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PART I. EPR STUDIES OF TETRASULFUR TETRANITRIDE IN SULFURIC ACID

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PART II. THE REACTION OF TETRASULFUR TETRANITRIDE WITH SULFURIC ACID

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February 1970

AEC Contract No. W-7405-eng-48

*Filed as a Ph. D. Thesis

LAWRENCE RADIATION LABORATORY
UNIVERSITY of CALIFORNIA BERKELEY

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Abstract

The solutions formed by the dissolution of tetrasulfur tetranitride in sulfuric acid have been studied by electron paramagnetic resonance (epr). The main radical species, which was determined from a transference study to be positively charged, has a five-line spectrum, due to two equivalent nitrogens, with g = 2.0109 and A_N = 3.21 gauss. A study using sulfur-33 enriched S_4N_4 showed that the radical contains two equivalent sulfur atoms with A_S = 8.9 gauss. The spectrum has been assigned to the radical $S_2N_2^+$. In 95% sulfuric acid the five-line spectrum decays to a spectrum containing three lines with relative intensities 1:2:1. This spectrum has g = 2.0152 and a proton coupling constant of 1.05 gauss. A sulfur-33 coupling constant determined from weak satellite lines is A_S = 8.5 gauss. The identity of this radical species is uncertain.

Introduction

The epr spectra of the solutions formed by the dissolution of S_4N_4 in concentrated sulfuric acid were first reported by Chapman and Massey[1] in 1962. Freshly-prepared solutions gave a spectrum of five lines with an intensity ratio of 1:2:3:2:1 and a separation of 3.32±.04 gauss. This spectrum is consistent with a radical containing two equivalent nitrogen atoms. A transference study by Chapman and Massey showed that the species was positively charged, and they suggested that the radical was SN_2^+.

In a later study, McNeil, Murray, and Symons[2] also observed the same five-line spectrum. They calculated spin populations from their observed hyperfine coupling constants, and concluded that there should be an appreciable spin population on the sulfur atom. However, using the method of Wälsh[3] they predicted that SN_2^+ would have a linear structure. They further predicted that there would be no spin population on the sulfur atom. Since the latter prediction was inconsistent with their calculated spin populations, they proposed that the observed radical was the cyclic $S_2N_2^+$ species.

Both groups of researchers reported that in 95% sulfuric acid a three-line spectrum appeared as the five line spectrum decayed. These lines were reported to have an intensity ratio of 1:1:1 and a splitting of approximately 1 gauss. Such a spectrum is consistent with a radical species containing only one nitrogen. Chapman and Massey were unable to determine the electrical charge of the species and proposed SN as a possible species.

We have further studied the esr spectra of these solutions to learn more about the nature of these radicals as well as their relative importance in the overall reaction of S_4N_4 with sulfuric acid.

Experimental Procedures

Two solvents were employed: concentrated sulfuric acid (Baker and Adamson 95% reagent grade) and 100% sulfuric acid. The reactions were slightly different in these solvents. Sulfuric acid (100% H_2SO_4 unless otherwise specified) was prepared from Baker and Adamson reagent grade concentrated sulfuric acid and Baker and Adamson reagent grade 15% fuming sulfuric acid. The exact composition of the solvent was adjusted until a maximum in the freezing point was obtained.

The S_4N_4 was prepared by the method of Villena-Blanco and Jolly.[4] The product was recrystallized from benzene until a constant melting point of 186° was obtained and then stored under vacuum until needed.

Tetrasulfur tetranitride enriched in ^{33}S was also prepared for these experiments. Sulfur (48.6% ^{33}S) was obtained from Oak Ridge National Laboratory. Three mg. of sulfur was placed in a conical 15 ml test tube equipped with a standard taper joint. The tube was connected through a stopcock to a standard vacuum line and evacuated. Approximately 700 torr of chlorine was placed in the tube and the stopcock was closed. After several hours all the solid sulfur was converted to volatile compounds, presumably a mixture of sulfur chlorides. The tube was placed in a -112° bath, and all the excess chlorine was pumped off. Then 8.5 ml of carbon tetrachloride was condensed into the tube at -196°. The vessel was then filled with a nitrogen atmosphere, warmed to room temperature and disconnected from the vacuum line. Purified ammonia was immediately bubbled through the solution. After four hours of bubbling, the carbon tetrachloride solution was filtered to remove all the ammonium chloride as

well as most of the sulfur which are products of the reaction. The filtrate was evaporated to dryness and the product S_4N_4 given no further purification. Several trial preparations with sulfur in natural abundance, checked by epr spectra, showed no radical impurities.

The reactions were always run under vacuum. Usually the S_4N_4 was added slowly to H_2SO_4 which was cooled to 0° in order to prevent any local overheating. With the $^{33}S_4N_4$, the smaller sample size made it more convenient to add the sulfuric acid to the S_4N_4.

The polarity of the radicals was determined in a transference study using electrolysis in a cell which consisted of five compartments separated by sintered glass discs. Solvent was placed in the four outer compartments, and the solution being studied was placed in the center compartment. For 95% H_2SO_4 5 V d.c. was applied, while for 100% H_2SO_4 15 V d.c. was needed in order to obtain a sufficient current. The charge on a species was deduced from the direction of migration as detected by the epr spectra.

Epr measurements were made using a Varian V4502 epr spectrometer, equipped with a nine-inch Fieldial regulated magnet and 100 KHz field modulation and detection. For routine work, samples were held in a quartz flat cell (Varian V4548 aqueous solution sample cell). A V4531 multipurpose cavity was used.

Spectra were recorded both in analog form for routine analysis and in digital form for computer processing of the spectra. The spectra were digitized by attaching a Honewell model S6114 automatic data logging system to the spectrometer. This system consists of a frequency counter

(HP 5245L), a digital voltmeter (Honeywell-EI- Multimeter, model 630S), an output control unit (Honeywell-EI model 825) and an incremental magnetic tape recorder (Kennedy, model 1400). A voltage-to-frequency converter (Vidar, model 240) was used to provide magnetic field information from the x-axis transmitting potentiometer of the Fieldial unit. The magnetic field was calibrated using an nmr magnetometer.

The digitized spectra were processed by computing a least squares fit to the spectra. With this process good values could be obtained for the linewidth, line position, and intensity. The least squares technique is especially important in determining line intensities of unresolved lines which have different linewidths. Errors due to baseline drift and overlapped lines are automatically accounted for by the lineshape analysis. This technique is not subject to the errors (due to approximations) of the usual integration methods.

Radical concentrations were determined by a comparison technique. A resonant cavity (Varian, V4534) was doped with a sample of manganese(II) in magnesium oxide. The manganese reference standard, in a small capillary tube, was taped to the side of the resonant cavity so that it was in both the microwave field and the modulation field. This sample gave epr signals which were resolved from those of the radical of interest. The manganese standard was calibrated with a sample of vanadyl acetylacetonate dissolved in dichloromethane and the radical spectra were compared with the manganese signals. The epr signal intensities were determined by a least squares fit to the digitized spectra.

Results and Discussion

The epr study of the reaction products of tetrasulfur tetranitride in 100% sulfuric acid produced the same spectrum as had previously been reported from 95% sulfuric acid. This spectrum consisted of five lines with an intensity ratio of 1:2:3:2:1 (Fig. 1). The lines showed a trend in linewidth: the narrowest line was on the low-field side and the broadest line was on the high field. This spectrum was fit using a modified version of the least-squares technique described by Bauder and Myers.[5] Assuming a Lorentz lineshape with variable widths for the lines, and a second-order spin Hamiltonian, the radical was found to have g = 2.0107 and a hyperfine coupling constant of 3.21 gauss.

Further study of the spectrum revealed several very low-intensity lines (each less than 1% of the intensity of the major spectrum) which were symmetrically disposed about the major five-line spectrum. These lines, like the major five lines, showed distinct variations in linewidths from low to high field (Fig. 2). Moreover, the lines both on the low field side and on the high field side were separated by approximately the same splitting as the major lines.

These low intensity lines appear to have the same g value as the five line spectrum and are believed to be due to ^{33}S in natural abundance. Sulfur-33 has a nuclear spin I = 3/2, and is a stable isotope of 0.74% natural abundance. If these peaks are due to ^{33}S, then, the number of sulfur atoms in the radical could, in principle, be determined by a comparison of the intensities of the satellite lines to the main lines. However, an attempt to perform this comparison failed. The low intensity of the satellite lines compared with the main lines as well as the

variation in the linewidths, and the lack of resolution, made such a comparison very difficult. The relative intensities of the lines could not be determined with any precision.

In order to establish the number of sulfur atoms in the radical, S_4N_4 enriched in ^{33}S was used. The spectrum resulting from the enriched sample is shown in Fig. 3. From this spectrum, it can be concluded that the radical must possess more than one sulfur. The hyperfine pattern is much too complicated for a species with only one sulfur atom. Because of the numbers of parameters required to describe the spectrum, the spectrum could not be fitted with a least squares technique. However, it was possible to simulate the spectrum quite closely by assuming a radical containing two equivalent sulfur atoms (see Fig. 4). The sulfur hyperfine coupling constant obtained is 8.9 gauss.

The epr studies have shown that the radical contains two equivalent nitrogen and two equivalent sulfur atoms. The concentration of the radical was also determined from the epr studies. The solutions employed were approximately 0.001 M in S_4N_4. The spectrum was taken 40 minutes after the reaction began and the subsequent slow decay was observed. After 40 minutes the epr results showed that 0.27 radicals were produced per S_4N_4. If the decay is extrapolated back to zero time, the yield is increased to 0.28. Thus, its formation must be considered to be a reaction of reasonable importance.

The species having the five-line spectrum can also be made from sulfur-nitrogen compounds other than S_4N_4. Chapman and Massey reported that they observed the same spectrum with S_2N_2, S_4N_2, $S_4N_4H_4$, $Co(S_2N_2H)_2$ and $S_3N_2O_2$ in concentrated sulfuric acid.[1,6] We have confirmed the results

with $S_3N_2O_2$ and have shown that, with $S_3N_2O_5$ in 100% sulfuric acid, the same species is formed. Thus, it appears that the radical is a common decomposition product of many sulfur nitrogen compounds in sulfuric acid. All of these intial compounds have one thing in common: alternating sulfur and nitrogen atoms.

The charge of the five line radical was checked by placing its solution in the center compartment of a five compartment transference cell. A potential of 15 V d.c. was applied for two hours with the cell kept in a 10° bath. When the epr spectra of the three central compartments were examined it was found that the radical migrated preferentially toward the cathode. This confirmed the results of Chapman and Massey who showed that the radical was positively charged.

The epr determinations have shown that the radical has two equivalent nitrogens and two equivalent sulfurs. However, this result cannot preclude the possibility of a species containing oxygen, other non-equivalent sulfurs or even hydrogen having no appreciable free electron density. Even if there were only sulfur and nitrogen in the radical, $SNNS^+$ and $NSSN^+$ would satisfy the epr results, although they both require a rearrangement of "S-N" fragments. However, the relative ease of formation from so many widely diverse compounds would indicate that its structure is most probably a ring of alternating sulfur and nitrogen atoms.

Although the earlier investigators reported the appearance of a three-line spectrum when the five-line spectrum decayed, the three-line spectrum was never observed when S_4N_4 was reacted with 100% sulfuric acid. However, it was possible to produce the three-line spectrum (see Fig. 5) by using 95% sulfuric acid. The five-line species was completely con-

verted to the three-line species after several weeks at room temperature or a couple of hours at 100°. Chapman and Massey reported that the spectrum had g = 2.016 with a coupling constant of about 1 gauss, and the lines had relative intensities of 1:1:1. On the basis of this they suggested that the species might be SN.

However, the present work shows that the relative intensities are approximately 1:2:1. These intensities are consistent with a species containing two equivalent hydrogen atoms. Furthermore, some very weak lines are present on both the low field and the high field sides of the main three line spectrum. These lines are equidistant from the main lines and exhibit the same pattern. Thus, they are thought to arise from a ^{33}S hyperfine interaction. The number of sulfur atoms in the radical species could not be determined because the signal intensities were too weak. The spectral parameters determined from a least squares fit to the spectrum were g = 2.0152, A_H = 1.07 gauss, and A_S = 8.5 gauss. The spectral parameters for this species as well as the five line species are presented in Table I.

TABLE I

Hyperfine Coupling Constants and g-values for Radicals Derived from S_4N_4

S_4N_4 in H_2SO_4	g	A_N[a]	A_H[a]	A_S[a]	Reference
(five line)	2.011	3.32		--	1
	2.0112	3.20		--	2
	2.0109	3.21		8.9	this work
S_4N_4 in H_2SO_4	2.016		ca.1	--	1
(three line-Decomp.)	2.0177		1.39	--	2
	2.0152		1.07	8.5	this work

[a]Hyperfine coupling constants are reported in gauss.

To further substantiate this interpretation of the three-line species, the dissolution was done in deuterated sulfuric acid. If the triplet spectrum is due to hyperfine interaction with protons, the spectrum resulting from deuteron interaction would, in principle, be a quintet, with one-third the spread of the three line spectrum. However, because the splitting would be smaller than the linewidth, the spectrum would consist of a single unresolved line. The dissolution produced the same five line spectrum as reported previously. However, when the five-line species decayed, the spectrum observed was a single line with a width which was less than the spread of the triplet spectrum. Since the line does not have a Lorentz lineshape, it probably consists of unresolved hyperfine structure. These results establish that the three-line spectrum is caused by hyperfine interaction with two hydrogens.

A solution of the species giving rise to the three line spectrum was placed in the center compartment of the five compartment transference cell. A potential of 5 V d.c. was applied for two hours. An examination of the three central compartments showed that the radical migrated to the cathode. This established that the species was positively charged as might be expected.

The concentration of the three line species was determined by comparison with the same manganese internal standard used previously. The yield was less than 0.01 per $S_2N_2^+$ or less than 0.0028 per S_4N_4. The growth of the three line species does appear to correlate with the decay of $S_2N_2^+$ but from its very small yield it seems to be of a relative unimportance.

These results indicate that the decomposition product contains two equivalent hydrogen atoms, at least one sulfur atom and is also positively

charged. The product probably contains oxygen, but it is unlikely that it contains nitrogen. The high g-value and the small hydrogen coupling constant indicate that the radical is probably a π-radical. However, from the available data it is impossible to determine its exact composition and the identity of the species is open to speculation.

Acknowledgements

We would like to acknowledge Professor Rollie J. Myers for his advice and many helpful discussions.

This work was done under the auspices of the Atomic Energy Commission.

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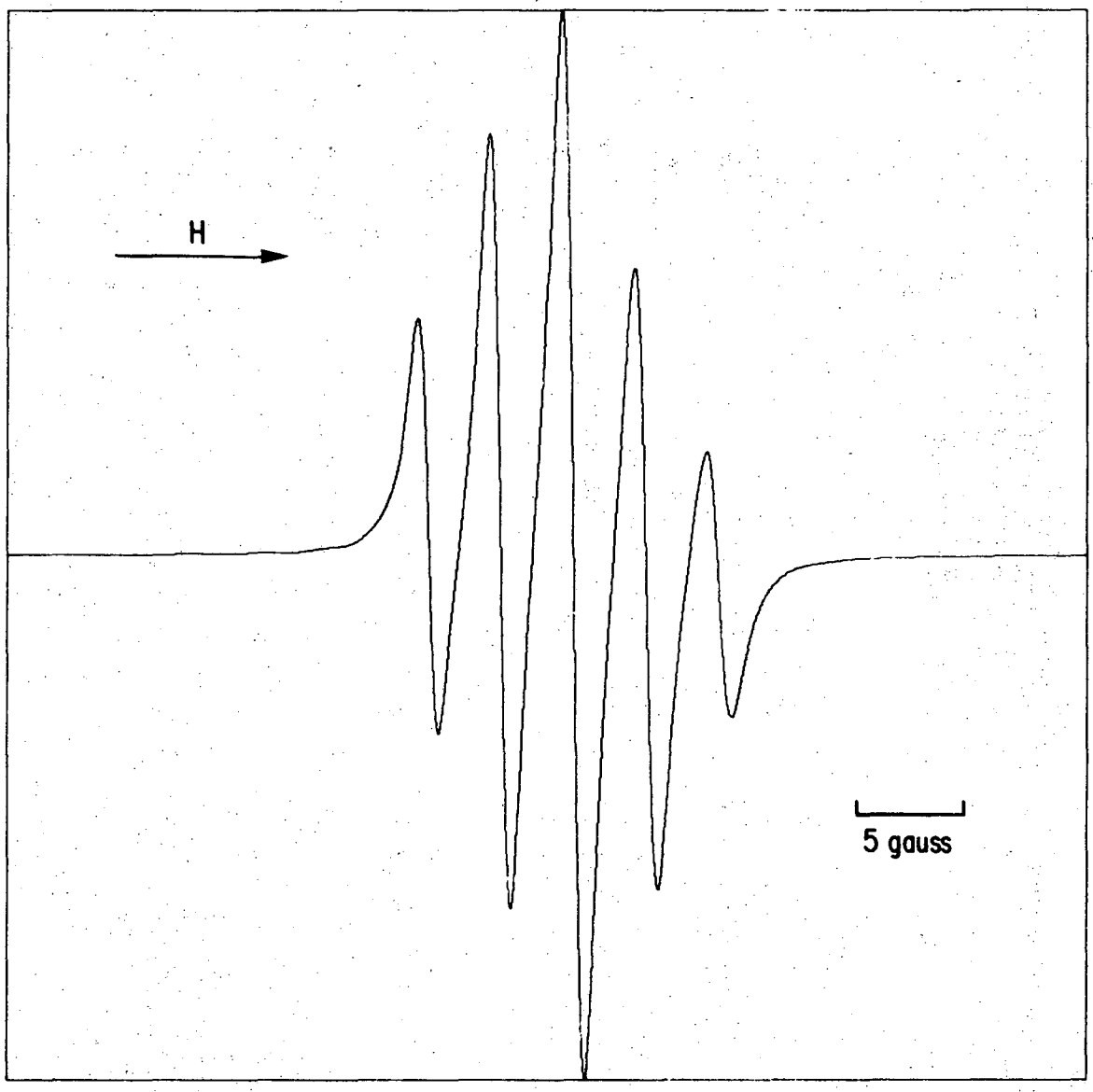

Fig. 1 EPR spectrum of $S_2N_2^+$ in H_2SO_4.

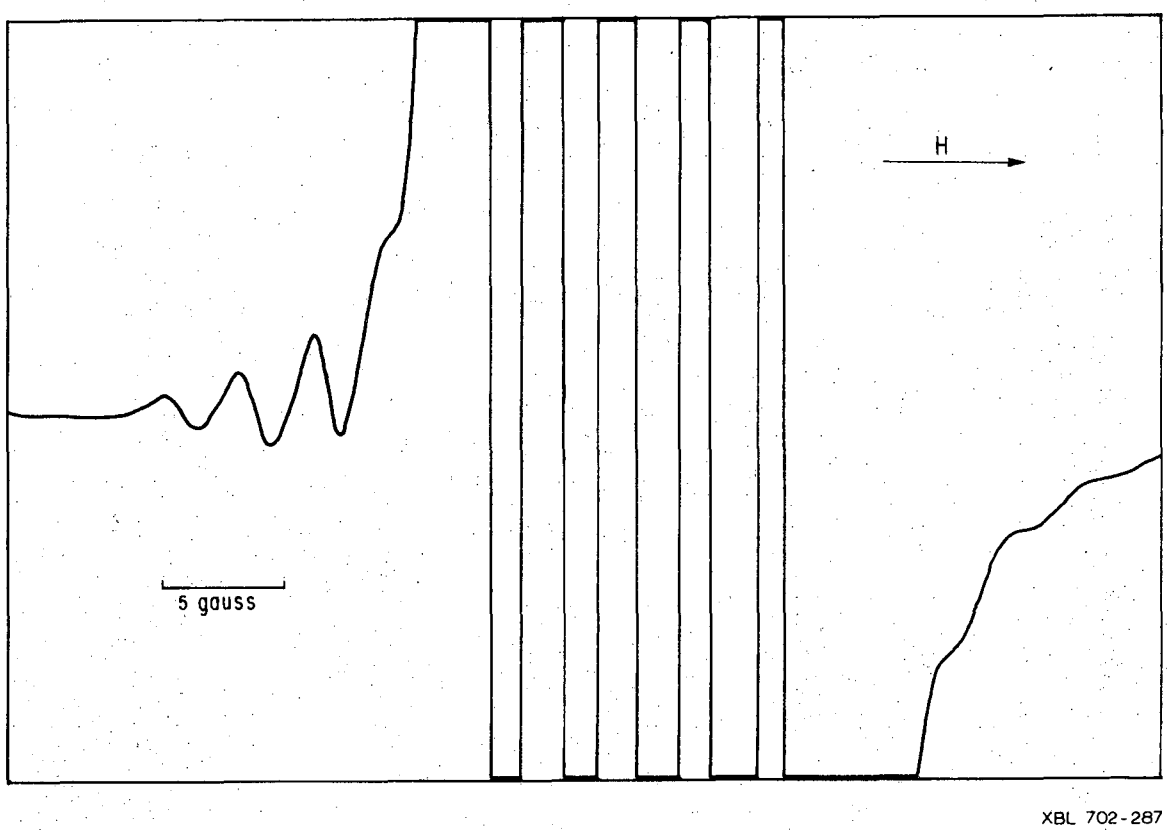

Fig. 2. Sulfur-33 satellite lines in the epr spectrum of $S_2N_2^+$ in H_2SO_4

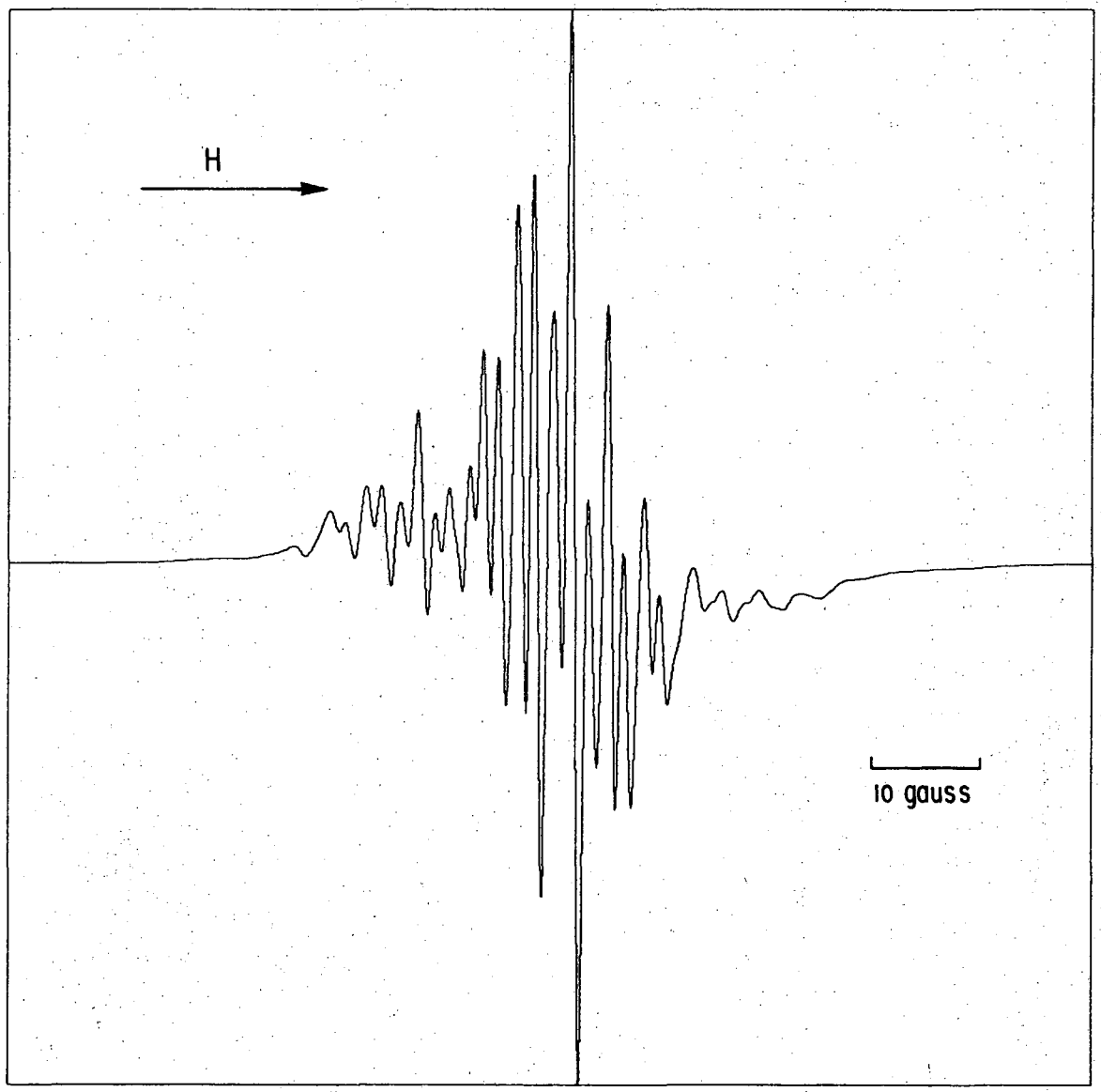

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Fig. 3. EPR spectrum of ^{33}S enriched S_4N_4 in H_2SO_4

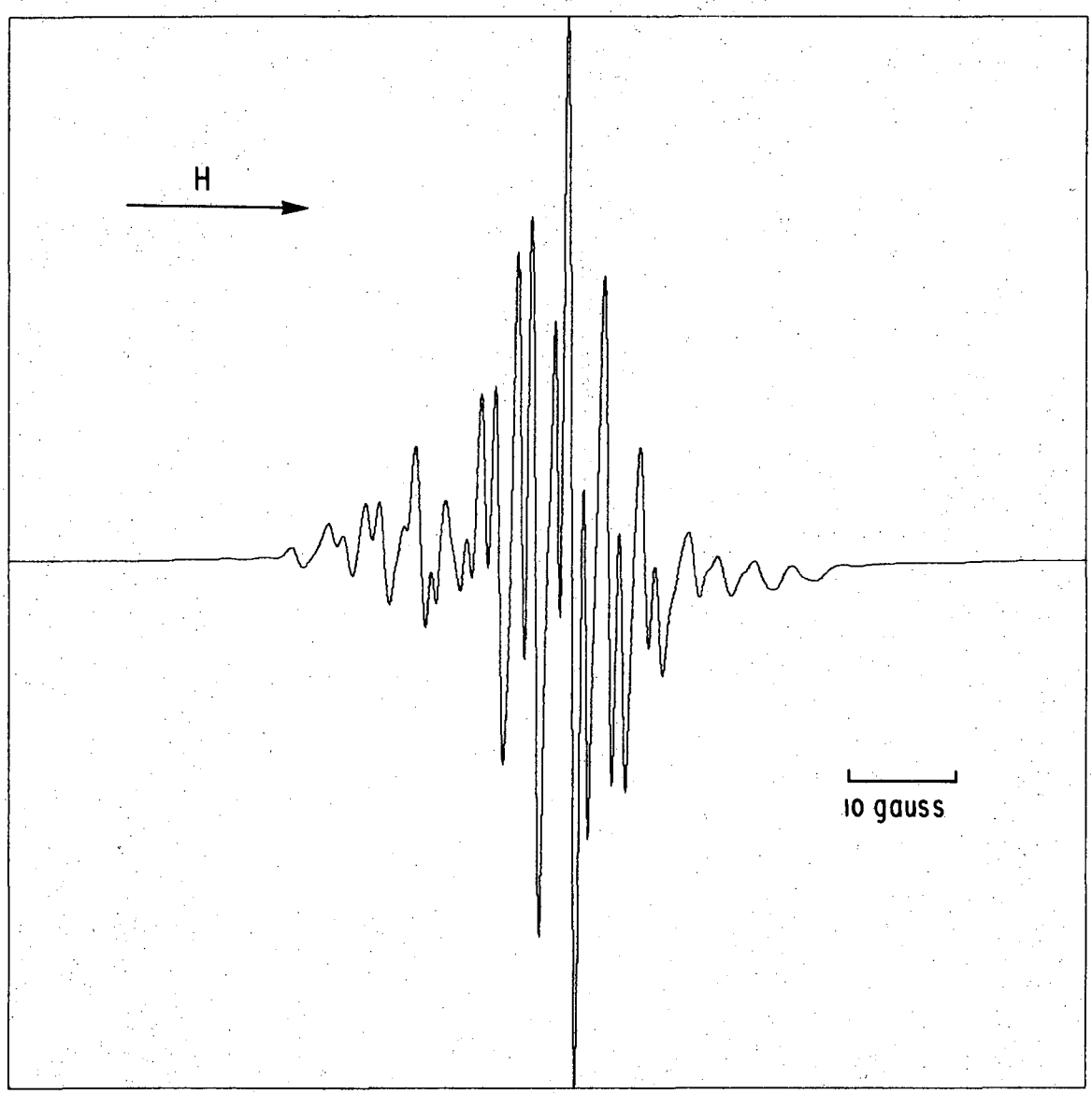

Fig. 4. Calculated epr spectrum of ^{33}S enriched $S_2N_2^+$

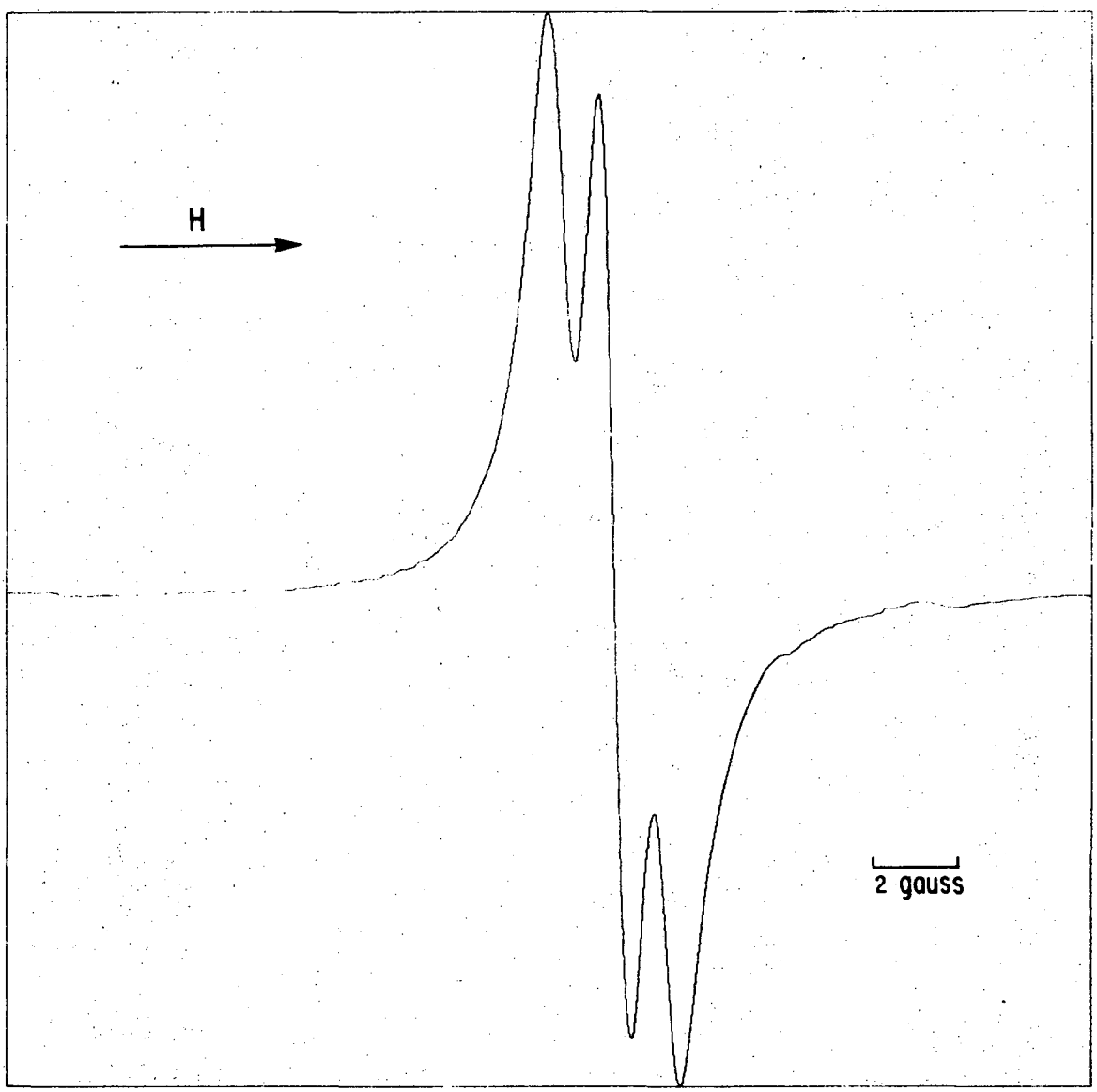

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Fig. 5. Three-line epr spectrum from S_4N_4 in concentrated H_2SO_4

PART II. THE REACTION OF TETRASULFUR TETRANITRIDE WITH SULFURIC ACID

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Abstract

The stable reaction products of tetrasulfur tetranitride with 100% sulfuric acid have been studied by several analytical techniques. The products are sulfur dioxide, sulfamic acid, varying amounts of bisulfate, disulfate and ammonium ion, as well as an uncharacterized cation with an intense uv and complex visible absorption spectrum. It was not possible to determine a completely balanced equation.

Introduction

The chemistry of tetrasulfur tetranitride (S_4N_4) dates back to 1835, when Gregory[1] isolated the compound from the reaction of disulfur dichloride with ammonia. Since then, many researchers have studied this parent compound and its large family of derivatives.[2]

Goehring and her co-workers[3] have reported the preparation of sulfur trioxide adducts of S_4N_4. Depending on the ratio of reactants, either $S_4N_4 \cdot 2SO_3$ or $S_4N_4 \cdot 4SO_3$ can be formed. When excess sulfur trioxide is used, the sulfur nitride complex is oxidized to $S_3N_2O_5$ and sulfur dioxide is evolved. Subsequent hydrolysis yields additional sulfur dioxide as well as ammonia, sulfuric acid and sulfamic acid.

The homogeneous acid hydrolysis of S_4N_4 has been reported to proceed by a different route. Nair and Murthy,[4] using dioxane that was 4 M in acid as solvent, were able to study the hydrolysis products without resorting to a heterogeneous medium.[5] Their results showed that all the nitrogen ended up as ammonia. The sulfur, on the other hand, ended up as varying non-stoichiometric amounts of sulfur dioxide, hydrogen sulfide and elemental sulfur.

The stoichiometry of the reaction of S_4N_4 with sulfuric acid might be expected to be intermediate between those of the two aforementioned reactions. The reaction of S_4N_4 with concentrated sulfuric acid was first reported by Chapman and Massey,[6] who observed two radical species in solution. The study by Lipp, Chang, and Jolly[7] showed that, in 100% sulfuric acid, only one of the radicals was formed. The species was shown to be $S_2N_2^+$, probably in the form of a ring of alternating sulfur and nitrogen atoms.

Sulfuric acid is known to be a stabilizing solvent for many reactive species which are unstable in aqueous solution. These would include NO^+,[8] NO_2^+,[9] Se_4^{2+},[10] as well as scores of aromatic radical cations.[11] The use of sulfuric acid as the solvent as well as a reactant in this study might allow for the stabilization of several unusual and otherwise unattainable products. It was with this in mind that a study of the total net reaction of tetrasulfur tetranitride with sulfuric acid was begun in this laboratory.

In order to systematically investigate the S_4N_4-H_2SO_4 reaction, 100% sulfuric acid was used as the solvent instead of ordinary concentrated (95%) sulfuric acid. More methods of analysis would thus be applicable, and a fuller understanding of the reaction would be possible. The analytical procedures employed successfully included esr, nmr, conductivity, cryoscopy, uv-visible spectroscopy as well as classical chemical analysis.

Experimental

General.- The 100% sulfuric acid (written as just H_2SO_4- any other concentrations will be specified) was prepared from concentrated H_2SO_4 (95%) Baker and Adamson Reagent Grade plus 15% fuming H_2SO_4 Baker and Adamson Reagent Grade. The solution was first adjusted to the point where fuming just stops by the "fair and foggy" method.[12] Exactly 100% was obtained by a readjustment with either slightly aqueous or slightly fuming H_2SO_4. The exact point was established by using the maximum freezing point as the end point indicator.[13] The method of determining freezing point will be explained in the section on cryoscopy.

The S_4N_4 used was prepared by the method of Villena-Blanco and Jolly.[14] The S_4N_4 was recrystallized from benzene until the melting point leveled off at 186°. The product was then stored under vacuum until needed.

The reactions of S_4N_4 with H_2SO_4 usually were studied on a standard vacuum line. The H_2SO_4 was first degassed, and the S_4N_4 was slowly added from a tipping side-arm. The reaction was quite exothermic. In order to prevent local heating the solution was stirred with a magnetic stirrer and kept in an ice bath as long as there was evidence of reaction.

Conductivity.- It has been shown by Gillespie et al.[15] that very accurate determinations of the bisulfate ion concentration in H_2SO_4 can be achieved by conductivity measurement. The ionic mobility of bisulfate ion is so much higher than that of any other species[16] that the conductance can be considered to be a measure of just that ion's concentration.

The conductivity cell (Fig. 1) used in this study was of the basic design of Gillespie.[17] The solutions were maintained under an atmosphere of dry nitrogen and the cell was placed in a thermostatted bath at 25±.005°. The measurements were made with an a.c. Wheatstone Bridge using a 1000 cps oscillator as the signal source and a Tektronix Type 532 oscilloscope as the balance point detector. A balance point to better than 1 ohm in 2,500 ohms could be obtained.

The cell was calibrated with Reagent Grade ammonium sulfate. First a known amount of H_2SO_4 was added to the cell from a weight buret, and the conductivity was measured. Then a known amount of ammonium sulfate was added from the side arm. When the ammonium sulfate had completely dissolved, the conductivity was again measured. Further aliquots of H_2SO_4 were added, and, after mixing, the conductivity of the solution was measured.

A plot of ammonium sulfate concentration versus conductivity was then drawn. The process was repeated twice more for overlapping ranges of concentration to check the reproducibility and to extend the concentration range. The results of overlapping runs were consistent to better than 0.2%. The concentrations of bisulfate ion in the S_4N_4 solutions used in this study were determined by measuring the conductivity of the solution and noting the appropriate bisulfate ion concentrations that would give those conductivities. The calibration plot is shown on Fig. 2.

Cryoscopy.- The freezing point depression method has been shown by Gillespie et al.[18] to be a very accurate method for determining the total concentration of all species in H_2SO_4 solutions. The cryoscopic

segments of the curve. These segments correspond to the temperature regions in which the liquid is in contact with the solid H_2SO_4 and in which the solid is completely melted. An example of such a plot is shown in Fig. 4.

The freezing point of the pure sulfuric acid was found to be 10.409° and was reproducible to ±0.002°. The quartz thermometer used in this study was very accurate for relative temperatures over a small range, but was not as precise for the true temperature. Therefore, the freezing point used to calculate the freezing point depression was the one determined in this study rather than the reported value of 10.371°.

The total number of species in solution was then calculated using the method of Gillespie.[18]

$$\nu = \theta(1+.002\theta)/(6.12\times m^S) - m_d/m^S$$

where ν = total moles of species in solution per mole of solute

θ = freezing point depression (from ideal undissociated value which is 0.245° higher than true freezing point of pure H_2SO_4).

m^S = stoichiometric concentration of solute in mole/kg of solvent.

m_d = total concentration of self-dissociation species (H_2O, H_3O^+, H^+, $H_2S_2O_7$)

m_d Values were determined from the tables in Bass, Gillespie and Robinson[18] from the known concentration of HSO_4^- in the solution.

NMR. - The nmr measurements were all made using a Varian A-60 spectrometer. To calibrate the intensity of the signals it was necessary to

employ an internal standard. Our choice was $[Co(NH_3)_6]_2[SO_4]_3$ which is soluble in H_2SO_4 and which gives one moderately sharp peak. The $[Co(NH_3)_6]_2[SO_4]_3$ was itself calibrated with purified $(NH_4)_2SO_4$ as a check on the accuracy of the method. The results consistently showed less than 2% error.

UV-Visible.- The uv and visible spectroscopy were performed on a Cary 14 spectrophotometer using quartz cells. Various path lengths from 0.1 mm to 5 cm were used in order to maintain reasonable absorption for a wide range of absorbances.

Ionic Polarity.- In order to determine the polarity of the species in solution, an electrolysis cell was employed. The cell, shown in Fig. 5, contained five compartments separated by medium-porosity glass frits. Solvent was placed in the four outer compartments and the solution being studied in the center.

A d.c. potential of 15 volts was applied across the cell for several hours. It was found necessary to have a five-compartment cell because the solution turned cloudy at the electrodes. The cell was kept in a cold water bath to prevent decomposition of the solution. By examining the three central compartments the charge on the species in question could be deduced by observing with uv-visible spectroscopy the direction in which it preferentially migrated.

Results

General.- When S_4N_4 and H_2SO_4 were mixed under vacuum, gas evolution began immediately. This gas was identified by ir and mass spectrometry as pure sulfur dioxide. When the solution was kept at room temperature or below, the sulfur dioxide was evolved slowly, and, after a few hours or a few days, depending on the concentration of S_4N_4, the amount of sulfur dioxide condensed invariably leveled off at 2.00±0.02 moles per mole of S_4N_4. The final ratio was the same regardless of the concentration, as long as there was sufficient H_2SO_4 to react with all the S_4N_4.

When a sample of S_4N_4 enriched in ^{33}S to the extent of 48.6% was treated with sulfuric acid, the resulting sulfur dioxide showed that it came completely from the S_4N_4. The sulfur ratios were determined on a C.E.C. Model 21-620 mass spectrometer, and the results showed no deviation between the $^{33}S/^{32}S$ ratio in S_4N_4 and in resulting sulfur dioxide.

In fairly concentrated solutions (above 0.01 mole/kg of solvent*) in S_4N_4 a fine precipitate was formed. The precipitate was isolated and shown to be sulfamic acid (NH_3SO_3). The determination of the total amount of sulfamic acid precipitated was accomplished by a standard Kjeldahl analysis. Several test runs were done to show that the nitrogen in the sulfamic acid was quantitatively converted to ammonium ions when the acid was heated with concentrated sulfuric acid.

The solutions from which the sulfamic acid precipitate was isolated and analyzed were all prepared as approximately 0.15 molal in S_4N_4.

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*Most concentrations used in this study are molal (moles/kg of solvent) and abbreviated as m.

The results varied from 1.40 to 1.46 NH_3SO_3/S_4N_4 as can be seen on Table I.

Table I

Analysis of NH_3SO_3 by Kjedahl Method

Concentration of S_4N_4 (molal)	NH_3SO_3/S_4N_4	NH_3SO_3/S_4N_4 solubility corrected
0.159	1.40	1.47
0.145	1.45	1.51
0.153	1.40	1.47
0.151	1.41	1.47

Since a precipitate was formed when a solution of greater than 0.01 molal in S_4N_4 was prepared, a limit on the sulfamic acid solubility can be set. The solubility correction of 0.01 molal when applied to the sulfamic acid precipitate shows a very high reproducibility. Thus, within the limits of experimental error the amount of sulfamic acid formed can be set at 1.49±0.02 moles of NH_3SO_3 per mole of S_4N_4.

A small amount of elemental sulfur was always produced in these concentrated solutions. It had no appreciable solubility in sulfuric acid and was collected with the sulfamic acid precipitate. Water washings removed all the sulfamic acid and the weighed residue gave approximately 0.15 moles of sulfur per mole of S_4N_4.

NMR - The nmr spectrum of the solution of reaction products after the sulfamic acid was filtered consisted of a triplet at 6.3 ppm downfield from TMS with a splitting of 53 cycles assignable to ammonium ion. When the spectrum was taken shortly after the reaction had begun a very broad triplet could be seen. The broadening was due to the presence of the paramagnetic species $S_2N_2^+$ in solution. As the radical

decomposed the nmr signal sharpened considerably until it had a width at half height of approximately 4 cps, which is almost as sharp as the ammonium ion signal in pure sulfuric acid.

The intensity of the signal was determined by using $[Co(NH_3)_6]_2(SO_4)_3$ as an internal standard. The $Co(NH_3)_6^{3+}$ gives a single absorption at 3.5 ppm with a halfwidth of 10 cps. Eight separate integrations were taken of each peak and the average of the ammonium ion peak integrations were compared to those for the known concentration of $Co(NH_3)_6^{3+}$.

The ammonium ion concentrations determined by this method showed a rather large variation between consecutive reactions. The results are tabulated on Table II.

Table II

Analysis of NH_4^+ by nmr

Concentrations S_4N_4(m)	NH_4^+/S_4N_4
0.1434	1.20
0.1512	1.32
0.1530	1.56
0.159	1.45
0.170	1.50
0.333	1.43

There appears to be no trend in the data, and the wide variations in the results cannot be attributed to experimental error, which is approximately ±5%.

The fact that there is a reasonably large variation in the results between runs must be attributed to a general non-reproducibility of the reaction stoichiometry. There are probably two decomposition reactions taking place simultaneously, and variations in the rate of each reaction

can cause measurable shifts in the concentrations of the species being measured.

Conductivity and Cryoscopy.- Conductivity measurements were performed on solutions of various concentrations ranging from 0.012 m to 0.16 m in S_4N_4. For solutions less than 0.02 m the number of moles of HSO_4^- in solution per mole of S_4N_4 added ranged from 0.94 to 1.00. At higher concentrations the relative yield of HSO_4^- decreased quite markedly. At the highest concentration the mole ratio was as low as 0.52, with intermediate values showing a consistent trend in the HSO_4^- in solution.

These HSO_4^-/S_4N_4 ratios can be shifted by simply diluting the solution with sulfuric acid. By dilution from 0.15 m to 0.036 m the HSO_4^-/S_4N_4 ratio was shifted from 0.527 to 0.916. This confirmed the previous observations for reactions in dilute solutions.

For many of the above-mentioned solutions cryoscopic and conductivity measurements were performed simultaneously. The absolute change upon dilution was much larger for the total number of species than for bisulfate. They both have higher relative yields per S_4N_4 at lower concentrations, but the different extent in their variations can rule out a simple ionic association as being the major factor. Over the sixfold change in concentration, the total number of species in solution changed from approximately 4.3 to 5.1. At intermediate concentrations a consistent progression was observed, as shown by the data in the third column of Table III.

Table III

Conductivity and Cryoscopy Results

Concentration S_4N_4 (molal)	HSO_4^+/S_4N_4	Total number of species per S_4N_4
0.1434	0.533	4.38
0.0482	0.782	4.85
0.1512	0.527	4.33
0.0501	0.744	4.94
0.0260	0.916	5.10
0.1530	0.529	4.38
0.0519	0.738	4.97
0.0257	0.870	5.20

At high concentrations the results are very consistent, but there is some scatter upon successive dilutions. At these low concentrations the percentage error increases, which could account for some of the divergence. However, the overall decreases at higher concentrations cannot be simply explained.

The HSO_4^-/S_4N_4 ratio of about 0.5 is considerably smaller than the NH_4^+/S_4N_4 ratio of approximately 1.4. Clearly an additional anion must be present in solution to balance the charge of the ammonium ion, not to mention any additional positively charged species which might also be present.

This anion must be the conjugate base of an acid as strong as, if not stronger than, H_2SO_4. The only probable one, noting the stoichiometric restrictions, is $HS_2O_7^-$, the conjugate base of disulfuric acid ($H_2S_2O_7$). If $HS_2O_7^-$ were present, it would exist in equilibrium with HSO_4^-, and only upon addition of water to the solution would it show

any special reactivity which would allow its presence to be detected. This reaction would be:

$$HS_2O_7^+ + H_2O \rightleftharpoons H_2SO_4 + HSO_4^-$$

The addition of water should increase the HSO_4^- concentration but should have no effect on the total number of solute species to the extent that the reaction proceeded to the right. Thus, by determining the melting point of the solution upon successive additions of small increments of water, a cryoscopic titration could be performed. Provided the reaction proceeded quantitatively according to the above expression, a break point would be expected when added H_2O = initial $HS_2O_7^-$, and the melting point would immediately fall sharply with successive water increments. If no $HS_2O_7^-$ were present the freezing point would be expected to drop sharply upon the first water addition.

When water (in the form of concentrated H_2SO_4) was added to the solutions of S_4N_4 in H_2SO_4, a rather unexpected result was obtained. The melting point of the solution rose rather sharply, leveled off at a maximum and then decreased upon further addition of water. A plot of m.p. vs added H_2O for one of these titrations is shown on Fig. 6. The maximum m.p. in this case corresponded to 1.3 moles of water added per mole of S_4N_4 initially used. The solution used for the titration was 10.67 M (moles of water per liter of solution).

The shape of the titration curve could however be explained by the presence of disulfuric acid ($H_2S_2O_7$) in equilibrium with its conjugate base according to equilibrium expression (A).[18]

$$(A) \quad H_2S_2O_7 \rightleftharpoons H^+ + HS_2O_7^-$$

If a significant amount of $H_2S_2O_7$ was present the melting point would

rise upon adding water. This would be due to the net decrease in species as disulfuric acid and water reacted to form solvent sulfuric acid.

Assuming that there is no ion pairing in these solutions, and using the measured values of the HSO_4^- concentration at two different dilutions it is possible to calculate the concentrations of all the self-dissociation species. The four independent equilibria[18] are given below:

(A) $H_2S_2O_7 \rightleftharpoons H^+ + HS_2O_7^-$

(B) $H_2O + H_2SO_4 \rightleftharpoons H_3O^+ + HSO_4^-$

(C) $2H_2SO_4 \rightleftharpoons H_3O^+ + HS_2O_7^-$

(D) $H_2SO_4 \rightleftharpoons H^+ + HSO_4^+$

Provided the equilibrium constants are known, the concentration of each species can be determined. It is then possible to calculate the net change in each of these species upon subsequent additions of water and thus determine what the theoretical titration curve should look like. There are only two assumptions made in these calculations. First, that there is no ion pairing and second, that only the four equilibria (A, B, C, and D) are involved. The concentrations of two species are determined by iterative calculations, and from these values the concentration of every other self dissociation species can be calculated.

On Fig. 7 the experimental points (corrected for the volume change) are plotted. The dotted line is the titration curve expected using the equilibrium constant values of Gillespie et al.[21] (which are $K_A = 1.4 \times 10^{-2}$ mole/kg, $K_B = 1$ mole/kg, $K_C = 3.5 \times 10^{-5}$ mole^2/kg^2, $K_D = 1.7 \times 10^{-4}$ mole^2/kg^2). When these constants are used in the

calculations there is a very poor fit to the experimental points. In addition, the calculated value of the disulfate ion concentration is so low that still another anion would be needed to maintain charge neutrality.

If indeed there is no ion pairing, then the equilibrium constants must be considerably different for these complex solutions. Judicious choice of constants would allow several close approximations to the titration curve. If however, an additional constraint is placed such that the remaining species left in solution are all of unit positive charge then the fit gives essentially one solution. Slight shifts in the constants that give equally good fits to the curve also give almost identical concentrations of each species.

An example of the calculated change in melting point upon addition of water is shown by the solid line in Fig. 7. This represents the best fit obtained to the experimental points. However, it was found necessary to change the constant for equilibrium B by a considerable amount in order to obtain this result. A value of $K_B = 0.004$ moles/kg was used instead of the literature value of 1 mole/kg. The other constants were $K_A = 3 \times 10^{-3}$, $K_C = 1 \times 10^{-5}$, and $K_D = 3.5 \times 10^{-5}$.

If limitations are set on the deviations from the accepted values of the constants then a close approximation to the titration curve becomes impossible. An example of an attempt, trying to fit the experimental values by this means is shown on Fig. 8 as the dashed line. The constants used for this calculation were $K_A = 7 \times 10^{-3}$, $K_B = 0.2$, $K_C = 2 \times 10^{-4}$, $K_D = 1.7 \times 10^{-4}$.

In order to determine the validity of the method of calculating the titration curve a check was made. Disodium hydrogen pyrophosphate

($Na_2H_2P_2O_7$) has been shown[22] to react with sulfuric acid according the expression:

$$Na_2H_2P_2O_7 + 5H_2SO_4 \rightarrow 2Na^+ + 2P(OH)_4^+ + 3HSO_4^- + HS_2O_7^-$$

Concentrations high enough to maintain what was felt to be a comparable $HS_2O_7^-$ concentration caused a very large and not easily manageable freezing point depression. It was therefore decided to use sodium metaphosphate trimer $(NaPO_3)_3$ which was shown in this study to have an equivalent reaction.

$$NaPO_3 + 3H_2SO_4 \rightarrow Na^+ + P(OH)_4^+ + HSO_4^- + HS_2O_7^-$$

At 0.1415 molal in $NaPO_3$ the HSO_4^- concentration and the total moles per mole of solute were 0.982 and 3.8 respectively. Thus the reaction does proceed essentially as written above.

The solution of sodium metaphosphate was treated in the same manner as the solutions of S_4N_4 in sulfuric acid. A cryoscopic titration was performed using the same water solution (10.67 M) and the resulting titration curve is shown on Fig. 8. The points are the experimental data. If the initial slope and the final slope are extrapolated they intercept at 0.96 waters per sodium metaphosphate.

Employing a similar calculation technique as before a theoretical curve can be determined. The heavy line in Fig. 8 represents such a curve assuming no ion pairing and using the accepted equilibrium constants. The theoretical curve shows an initial increase while the experimental show a slight decrease. However, the extrapolation of the initial and final slopes does give the same value of 0.96 waters per sodium metaphosphate.

The stability of $P(OH)_4^+$ in sulfuric acid is not known. Its dissociation might be dependent upon the acid strength of the solution and thus it might be dissociated as water is added. In this manner the intercept would be the same but both the slopes would be lower, as is observed. No attempt was made to approximate the experimental fit more closely. The use of Gillespie's constants showed a reasonable approximation considering the uncertain nature of the solution. This fact points to the necessity of attributing many of the observed effects in the S_4N_4 solutions to ion pairing or a similar type of ion association.

The major problem with calculating ion pairing effects is that the known species show no tendency to ion pair at these concentrations. A solution of ammonium bisulfate of comparable concentration was prepared from ammonium sulfate in sulfuric acid. Cryoscopy showed that there were 3.99 total species produced per mole of ammonium sulfate. The conductivity is calibrated with ammonium sulfate which presupposes the complete dissociation in the concentration range of interest. Thus, to the limits of the techniques employed there was no ion pairing by the ammonium and bisulfate ions.

The Kjeldahl analysis for sulfamic acid (1.49 NH_3SO_3/S_4N_4) and the nmr analysis (1.2-1.6 NH_4^+/S_4N_4) for ammonium ion can account for between 2.7 to 3.1 nitrogens per S_4N_4. Thus there is still 0.9 to 1.3 moles of nitrogen per mole of S_4N_4 as yet unaccounted for. When these analyses were performed the radical $S_2N_2^+$ produced by this reaction had decayed essentially to zero so the nitrogen must be in solution in a different form. In order to obtain some information about these species some spectroscopic investigations were initiated.

UV-Visible Spectroscopy.- A freshly-made solution of S_4N_4 in sulfuric acid is bright canary-yellow; after about an hour the color fades to a pale orange. It was felt that a study of the uv-visible absorption might help to identify the various species in solution.

Immediately after mixing the reactants, a rather complex spectrum is observed. There is a broad peak at 4560 Å, a multiplet centered around 4000 Å, an intense absorption at 3260 Å, and an extremely intense absorption at 2140 Å. The peaks at 4560 Å and 3260 Å both decay rapidly according to first-order rate laws. Their respective half lives are 22 minutes and 40 minutes. As the peak at 3260 Å decays, a shoulder at 3510 Å becomes apparent, and the latter peak decays by first-order kinetics with a half-life of 48 hours. These absorptions always show first-order decay; however, the half-times vary with the reaction condition. When the sample is not continuously evacuated to remove all evolved sulfur dioxide, the half-lives are those reported. However, when evacuated, the bands decay much more rapidly. It is hard to observe the peaks at 3260 Å and 4560 Å after extensive pumping because of their more rapid decay rates. After two days of pumping, the peak at 3510 Å is completely gone, whereas an unevacuated sample had a two-day half-life.

The effect of sulfur dioxide in the reactions has not been investigated, and the exact nature of the transient species corresponding to the absorption bands has not been determined. The absorptions at 3260 Å and 4560 Å could very well be due to S_4N_4 or an adduct of S_4N_4 with H_2SO_4 where the S_4N_4 ring was still intact. S_4N_4 in an inert solvent like CCl_4 or decane shows one very intense absorption at

2560 Å, but it might shift considerably in a highly polar solvent such as sulfuric acid.

The spectrum remaining after four days of pumping on a sample is shown in Fig. 9. The multiplet in the visible region and the single peak in the uv region always appear together in the same ratio and show no further change on standing. Assuming that the absorption corresponds to one species per S_4N_4 the maximum extinction coefficient in the visible is 58 and in the uv 27,000 l mole^{-1} cm^{-1}.

The stable spectrum did not correspond to any reported species. However, the appearance of the splitting in the visible spectrum is quite unexpected in such a highly polar and highly hydrogen-bonding solvent. The greater orientation of solvent molecules in highly polar solvents tends to obscure vibrational fine structure.[31] However, the spectrum of nitrous acid in aqueous sulfuric acid, shown in Fig. 10, shows some resemblances. The multiplet and the intense singlet have been assigned to HONO and NO^+ respectively. By adjusting the sulfuric acid concentration, the relative concentrations of these two species can be altered by shifting the following equilibrium:[23]

$$HONO + H^+ \rightleftharpoons NO^+ + H_2O$$

At sulfuric acid concentrations above 70%, essentially all of the nitrous acid is converted to NO^+.

The nature of these species might be accertainable by comparison of the visible spectrum to that of HONO. The fact that they both show the same type of splitting in a solvent which has such a high dielectric strength already makes them exceptional. The splitting between the two lowest-energy peaks in HONO is 1015 cm^{-1}. Herzberg[24]

has pointed out that this frequency corresponds closely to the lowest-energy vibration of free NO at 958 cm^{-1}. Thus he decided that HONO acts as a pseudo diatomic molecule in its vibrational motion.

The splitting between the two lowest-energy peaks in the solution under study is 580 cm^{-1}. This corresponds rather well with the lowest frequency vibration of free NS. NS is not a stable molecule, but the lowest-energy vibrational splitting determined from its emission spectrum is 610 cm^{-1}.[25] This close similarity suggests that the species under study contains an NS terminal group. In which case what is observed is the vibrational motion of a pseudo diatomic NS.

If the reaction of S_4N_4 with sulfuric acid produced sulfur analogues of HONO and NO^+ such as HONS and NS^+ they would be expected to show a similar shift upon changing the sulfuric acid concentration. When the sulfuric acid strength was varied from 95% sulfuric acid to 15% fuming sulfuric acid there was only a 5% shift in the relative absorptions. Over this range both the water activity and hydrogen ion activity change by several orders of magnitude[26] and the relative intensities would be expected to reflect this change. The shift that we do see, slightly favoring the visible species in the more aqueous solvent, could be caused by a change in the extinction coefficient when we alter the properties of the solvent.

To check if a different equilibrium was involved in this system, just the bisulfate concentration was altered. When a twenty-fold excess of ammonium sulfate was added to the solution in 100% sulfuric acid, the ratio of the two absorptions changed only by a few percent. This result again could be accounted for by a change in the nature of the solvent.

Upon adjusting the temperature of the cell compartment from 5° to 40°, a change in the peak intensities would be observed if the peaks were due to two species in equilibrium and they had a non-zero heat of reaction. In this case there was essentially no shift in the relative peak heights over the entire temperature range. Thus, the two absorptions at 2140 Å and 4000 Å appear to be due to a single species in solution.

To check on the possibility of a single sulfur-nitrogen species having two such absorptions, the gas-phase electronic spectrum of NSCl was obtained. Solid $S_3N_3Cl_3$ exists in equilibrium with the gaseous monomer NSCl. $S_3N_3Cl_3$ was prepared according to the method of Schröder and Glemser by the reaction of Cl_2 with S_4N_4. The product was recrystallized twice from CCl_4 and gave a sharp melting point at 89° (literature 91°,[28] 98°[29]). A sample was transferred to a 2-cm quartz cell equipped with a ball joint. The cell was attached to a standard vacuum line, evacuated, and then sealed off. At room temperature (23°) the spectrum consisted of only one very strong peak at 2140 Å. The intensity of the absorption increased with time until the equilibrium vapor pressure was reached. By this time the peak was well off scale on the Cary 14 spectrophotometer. At 5° its absorbance stabilized at 2.33 and its extinction coefficient was calculated to be 11,300. As the temperature was raised, many sharp, weak absorptions appeared in the range 3600-4900 Å. At 60° at least 50 distinct absorptions with recurrent splittings could be seen (see appendix).

A gas phase sample might be expected to show many more vibrational splittings than a species in solution.[31] The fact that the solution

spectrum and NSCl gas both exhibit an intense absorption peak at the same wavelength in the uv and a complex multiplet in the visible supports the idea that one species containing an NS terminal group could account for both. The exact formulation cannot of course, be determined by this analogy.

Ionic Polarity.- The solution was placed in the central compartment of a five-compartment transference cell for a determination of the polarity of the species. Fifteen volts d.c. was applied for two hours with the cell in a 10° bath. The solutions from each compartment were then examined by uv-visible spectroscopy. The species was found to migrate to the cathode (negative electrode), and the relative intensities of the absorptions remained the same. This result established that the species is in fact positively charged, as would be expected in such a solution.

Isolation Attempts. - Several attempts were made to isolate the cation from solution. When the sulfuric acid concentration is lowered to 95% or less the species slowly decomposes. When the solution is mixed with excess water, hydrogen sulfide is evolved and sulfur is precipitated. Above 40° the species starts to decompose so that evaporation of the solvent (boiling point 310°) was infeasible.

Attempts were made to precipitate the species as a salt by saturating the solution with salts of suitable anions. Very few stable anions exist in 100% sulfuric acid at high concentrations. Among the few that do are: HSO_4^-, $HS_2O_7^-$, and $B(HSO_4)_4^-$ (the last formed from H_3BO_3 in sulfuric acid[30]). Solutions saturated with salts of each of these ions were added to concentrated S_4N_4 solutions, but in no case was any salt precipitated.

Attempts were made to precipitate the species by lowering the dielectric strength of the solvent. Sulfuryl chloride ($SOCl_2$) and nitromethane (CH_3NO_2) are both non-electrolytes, but up to their solubility limits there was no sign of precipitation (CH_3NO_2 does not ionize in sulfuric acid but it does react very slowly).

Even ion exchange chromatography was tried. When Dowex 50 resin is washed several times with sulfuric acid, the water is exchanged and the resin contracts. If the resin in the sulfuric acid form is employed it shows no selectivity for any of the species and the solution passes straight through the column.

The rapid decomposition of the reaction product when excess water was added indicated that it might be reactive enough to form derivatives in the sulfuric acid solution. When benzene was mixed with concentrated solutions from the reaction of S_4N_4 in sulfuric acid a red-violet solution was formed in the sulfuric acid phase. Upon the slow addition of water or methanol to the cooled solution, there was no decomposition to hydrogen sulfide, the color disappeared and a precipitate was formed.

After the precipitate was washed and vacuum dried it became obvious that it was a mixture of several species. Successive washings with hot dichloromethane removed most of one or more components, however, all the nitrogen containing species were insoluble. It was not possible to purify the remaining solid because it was soluble only in sulfuric acid (giving a green solution). Successive precipitations from sulfuric acid left a solid which melted at approximately 280° and from elemental analysis, contained only 1.3% nitrogen.

Similar reactions yielding highly colored solutions were observed with toluene, chloro-benzene, and para-xylene. As in the case with the benzene products, isolation attempts were unsuccessful. Thus it appears that the unknown species in solution is a very reactive electrophile, but its identification has been shown to be very difficult. Isolation of a pure derivative would help to prove the identity of this unknown product. Until then all procedures to establish its identity and concentration must be made by deduction and indirect measurements.

Discussion

A compilation of the analytical data is rather confusing. The only invariant quantity was the amount of sulfur dioxide evolved (2 per S_4N_4). The amount of NH_3SO_3 produced (1.5 per S_4N_4) was determined over a rather limited concentration range. There is no simple explanation for the large changes in the bisulfate concentration upon dilution and the total number of species. The changes as well as the shape of the cryoscopic titration curve can be explained, but it requires a complex re-evaluation of equilibrium constants and/or extensive ion interactions.

The uv spectrum shows that there is a species in solution at high concentration. If, for example, there were only 0.5 of this species produced per S_4N_4, the extinction coefficient would be 54,000 - a value which is almost unreasonably high. This species surely contains sulfur and nitrogen; it is positively charged, and it must be a major product of the reaction. If the results of the curve-fitting are used, a reasonable reaction expression can be written.

$$S_4N_4 + 6.8\ H_2SO_4 \rightarrow 2\ SO_2 + 1.5\ NH_3SO_3 + 1.5\ NH_4^+ + 1.6\ HS_2O_7^- + 0.4\ HSO_4^- + 0.3\ H_2S_2O_7 + 0.1\ S + 0.5\ S_6N_2O_8H^+$$

This equation takes into account the results of the Kjeldahl analysis (sulfamic acid), and average of the nmr results (ammonium ion), the cryoscopy determinations (total species in solution) as well as the shape of the cryoscopic titration curve. However, there is no real significance to the consititution of this last species.

If ion pairing is allowed between the unknown species in solution and HSO_4^- and $HS_2O_7^-$ the complexity increases markedly. For every diffe-

rent ion-pairing constant attempted a different balanced equation would have to be written, each having no greater validity than the others.

The fact that this reaction is so complex as well as somewhat irreproducible makes a complete solution to this problem very difficult. It was originally hoped that via these numerous analyses a consistent remainder from the materials balance could be obtained which would correlate with the uv-visible spectrum. In this manner a definitive balanced equation could be written.

This goal obviously has not been attained. The nature of the undetermined species with the enormous extinction coefficient may prove to be very interesting. It is stable in sulfuric acid for many months without decomposition. If its stability requires a sulfuric acid medium, then all reactions involving this species will have to be in that solution.

In conclusion, it would seem that a prerequisite to completely solving this reaction is the determination of the identity of this unknown species. Once that is achieved, then some reasonable ion pairing constants can be determined and the reaction can be balanced. Until then the number of variables remains too large to permit determination of the one exact solution.

Appendix

The visible spectrum of NSCl is shown on Fig. 11. The spectrum was taken at 60° in a 2.05 cm quartz cell. The wavelengths of the discernible maxima in the region 3750 Å to 4900 Å are given on Table IV. All wavelengths were calibrated with a mercury lamp source. The peaks tend to come in repeating groupings over the entire range, with recurrent splittings and intensity patterns. Using the previously determined vapor pressure of NSCl[29] the maximum extinction coefficient was calculated to be approximately 10. At 80° several additional low intensity absorptions at higher wavelengths can be observed. However, they are accompanied by decomposition which can be seen as a very broad absorption in the visible region.

TABLE IV

Wavelength (Å) of the Absorption Maxima of NSCl (g) at 60°

4863	4217
4814	4205
4800	4193
	4181
4754	4170
4708	4160
	4134
4665	4100
4637	
4624	4079
	4066
4594	4056
4580	4047
4537	4034
	4021
4497	4011
4456	
4435	3999
4415	3979
	3946
4395	3915
4383	
4377	3898
4356	3885
4343	3867
4305	3836
	3806
4270	
4255	3777
4233	3749

Acknowledgements

I would like to thank Professor William L. Jolly for his constant guidance and interest in this study and for many helpful suggestions. I am indebted to Jim Chang for his great assistance on many facets of this problem. I would also like to acknowledge the entire Jolly group for their suggestions and for having been a sounding board for each new interpretation that was proposed.

My foremost thanks go to my wife Jo Jo, who not only did most of the typing but also kept me from getting discouraged throughout the final phases of this work.

This work was done under the auspices of the United States Atomic Energy Commission.

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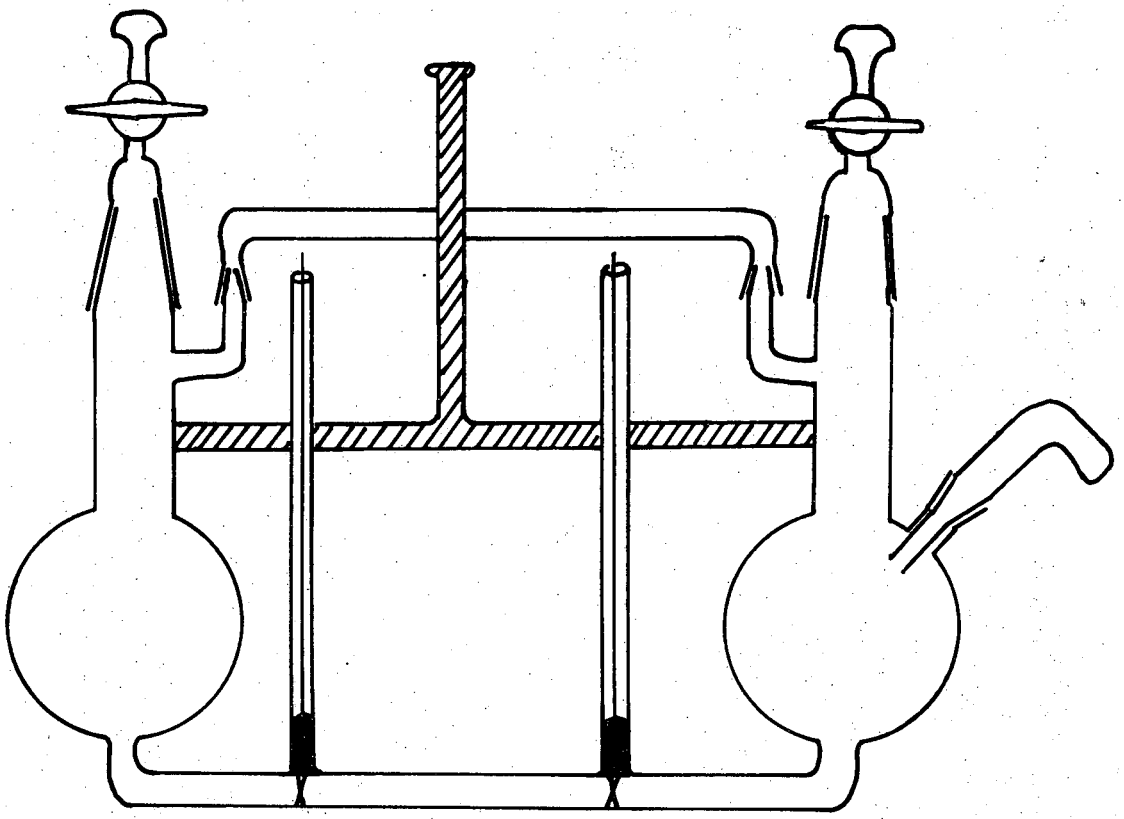

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Fig. 1. Conductivity cell

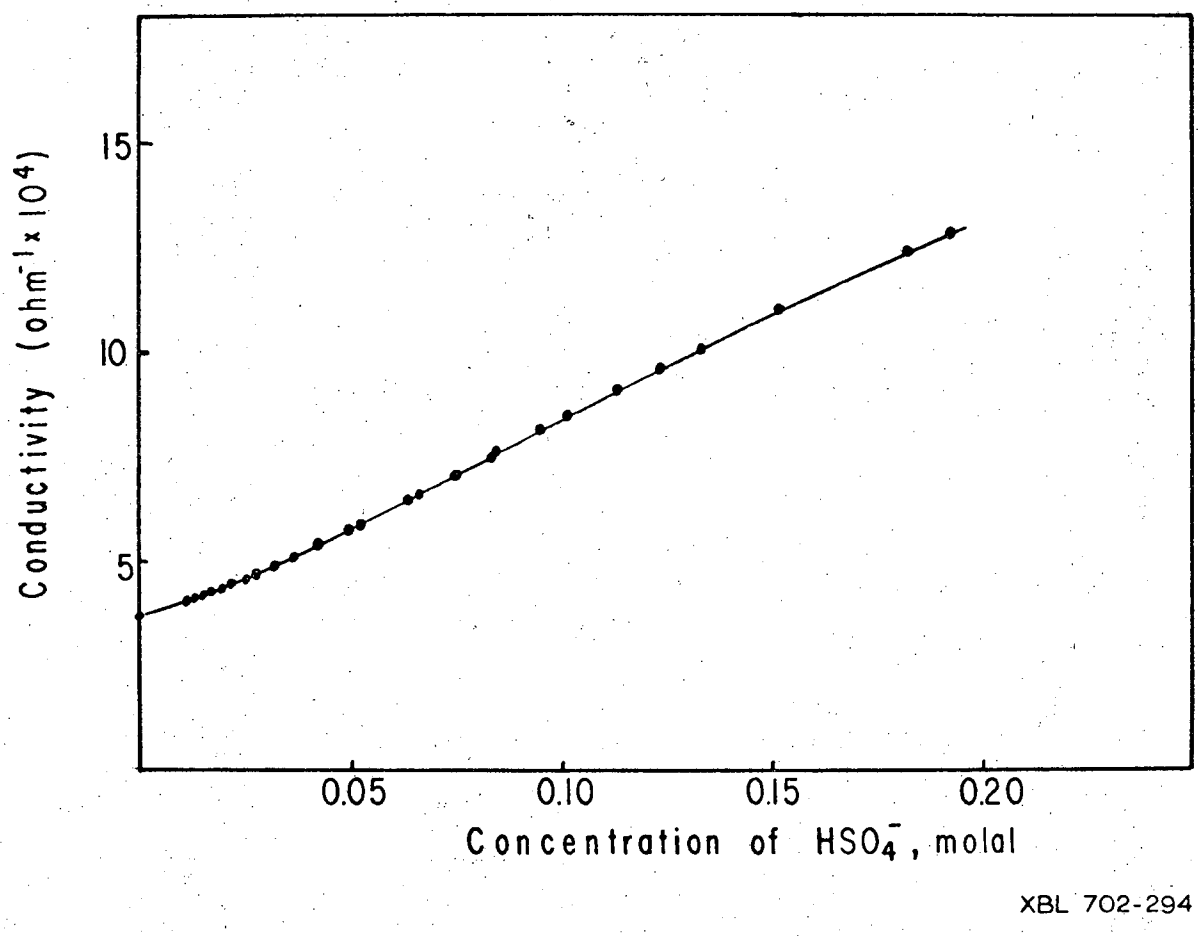

Fig. 2. Ammonium sulfate conductivity calibration

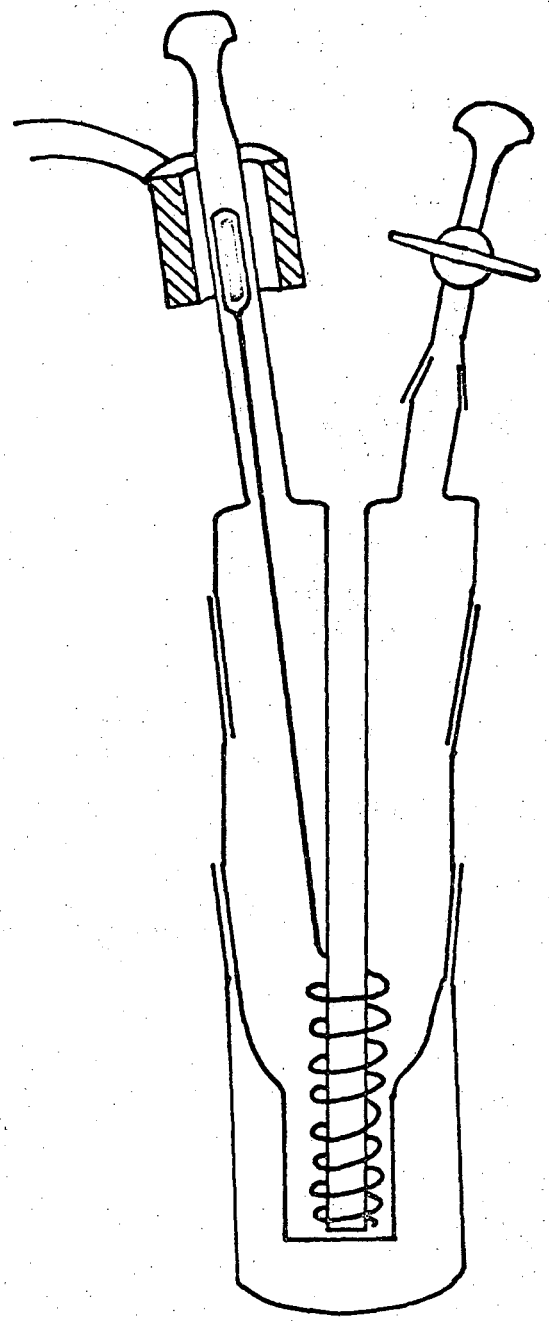

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Fig. 3. Cryoscopy apparatus

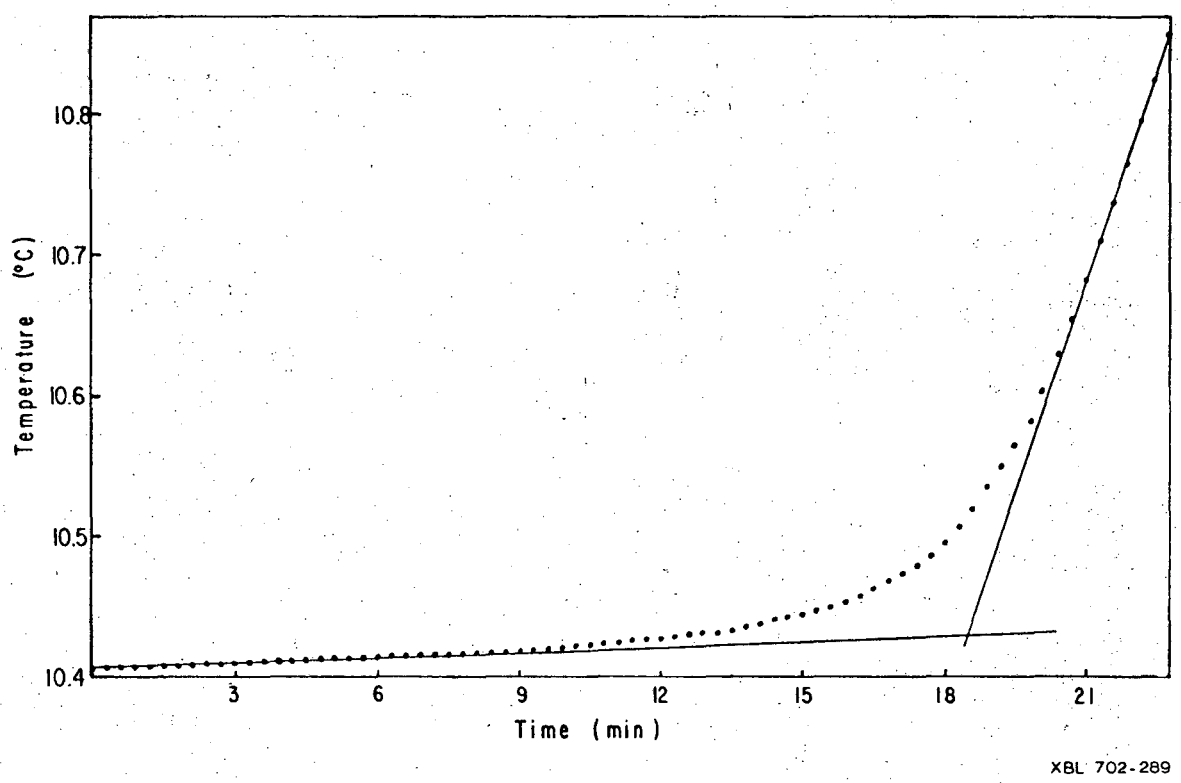

Fig. 4. Melting point curve of sulfuric acid

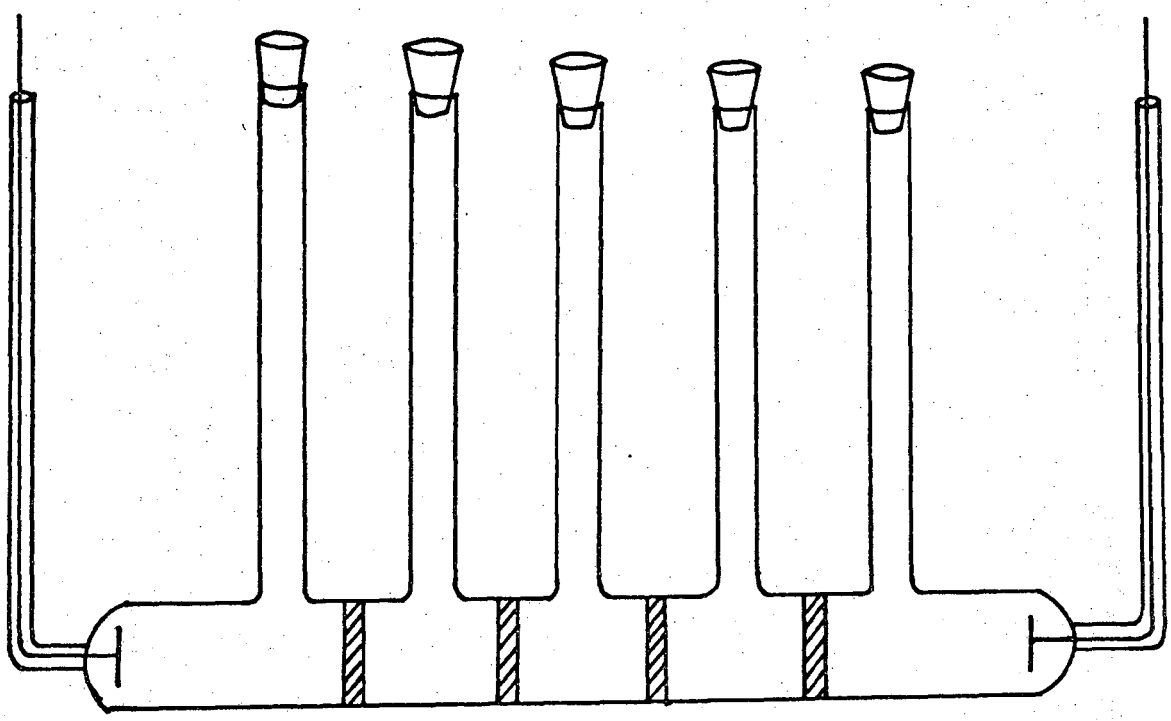

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Fig. 5. Electrolysis cell

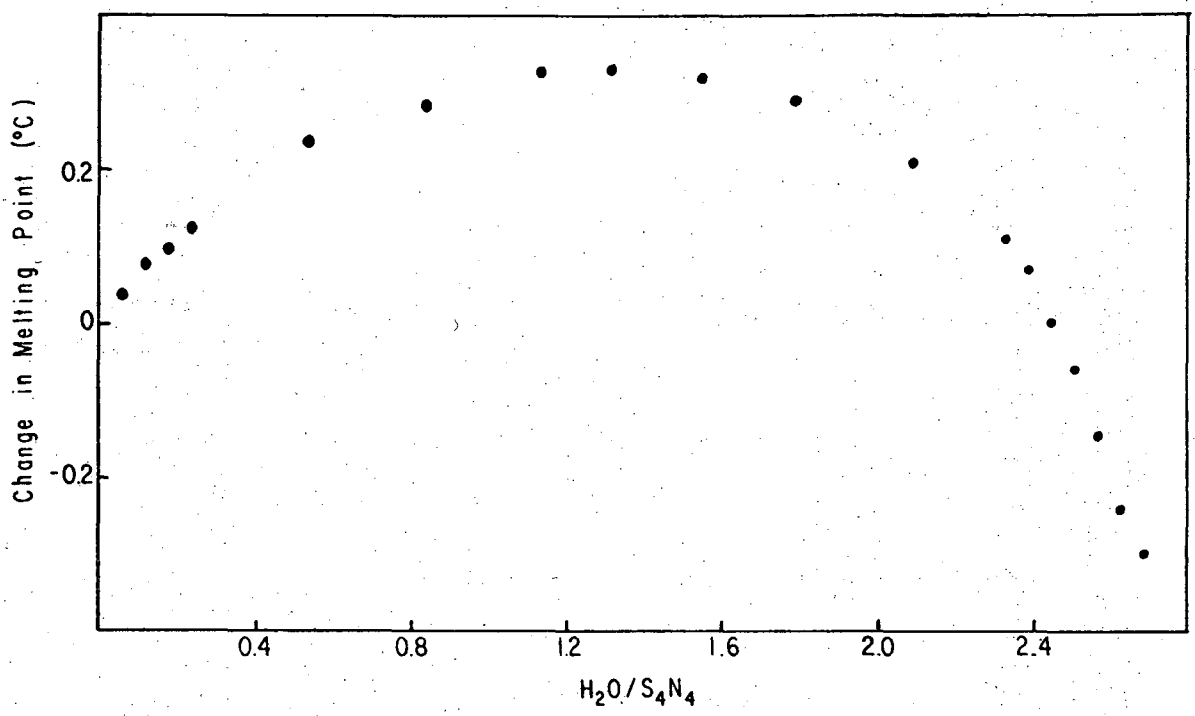

Fig. 6. Cryoscopic titration: water added to 0.15m S_4N_4 in H_2SO_4

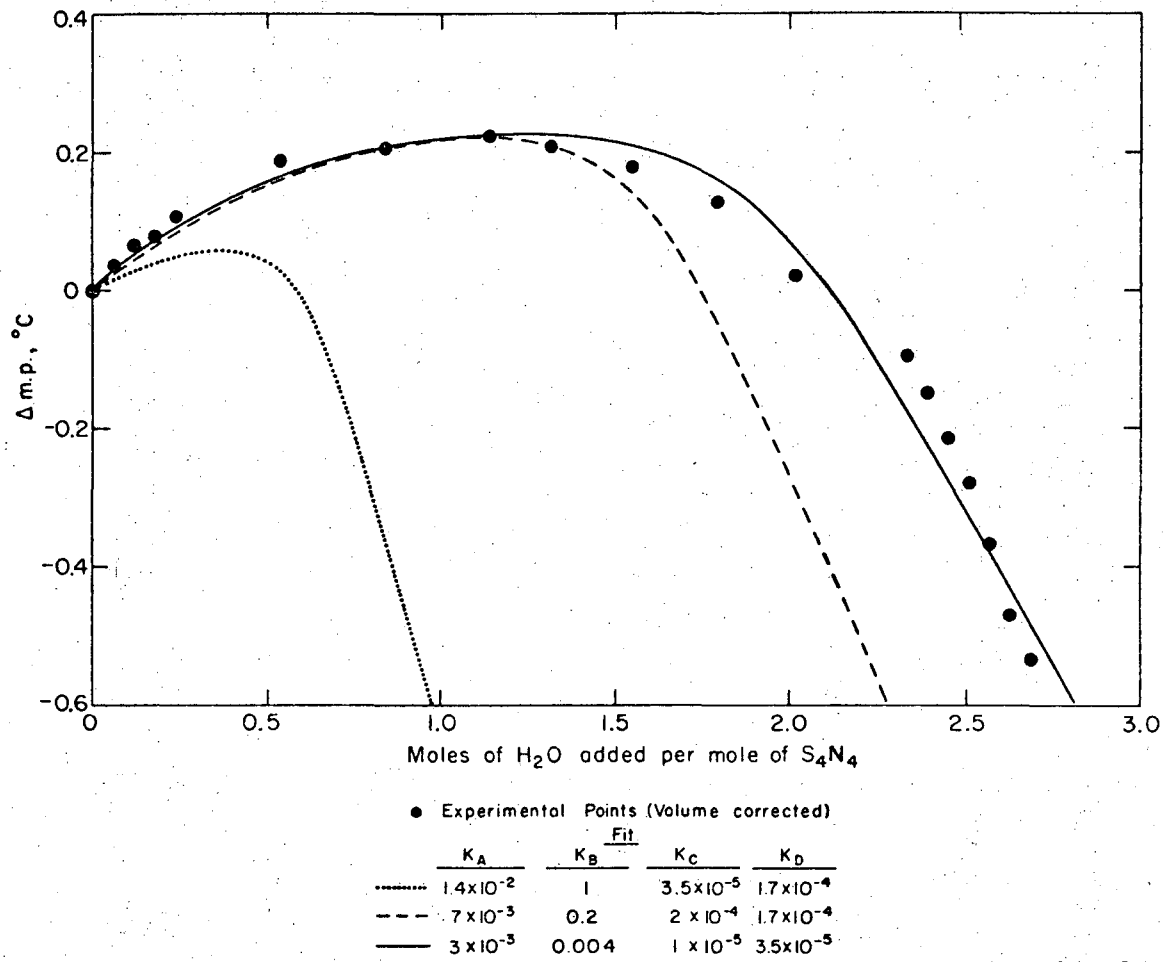

Fig. 7. Cryoscopic titration: 0.15m S_4N_4 in H_2SO_4

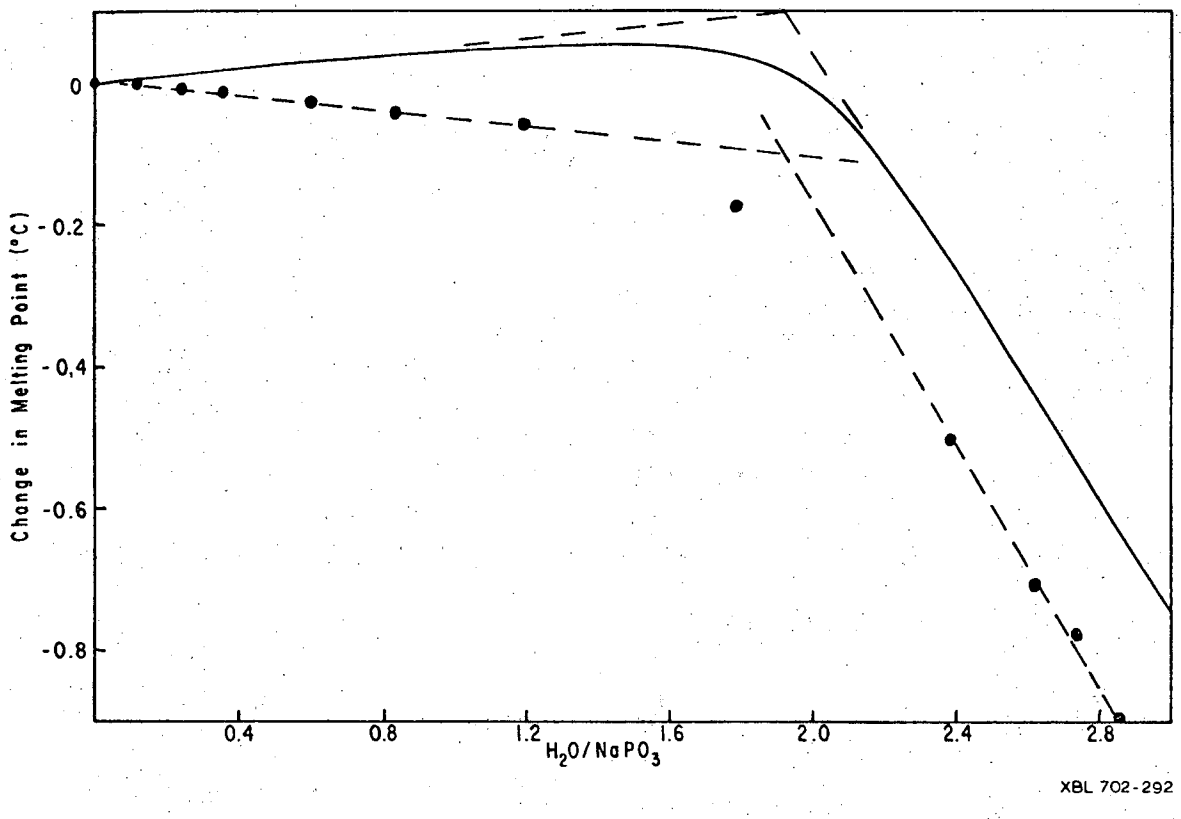

Fig. 8. Cryoscopic titration: water added to 0.14m $NaPO_3$ in H_2SO_4

· Experimental points

——— Fit using $K_A = 1.4\times10^{-2}$, $K_B = 1$, $K_C = 3.5\times10^{-5}$, $K_D = 1.7\times10^{-4}$

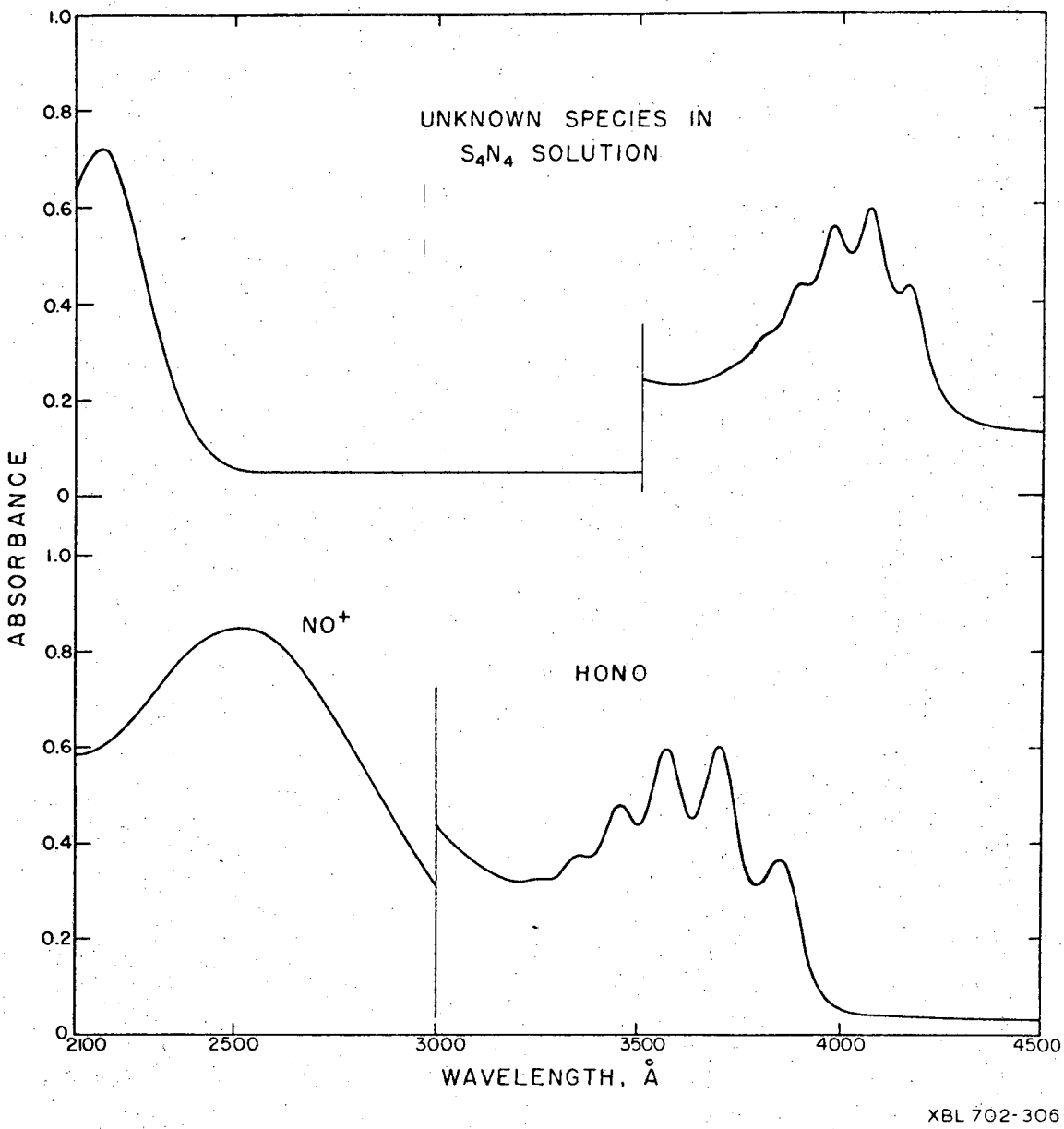

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Fig. 9. Upper: 2×10^{-3} M S_4N_4 in 100% H_2SO_4, uv spectrum taken in 0.013 cm cell, visible spectrum taken in 5.00 cm cell
Lower: 4×10^{-3} M $NaNO_2$ in H_2SO_4, uv spectrum (NO^+) taken in 0.050 cm cell in 71% H_2SO_4, visible spectrum (HONO) taken in 5.00 cm cell in 44% H_2SO_4

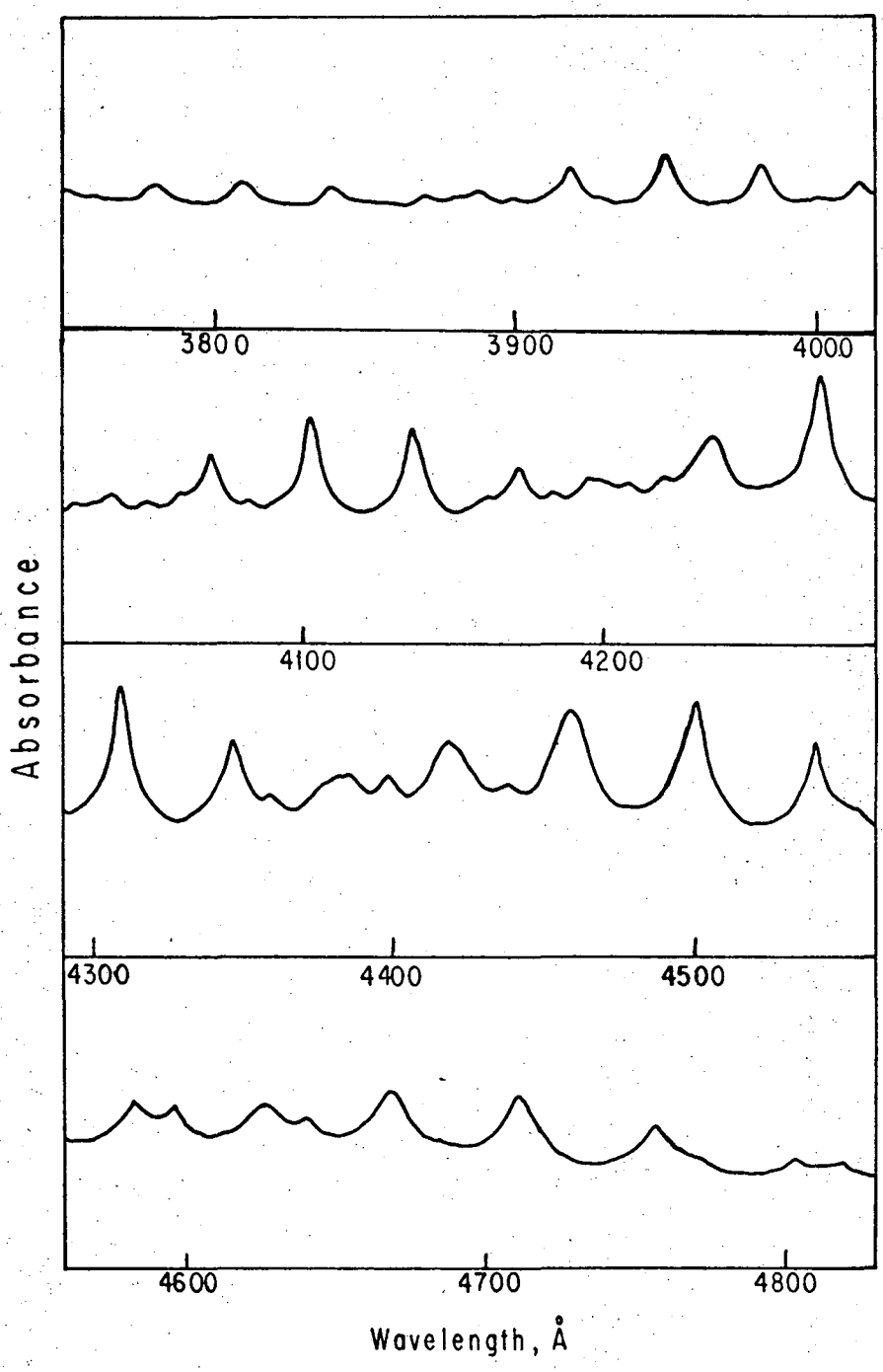

Fig. 10. Visible absorption spectrum of NSCl(g). Spacing between horizontal lines corresponds to 0.35 absorbance units.

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