The average value, 8 ± 2 cal mol^{-1} $°K^{-1}$, will be adopted at 25°. This new value is consistent with the known entropy of the smaller sulfate ion, 4.8 cal mol^{-1} $°K^{-1}$.

The average of the three separate values for the standard enthalpy of formation of thiosulfate is −157.7 ± 0.2 kcal mol^{-1}. It is believed that this value is superior to the presently adopted[15] one of −155.9 kcal mol^{-1}. The calculated standard free energy of formation for $S_2O_3^{2-}(aq)$ is −130.1 ± 1.8 kcal mol^{-1}.

Thermodynamic Functions for $S_4O_6^{2-}(aq)$.—The standard enthalpy of formation of $S_4O_6^{2-}(aq)$ is based on the calorimetric studies by Zimmermann and Latimer[36] on the heat of oxidation of $S_2O_3^{2-}$ by I_3^-, which was observed to be −8580 ± 250 cal mol^{-1}. Using a new[37] value for the enthalpy of formation of $I^-(aq)$, −13,550 cal mol^{-1}, and the most recent value[42] for the heat of reaction of $I^-(aq)$ with I_2 to give $I_3^-(aq)$, 1.074 ± 0.012 kcal mol^{-1}, the standard enthalpy of formation of $S_4O_6^{2-}$ becomes −298.2 ± 1.2 kcal mol^{-1}. From the previously determined entropy given earlier in this communication of 61.5 ± 0.4 cal mol^{-1} deg^{-1}, the standard free energy of formation of $S_4O_6^{2-}$ becomes −252.4 ± 1.2 kcal mol^{-1}.

Potential of the $S_4O_6^{2-}$–$S_2O_3^{2-}$ Electrode.—The potential for the electrode reaction

$$S_4O_6^{2-} + 2e^- = 2S_2O_3^{2-} \quad E°_{25°} = 0.169 \pm 0.010$$

can be calculated from the free energies determined above for $S_4O_6^{2-}(aq)$ and $S_2O_3^{2-}(aq)$. This potential differs somewhat from the one adopted by Latimer[30] of 0.08 V from less complete and less accurate data.

V. Summary of Data

The new thermodynamic data obtained in this research are summarized in Table VI.

TABLE VI

SUMMARY OF THERMODYNAMIC FUNCTIONS[a]

Species	$\Delta H_f°$ [b]	$\Delta F_f°$ [b]	$S°$ [c]
$H_2SO_3(aq)$	*−145.51*	*−128.56*	*55.5*
$HSO_3^-(aq)$	−151.12	*−126.15*	28.6
$SO_3^{2-}(aq)$	−152.4	*−116.3*	−8.3
$S_2O_3^{2-}(aq)$	−157.7	−130.1	8
$S_4O_6^{2-}(aq)$	−298.2	−252.4	61.5
$CaSO_3 \cdot {}^1/_2H_2O(c)$	−313.0	−286.2	(31)
$K_2S_4O_6(c)$	−429.36	−389.31	74.01
$I^-(aq)$	−13.55	−12.330	25.4

[a] Italicized and auxiliary thermodynamic functions are from ref 15. [b] In kcal mol^{-1}. [c] In kcal mol^{-1} $°K^{-1}$.

Acknowledgment.—The authors are indebted to Dr. Kristina Arvidsson who assisted in the low-temperature heat-capacity measurements. We gratefully acknowledge the support of the U. S. Atomic Energy Commission and the National Science Foundation which made this work possible.

[36] H. W. Zimmermann and W. M. Latimer, *J. Amer. Chem. Soc.*, **61**, 1554 (1939).

[37] Unfortunately there are a variety of values for the standard enthalpy of formation of $I^-(aq)$. The recently adopted value by the Bureau of Standards[15] is −13,190 cal mol^{-1}. Howard and Skinner[38] have obtained data for $HI \cdot 50H_2O$ which, when corrected to infinite dilution, give −13,790 cal mol^{-1}. Actually the thermodynamic functions for $I^-(aq)$ can probably best be fixed from the extensive cell data. The standard free energy of formation of $I^-(aq)$ is accurately known to be −12,330[15] cal mol^{-1} from cell data on the iodine–iodide electrode. The standard entropy of $I^-(aq)$ can be obtained from a third law analysis[22] of the silver–silver iodide electrode in HI solutions. Measurements on this electrode[39,40] have extended over 50°, and can be combined with heat capacities of the pure substances[15,18] and the estimated heat capacities for HI(aq)[21] for a third law analysis.[22] $\Delta S°$ for the silver–silver iodide cell reaction was found to be 7.6 ± 0.2 cal mol^{-1} deg^{-1}, from which the standard entropy of $I^-(aq)$ becomes 25.4 ± 0.2 cal mol^{-1} deg^{-1} at 25°, using available auxiliary data.[15] The free energy and entropy combine to give standard enthalpy of formation of −13,550 cal mol^{-1} for $I^-(aq)$, which value will be adopted. This value is near the mean of the other proposed values and is essentially the same as that tentatively adopted by a recent international committee,[41] −13.60 ± 0.20 kcal mol^{-1}.

[38] P. B. Howard and H. A. Skinner, *J. Chem. Soc. A*, 1536 (1966).

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Polyatomic Cations of Sulfur. III. Solutions of Sulfur in Oleum

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It is shown by absorption spectra, esr spectra, and cryoscopic measurements that solutions of sulfur in oleum are, with time and with increasing SO_3 concentration, successively oxidized to S_{16}^{2+}, S_8^{2+}, S_4^{2+}, and SO_2. Esr measurements show that S_{16}^{2+} is in equilibrium with the radical ion S_8^+ and that S_8^{2+} is in equilibrium with the radical ion S_4^+.

Introduction

Colored solutions of sulfur in oleum have been known for a considerable time, the first report of such solutions apparently being by Bucholz in 1804.[1] Brown, green, and blue solutions have been described. Weber[2] and later Masson and Argument[3] attributed the blue color to the supposed compound S_2O_3 which had been found to have a greenish blue color and to dissolve in oleum to give a blue solution. Auerbach[4] made cryoscopic measurements on solutions of sulfur in oleum and concluded that it was dissolved as S_2 molecules but later Brayford and Wyatt[5] came to the tentative conclusion from their cryoscopic measurements that sulfur is present in 45%

[1] C. F. Bucholz, *Gehlen's Neues J. Chem.*, **3**, 7 (1804); "Gmelin's Handuch der anorganischen Chemie," Vol. 9, Part B1, 1953, p 179.

[2] R. Weber, *J. Prakt. Chem.*, **133**, 218 (1882); *Ann Phys. Chem.*, [2] **156**, 531 (1875).

[3] I. Masson and C. Argument, *J. Chem. Soc.*, 1705 (1938).

[4] R. Auerbach, *Z. Phys. Chem.* (*Leipzig*), **121**, 337 (1926).

[5] J. R. Brayford and P. A. H. Wyatt, *Trans. Faraday Soc.*, **52**, 642 (1956).

oleum largely as S_2O_3 although they found that the solutions were not stable with time. Symons[6] and more recently Lux and Bohm[7] studied the absorption spectra of solutions of sulfur in oleum. The latter authors concluded that at least four different species are formed at different oleum concentrations. They designated these as S_X (absorption maximum at 330 nm), S_I (absorption maximum at 273 nm), S_Z (absorption maximum at 400 nm), and $S_8(SO_3)_n$. Gardner and Fraenkel[8] showed by esr measurements that the blue solutions of sulfur in oleum contain two radicals with g values of 2.016 and 2.026. Later Symons, *et al.*,[9] examined the esr spectra of solutions of sulfur in 25 and 65% oleum and also showed that they contained two radical species for which they obtained the g values of 2.018 and 2.032.

Recently Giggenbach[10] has further investigated the esr spectra of solutions of sulfur in oleum. In oleum containing more than 40% SO_3 he obtained only one signal with $g = 2.013$ but in solutions in more dilute oleum an additional signal with $g = 2.026$ was also found to be present. On the basis of changes in the absorption spectra and the esr spectra with time Giggenbach attributed the blue color and the absorption peaks at 590 and 420 nm to the species giving the $g = 2.013$ esr signal which he tentatively concluded is a square-planar S_4^+ radical. Similarly he attributed peaks at 935, 720, and 330 nm to the species having $g = 2.026$ which he assumed to be an open-chain S_n^+ radical.

Very recently Symons, *et al.*,[11] have extended their earlier work by studying the esr spectra of solutions of sulfur enriched with ^{33}S in 65% oleum and contrary to Giggenbach they concluded from their analysis of the spectra that the species having $g = 2.013$ is the S_8^+ radical with a cyclic structure like S_8.

In the first paper in this series[12] we have shown that sulfur may be oxidized with $S_2O_6F_2$, AsF_5, or SbF_5 to the cations S_{16}^{2+}, S_8^{2+}, and S_4^{2+} and that, in solution in SO_2 or HSO_3F, S_{16}^{2+} and S_8^{2+} are in equilibrium with radical species which were tentatively assumed to be S_8^+ and S_4^+, respectively. In the second paper[13] the presence of the S_8^{2+} cation in the compound $S_8(AsF_6)_2$ was confirmed by a crystal structure determination and it was shown that the cation has a bicyclic structure with an exo,endo conformation.

It seemed reasonable to suppose that these same cationic species are formed in the colored solutions of sulfur in oleum and the present work was undertaken to obtain evidence for this supposition, to attempt to elucidate the nature of the species responsible for the esr spectra, and to resolve the differences between the conclusions of earlier workers.

Results and Discussion

Absorption Spectra of Solutions of Sulfur in Sulfuric Acid and Oleum.—A saturated solution of sulfur in 95–100% H_2SO_4 at room temperature was found to be colloidal as it exhibited a Tyndall effect. The colloidal solution gave an absorption spectrum (Figure 1A) which consisted of three bands at 224, 260, and 320 nm. On heating elemental sulfur in this solvent for 12 hr at 75° the resulting clear solution gave a spectrum which was identical with the spectrum of sulfur dissolved in hexane (Figure 1A). Clearly in this medium sulfur is present as S_8 molecules.

A freshly prepared 1.2×10^{-4} M solution of sulfur in 5% oleum had a very pale yellow color and had absorptions at 235, 335, 430, and 720 nm in addition to the 280-nm peak of SO_2 (Figure 1B). The intensities of these peaks decreased slowly with time and there was a corresponding increase in the intensity of the 280-nm SO_2 peak. We have previously obtained this same spectrum with peaks 235, 335, 430, and 720 nm from solutions obtained by oxidizing sulfur with an appropriate amount of $S_2O_6F_2$ in solution in HSO_3F and have shown that the solution contains the S_{16}^{2+} cation. We conclude therefore that 5% oleum oxidizes sulfur rather rapidly to the S_{16}^{2+} cation. The observation of the 280-nm SO_2 peak in the fresh solutions confirms that oxidation does indeed take place. Lux and Bohm[7] had previously observed a peak at 233 nm in solutions of sulfur in 5% oleum which they attributed to the compound $S_8(SO_3)_n$. After 6 hr we observed a new weak peak at 590 nm which increased somewhat in intensity on further standing. It has been shown in our earlier paper[12] that further oxidation of solutions of S_{16}^{2+} in HSO_3F with $S_2O_6F_2$ leads to the formation of blue solutions with a strong absorption at 590 nm and we have shown that these solutions contain the S_8^{2+} cation. This cation has been shown to be present in the compound $S_8(AsF_6)_2$ by X-ray crystallography and its structure has been determined.[13] We have now shown that the reflectance spectrum of this solid has a strong peak at 590 nm thus confirming that the blue color of the solutions and the 590-nm absorption are indeed due to the S_8^{2+} cation and not to the S_4^+ cation as supposed by Giggenbach or to the S_8^+ cation as claimed by Symons, *et al.* Thus we conclude that in 5% oleum the S_{16}^{2+} that is formed initially is very slowly further oxidized to S_8^{2+}. However, as we shall see, this species is not very stable in 5% oleum and is apparently extensively disproportionated to S_{16}^{2+} and SO_2. Thus all the sulfur in a solution in a dilute oleum is very slowly oxidized to SO_2.

A freshly prepared 9×10^{-5} M solution of sulfur in 10% oleum was pale green and had the spectrum shown in Figure 1C with absorption bands at 235, 335, 430, and 590 nm. On standing the bands at 235, 335, and 430 nm decreased in intensity and eventually disappeared and there was a corresponding increase in the intensity of the 280-nm SO_2 peak. The 590-nm peak also decreased slowly in intensity but was still present after 28 hr at which time the solution was a pale blue. It is clear that 10% oleum oxidizes a dilute solution of sulfur rather rapidly to a mixture of S_{16}^{2+} and S_8^{2+} and that these species are slowly further oxidized to SO_2.

A freshly prepared 4×10^{-5} M solution of sulfur in 15% oleum was blue and had the absorption spectrum shown in Figure 1D with bands at 280, 335, 430, and 590 nm. The intensity of the 335- and 430-nm bands associated with S_{16}^{2+} decreased rather rapidly in intensity while the 280-nm SO_2 band increased in intensity. Initially the 590-nm band of S_8^{2+} increased in intensity

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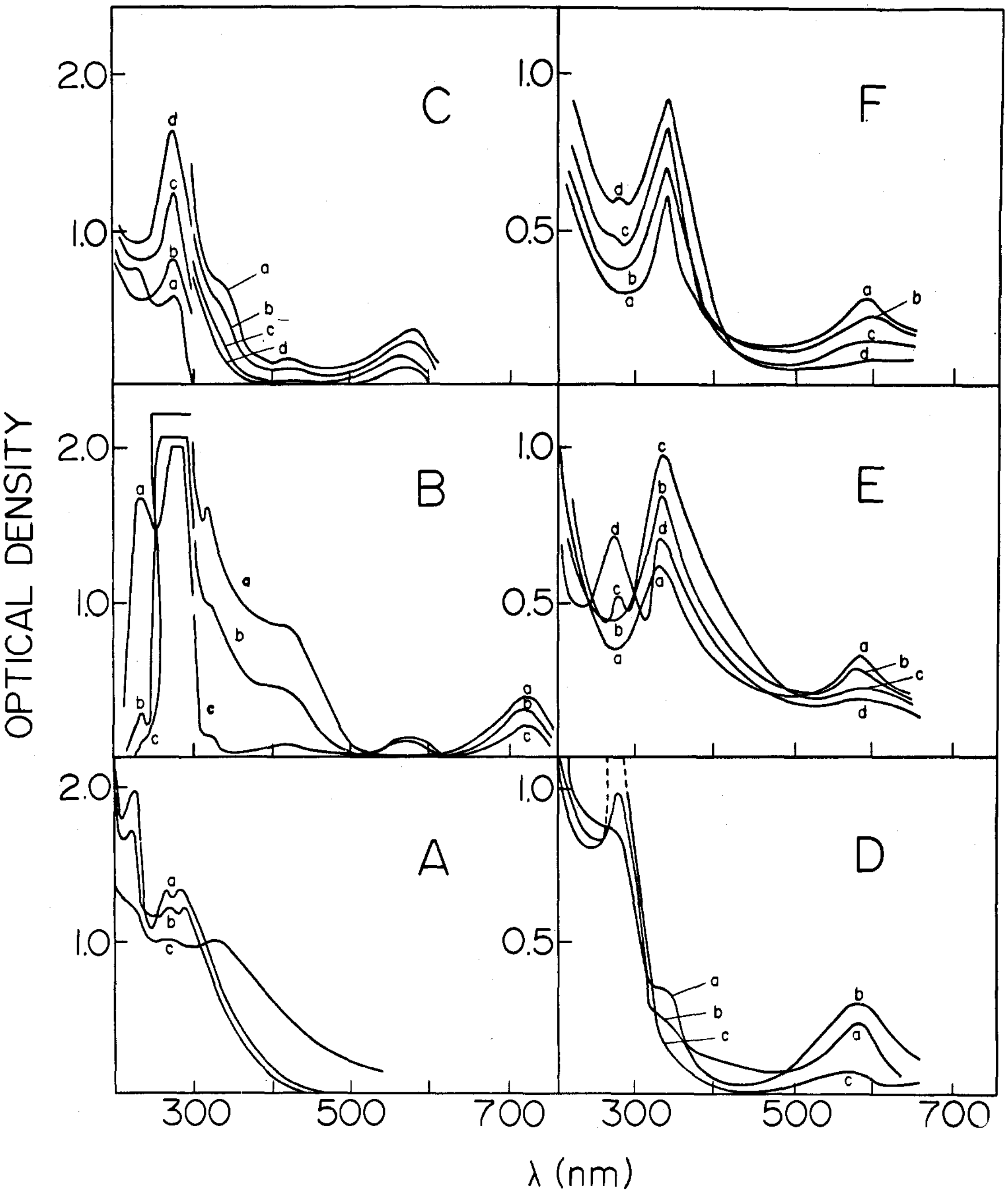

Figure 1.—Absorption spectra of solutions of sulfur in oleum. A: (a) S_8 in hexane; (b) S_8 in 95% H_2SO_4 after 12 hr at 75°; (c) colloidal solution of S_8 in 95% H_2SO_4. B: 1.2×10^{-4} *M* solution of sulfur in 5% oleum after (a) 0.5 hr; (b) 6 hr; (c) 23 hr. Above 300 nm optical density × 0.25. C: 9×10^{-5} *M* solution of sulfur in 10% oleum after (a) 0.5 hr; (b) 7 hr; (c) 17 hr; (d) 28 hr. Above 300 nm optical density × 0.1. D: 4×10^{-5} *M* solution of sulfur in 15% oleum after (a) 0.5 hr; (b) 12 hr; (c) 55 hr. E: 2.3×10^{-5} *M* solution of sulfur in 30% oleum after (a) 0.5 hr; (b) 6 hr; (c) 17 hr; (d) 23 hr. F: 1.4×10^{-5} *M* solution of sulfur in 45% oleum after (a) 0.5 hr; (b) 20 hr; (c) 72 hr; (d) 100 hr.

but then eventually also decreased in intensity. After a period of 5 weeks the blue solution had become colorless and only the SO_2 peak at 280 nm could be observed. The spectrum of a more concentrated (3.5×10^{-3} *M*) solution in 15% oleum was measured over a larger wavelength range and in addition to peaks at 280, 330, 420, 590, and 720 nm an additional peak at 945 nm was observed. It is shown later that the intensity of this latter peak varies with those of the 420- and 720-nm peaks and it may therefore be assigned to the same species as is responsible for these peaks. Again we conclude that 15% oleum oxidizes sulfur rapidly to a mixture of S_{16}^{2+} and S_8^{2+} and that, on standing, oxidation of S_{16}^{2+} to S_8^{2+} and SO_2 occurs. Finally after approximately 5 weeks all the sulfur in this particular solution was converted to SO_2.

A freshly prepared 2.3×10^{-5} *M* solution of sulfur in 30% oleum was blue and had the absorption spectrum shown in Figure 1E with bands at 330 and 590 nm and an SO_2 peak at 280 nm. With time the 330-nm peak increased in intensity at the expense of the 590-nm peak. In our previous study of the oxidation of sulfur with $S_2O_6F_2$ it was found that, in addition to S_{16}^{2+} and S_8^{2+}, the S_4^{2+} ion can also be obtained, and although it is not stable in solution in HSO_3F, it is stable in HSO_3F-SbF_5 and it has an absorption spectrum with a single peak at

330 nm. Thus we conclude that on dissolving sulfur in 30% oleum a mixture of S_8^{2+} and S_4^{2+} is obtained and that with time further oxidation of S_8^{2+} to S_4^{2+} occurs. Eventually however the 330-nm peak of S_4^{2+} diminished in intensity and the 280-nm peak of SO_2 increased in intensity because of the slow oxidation of S_4^{2+} to SO_2.

Freshly made dilute solutions of sulfur in 45 and 65% oleum are blue and were found to have absorption bands at 330 and 590 nm due to S_4^{2+} and S_8^{2+}, respectively (Figure 1F). On standing, the 590-nm peak disappeared and a rather weak 280-nm SO_2 peak grew somewhat in intensity. Thus in these concentrated oleum media S_8^{2+} is oxidized to S_4^{2+} which appears to be rather stable and is only very slowly oxidized to SO_2.

The absorption spectra experiments may be summarized as follows. In dilute oleum sulfur is rapidly oxidized to the S_{16}^{2+} cation and to some extent to the S_8^{2+} cation. This latter cation is however not particularly stable in dilute oleum and appears to disproportionate to S_{16}^{2+} and SO_2 until eventually all the sulfur is oxidized to SO_2. In more concentrated oleum S_8^{2+} is more stable but is slowly oxidized to S_4^{2+} which is the most stable cation in concentrated oleum.

Cryoscopic Measurements in 45% Oleum.—The freezing point depressions produced by solutions of sulfur in 45% oleum were measured. The freezing points were however not stable with time and the freezing point depression continually increased for several days. The observed freezing points were plotted against time and extrapolated to zero time to give the freezing points of fresh solutions. These results are shown in Figure 2. The solutions were initially a deep blue but the color diminished fairly rapidly and after several days the solutions were almost colorless. The initial freezing points of the solutions were only slightly lower than predicted for the formation of the S_8^{2+} ion according to the equation

$$8S + 6H_2S_2O_7 \longrightarrow S_8^{2+} + 2HS_3O_{10}^- + 5H_2SO_4 + SO_2$$

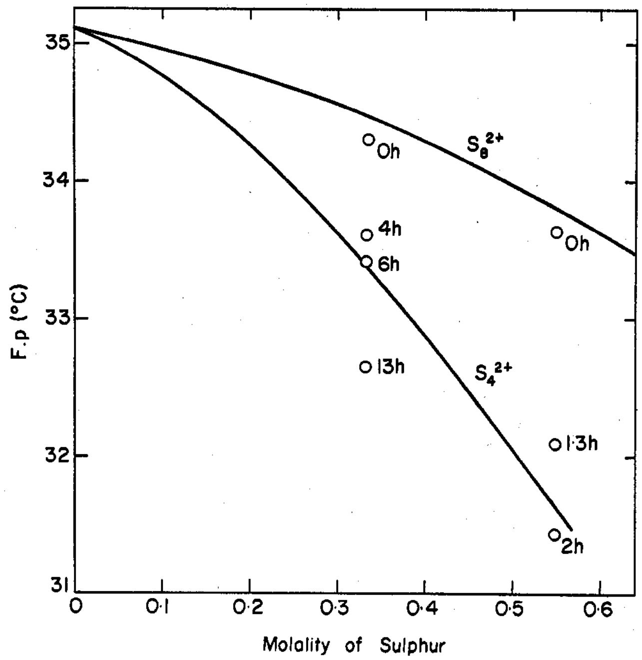

Figure 2.—Freezing points of solution of sulfur in 45% oleum ($H_2S_2O_7$).

The calculation of the expected freezing point curve for S_8^{2+} is exactly similar to that given previously for Se_8^{2+}.[14] We conclude that when sulfur dissolves in 45% oleum, the S_8^{2+} cation is formed very rapidly according to this equation. However the rapid decrease in the freezing points of these solutions shows that further oxidation occurs first to S_4^{2+} and then to SO_2. After 6 hr for the more dilute solution and after only 2 hr for the more concentrated solution, the freezing point had reached the value expected for quantitative formation of S_4^{2+} according to the equation

$$4S + 6H_2S_2O_7 \longrightarrow S_4^{2+} + 2HS_3O_{10}^- + 5H_2SO_4 + SO_2$$

However these solutions were still blue and evidently still contained S_8^{2+} so it is clear that some of the sulfur must have been oxidized to SO_2, in agreement with the absorption spectra measurements which showed that after several hours these solutions contained S_8^{2+}, S_4^{2+}, and SO_2.

Reaction of Sulfur with Liquid Sulfur Trioxide.—In a typical experiment, liquid SO_3 (20 g, 0.25 mol) was distilled onto powdered sulfur (1 g, 0.031 g-atom) in a glass tube with an exit protected from moisture by a P_2O_5 tube. As soon as the first few drops of SO_3 came into contact with sulfur, the latter turned bright red and then rapidly changed to a greenish blue material on further addition of SO_3. The reaction is apparently complete in a few minutes giving a greenish blue product which is insoluble in liquid SO_3. The excess SO_3 was decanted off. Any attempt to remove the last traces of SO_3 under vacuum resulted in complete decomposition of the product with the formation of elemental sulfur. It is interesting to note that there appears to be no reaction between sulfur and extremely dry SO_3 although in the presence of a trace of moisture the reaction is rapid. The product containing a little adhering SO_3 was dissolved in 65% oleum and the absorption spectrum of this solution was recorded as rapidly as possible. The resulting spectrum was identical with that in Figure 1F showing the presence in the solution of the S_8^{2+} and S_4^{2+} ions. The latter may have been present in the original solid or may have been formed by oxidation of S_8^{2+} in the oleum. A reasonable formulation for the blue solid which has a composition close to that of S_2O_3, as was reported by several of the early workers, is $S_8(HS_3O_{10})_2$ if it is assumed that the small amount of water that is needed to initiate the reaction is incorporated in the product. However the product may also contain other polysulfate anions and also a substantial amount of the S_4^{2+} ion probably in the form of the compound $S_4(S_4O_{13})$. This compound is expected to be white or pale yellow but only a small amount of the highly colored S_8^{2+} would be required to cause the product to have a dark blue color.

Electron Spin Resonance Measurements.—A concentrated red solution of sulfur in 30% oleum had two esr signals, a strong signal at $g = 2.027$ and a very weak signal at $g = 2.014$. When the red solution was oxidized with more 30% oleum to give a green solution, the intensity of the absorption (*i.e.*, the area under the absorption curve) at $g = 2.014$ increased relative to the $g = 2.027$ signal. From measurements on solutions of S in HSO_3F and of the compounds $S_{16}(SbF_6)_2$ and S_8-

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[14] J. Barr, R. J. Gillespie, R. Kapoor, and K. C. Malhotra, *Can. J. Chem.*, **46**, 149 (1968).

TABLE I

g VALUES AND ABSORPTION MAXIMA FOR SULFUR CATIONS

	S_{16}^{2+}	S_8^+	S_8^{2+}	S_4^+	S_4^{2+}
g	...	2.027	...	2.014	...
Abs max, nm	235 335	430 720 935	590	...	330

$(Sb_2F_{11})_2$ in SO_2 we have previously ascribed the signal at $g = 2.027$ to the radical S_8^+ arising from dissociation of S_{16}^{2+} and the signal at $g = 2.014$ to the S_4^+ radical arising from the dissociation of S_8^{2+}.[12] The present observations on oleum solutions are clearly in accord with these previous conclusions. On cooling a 3.5×10^{-3} *M* solution in 15% oleum to −37° the signal at $g = 2.027$ decreased in intensity rather markedly while that at $g = 2.014$ also decreased although the change in intensity was less marked. The decrease in the intensity of the $g = 2.027$ signal with decreasing temperatures was accompanied by a decrease in the intensity of the 430-, 720-, and 954-nm peaks while the peaks at 590, 335, and 235 nm remained unchanged in intensity. It seems reasonable therefore to assign the 420-, 720-, and 945-nm peaks to the S_8^+ radical leaving the 235- and 335-nm peaks as the characteristic absorptions of S_{16}^{2+}. The 590- and 330-nm peaks are due to S_8^{2+} and S_4^{2+}, respectively. These assignments of the esr signals and absorption maxima are summarized in Table I. Our conclusions differ somewhat from those of Giggenbach,[10] who has attributed the 590-nm peak and the $g = 2.014$ signal to the S_4^+ radical, the 430-nm peak to the dimer S_8^{2+}, and the $g = 2.027$ signal to an S_n^+ radical. Although we agree with the assignment of the $g = 2.014$ signal to S_4^+, our earlier results for the compounds $S_{16}(SbF_6)_2$ and $S_8(AsF_6)_2$ and our results in dilute oleums clearly indicate that the 430-nm peak is not associated with the 590-nm peak and that indeed the former is to be associated with S_8^+ and the latter with S_8^{2+}.

Symons, *et al.*,[11] have recently claimed, on the basis of experiments utilizing sulfur enriched in ^{33}S and contrary to the conclusions of Giggenbach and ourselves, that the radical present in blue solutions of sulfur in 65% oleum having a *g* value of 2.013 is the S_8^+ radical. They claimed that a detailed analysis of their spectra is inconsistent with the radical being S_4^+ but is consistent with it being S_8^+. They suggest moreover that the S_8^+ radical is in equilibrium with the diamagnetic S_{16}^{2+}. However our work shows that S_{16}^{2+} does not exist in 65% oleum as it is rapidly and completely oxidized to S_8^{2+} and S_4^{2+}. Thus the signal that is observed in 65% oleum is hardly likely to be due to S_8^+. Moreover our results show that when S_{16}^{2+} is present in more dilute oleums another esr signal is observed with $g = 2.027$. This we have assigned to the S_8^+ radical.

Our proposed assignments receive some confirmation from the spectra of the frozen solutions reported by Giggenbach.[10] At 90°K the signal attributed to S_4^+ gives a typical glass spectrum with $g_\perp = 2.0004$ and $g_\parallel = 2.0192$ indicating that the species giving rise to this signal has axial symmetry. This is consistent with S_4^+ having a square-planar structure like S_4^{2+}. On the other hand the signal at $g = 2.027$ splits into three signals with $g_1 = 2.0024$, $g_2 = 2.0311$, and $g_3 = 2.0421$ in the frozen solution at 90°K. This indicates that the radical giving rise to this spectrum does not have axial symmetry and this is consistent with the ion having a structure like that of S_8^{2+}.[12] Somewhat surprisingly the blue and red diamagnetic solids $S_8(AsF_6)_2$ and $S_{16}(AsF_6)_2$ also give esr signals which have *g* values identical with those observed by Giggenbach[10] for the frozen red and blue solutions in oleum. The crystal structure of $S_8(AsF_6)_2$ shows that it does indeed consist of S_8^{2+} and AsF_6^- ions[13] and one can only conclude that the esr spectrum is due to a very small amount of S_4^+ trapped in the crystal or adsorbed on the surface. Although the crystal structure of $S_{16}(AsF_6)_2$ has not been determined, other evidence strongly indicates that the species present in this solid and in the more dilute oleum solutions is indeed the diamagnetic S_{16}^{2+} ion[12] so that one is again forced to conclude that the esr signal with $g = 2.027$ is due to the S_8^+ radical which is present in solution in equilibrium with S_{16}^{2+} and is trapped in the crystal or adsorbed on the surface of the solid $S_{16}(AsF_6)_2$.

Experimental Section

Fuming Sulfuric Acid.—Oleums of known composition were obtained by distilling sulfur trioxide into a weighed amount of 100% sulfuric acid.

Sulfur was 99.999% grade (K & K Laboratories) and was stored over P_2O_5 in a dessicator.

Electron Spin Resonance Spectroscopy.—Esr spectra were obtained on a Jeolco Model JES 3BS-X spectrometer. The *g* values were obtained by comparison with a sample of Mn^{2+} in MgO ($g = 1.981$); they are accurate to ±0.001.

Cryoscopy.—Freezing point measurements in disulfuric acid were made as described previously.[15]

Spectrophotometric Measurements.—Measurements on solutions were made in 1-cm rectangular silica cells with inserts to give path lengths from 0.1 to 1 mm. Optical densities were measured against a reference cell containing solvent on a Cary Model 14 recording instrument. Measurements on solids were made using a reflectance attachment.

Acknowledgment.—We thank the National Research Council of Canada for financial support of this work. We thank Dr. O. C. Vaidya for carrying out the cryoscopic measurements in 45% oleum.

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