative probable error in the measurements based solely upon the distribution of values of the force of the field upon the sample, as a result of four or five determinations at each temperature, was about 3% at 850° and increased progressively to about 20% at 550° where the force was much smaller. Errors in temperature, field strength, and equilibrium data would increase the relative error at 850° to perhaps 7% but would be swamped by the observational error at the lower temperature. The error in the average $\chi_M T$ (excluding values at 550°) is thus about 10%.

The theory of Van Vleck[7] predicts that the molar susceptibility of molecules in the $^3\Sigma$ state, having small multiplet intervals, is

$$\chi_M = \frac{N\beta^2}{3KT}[4S(S+1)] = \frac{0.993}{T}$$

At 850° this leads to a value of 8.83×10^{-4} unit, in good agreement with the observed average of the two samples, $9.0 \times 10^{-4} \pm 0.6 \times 10^{-4}$. Neel[3] reported 5.4×10^{-4} unit.

The average value of $\chi_M T$, excluding the values at 550°, is 0.91 ± 0.09, compared to the theoretical value of 0.993.

These data serve to show that the ground state of diatomic sulfur is undoubtedly the triplet state, and further that the equilibrium data of Preuner and Schupp predict quite satisfactorily the proportion of S_2 in sulfur vapor between 550 and 850°.

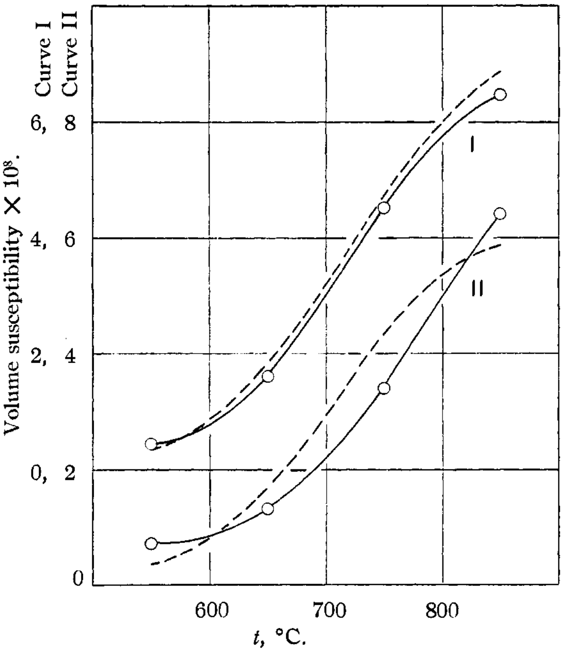

Fig. 1.—Volume susceptibility of S vapor: I, density 5.76 mg./cc.; II, density 4.74 mg./cc.; broken curves, calculated.

A similar study of the ground state of Se_2 is to be undertaken by this laboratory in the near future.

Summary

The molar susceptibility of S_2 at temperatures between 550 and 850° has been measured and found to agree with the theoretical value within the limits of experimental error. The existing equilibrium data predict satisfactorily the proportion of S_2 in sulfur vapor between 550 and 850°.

CORVALLIS, OREGON RECEIVED APRIL 21, 1949

[7] J. H. Van Vleck, "Electric and Magnetic Susceptibilities, Oxford University Press, Oxford, England, 1932, p. 266.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CALIFORNIA]

The Solubility of Nitrogen in Carbon Disulfide, Benzene, Normal- and Cyclo-hexane, and in Three Fluorocarbons

BY J. CHR. GJALDBAEK[1] AND J. H. HILDEBRAND

Introduction.—The extraordinary solubility relations of fluorocarbons have been the subject of three recent papers from this Laboratory; Scott[2] assigned figures for the "solubility parameters" needed in order to apply the modern theory of regular solutions, and showed their general consistence with the initially fragmentary data. Benesi and Hildebrand[3] determined the solubility of iodine in perfluoro-*n*-heptane, finding a value which, although only 0.027 of its solubility in normal heptane, is nevertheless consistent with theory. Hildebrand and Cochrane[4] determined liquid–liquid solubility curves for perfluoromethylcyclohexane with five organic liquids and likewise found reasonably good agreement with theory. The most illuminating investigation to undertake next appeared to us to be the solvent powers of these substances for gases. Their exceedingly low solvent power for a substance such as iodine implies high solvent power for gases, but there remained the question

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[1] Holder of a scholarship from the Danish Council for applied Science. Home address, Department of Inorganic Chemistry, the Pharmaceutical College of Denmark, Copenhagen.

[2] R. L. Scott, THIS JOURNAL, **70**, 4090 (1948).

[3] H. A. Benesi and J. H. Hildebrand, *ibid.*, **70**, 3978 (1948).

[4] J. H. Hildebrand and D. R. F. Cochrane, *ibid.*, **71**, 22 (1949).