POLYATOMIC CATIONS OF SULPHUR, SELENIUM AND TELLURIUM

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By

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SCOPE AND CONTENTS:

The preparation of compounds containing polyatomic cations of sulphur, selenium and tellurium has been investigated by using oxidising agents such as AsF_5, SbF_5, $S_2O_6F_2$ and SO_3. New compounds, containing polyatomic cations Se_8^{2+}, Se_4^{2+}, Te_{3n}^{n+}, Te_4^{2+} Te_n^{n+}, S_{16}^{2+}, S_8^{2+} and S_4^{2+}, and anions of very strong acids such as $Sb_2F_{11}^-$ and AsF_6^- were isolated and characterised by a combination of the stoichiometry of the preparation reactions, UV-visible spectrophotometry, Infrared and Raman spectroscopy and magnetic susceptibility measurements.

Solutions of sulphur in various concentrations of oleum were investigated in detail by UV-visible spectrophotometry and e.s.r. spectroscopy. Evidence is presented for the formation of the sulphur cations S_{16}^{2+}, S_8^{2+} and S_4^{2+} in these media, and for the presence of low concentrations of the radical cations S_8^+ and S_4^+.

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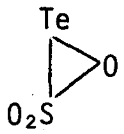
CHAPTER I

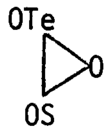
Introduction

(a) Historical

Coloured solutions of sulphur, selenium and tellurium have been known for a considerable time. The first report of the reaction of tellurium with concentrated sulphuric acid to produce a red solution was given by Professor Klaproth (1) in a paper titled "A Memoir on a New Metal Called Tellurium", read at a public sitting of the Academy of Science at Berlin in 1798. He pointed out that when tellurium is dissolved in concentrated sulphuric acid, a beautiful crimson red colour is formed. This colour disappears on heating and a white oxide of tellurium is deposited. Bucholz (2) in 1804 discovered that sulphur reacts with SO_3 to give brown, greenish-blue, and blue solutions. Magnus (3) and Fischer (4) in 1828 observed that selenium dissolves in fuming sulphuric acid to give a green solution which deposits elemental selenium when poured onto water. Fischer further observed the evolution of SO_2 and pointed out that selenium must have been oxidised. Weber (5) in his investigation of the reactions of sulphur, selenium and tellurium with SO_3, isolated blue, green and red compounds which analysed as S_2O_3, $SeSO_3$ and $TeSO_3$, respectively. Divers and Shimose (6) agreed with Weber's findings and further observed that on heating the green $SeSO_3$ a bright yellow amorphous mass is obtained which they considered as an allotropic form of the green material. Divers and Shimose also obtained a red solution by passing H_2Te through a saturated solution of TeO_2 in concentrated H_2SO_4 and on continued passing of H_2Te, an insoluble brown substance was produced, which according to these authors was not elemental tellurium. The authors suggested the following structures for the red and brown materials:



Red



Brown

Moles (7) investigated the green solution of selenium in SO_3 cryoscopically and obtained inconsistent results which he considered in terms of polymerisation of $SeSO_3$ to $(SeSO_3)_x$ in solution. Auerbach (8) attributed the green colour to an unoxidised form of polyatomic radicals. Cameron and Macallan (9) in 1890 reported that selenium readily dissolves in anhydrous selenic acid to give a green solution. By analogy with the green colour of selenium formed in concentrated H_2SO_4, they ascribed the green colour in selenic acid to Se_2O_3. A more recent paper describing the preparation of pure SeO_3 (10) states that selenium reacts with SeO_3 to give a green substance, probably Se_2O_3. Wiberly (11) et al. have suggested the use of the green selenium and red tellurium solutions as a spectrophotometric method of analysis for these elements. They found that strictly controlled heating is necessary for reproducible results.

Investigations of coloured solutions of sulphur have been much more comprehensive than those of the selenium and tellurium analogues. Vogel (12) in 1812 isolated a deep blue liquid, a bluish-green solid, and a brown liquid from the reaction of sulphur with SO_3. He considered these as definite compounds. Similar results were obtained by

Schweigger (13). A few years later, Wach (14) attempted to find the composition of the blue, green and brown solids and discovered that the amount of sulphur which reacted with SO_3 increased in that order. Fischer (15) and Rose (16) supported Vogel's view that the blue liquid contains a definite compound. Stein (17) disagreed with Fischer, Rose and Vogel's point of view and considered the blue colour of the solutions to be due to the presence of finely divided sulphur. Hofmann (18) and Ephraim (19) suggested that the supposed blue compound "S_2O_3" is a colloidal solution of sulphur in SO_3. Vogel and Partington (20) in 1925 investigated in detail the reaction of sulphur with SO_3 to give the blue compound and came to the following conclusions:

(a) Dry sulphur does not react with dry SO_3; a trace of moisture is essential for the reaction.

(b) Weber's formulation of the blue compound as S_2O_3 is correct.

(c) The earlier "colloidal solution" theory is incorrect; the blue material is a definite compound and not a "colloidal solution" of sulphur in SO_3.

These authors also investigated the complex decomposition products obtained when sulphur sesquioxide, "S_2O_3", is heated or reacted with alcohol or water. The products include sulphur, thionic acid, SO_2 and SO_3. A cryoscopic investigation of the blue solution of sulphur in oleum was made by Auerbach (8) who concluded that sulphur is dissolved as S_2 molecules, but later Brayford and Wyatt (21) who also attempted to make cryoscopic measurements, came to the tentative conclusion that sulphur is present in 45% oleum largely as "S_2O_3". The latter authors found however that the solutions are not stable with time. Symons et al. (22, 23) found that sulphur does not increase the conductivity of 65% oleum and hence concluded that it is neither protonated nor oxidised to a radical cation.

Ruff et al. (24) in 1906 reported that a white solid, $SSbF_5$, could be obtained from the reaction of antimony pentafluoride, SbF_5, with sulphur. Aynsely, Peacock and Robinson (25) in 1951 reported that blue, yellow and red solutions were obtained when sulphur, selenium and tellurium respectively dissolved in SbF_5. They obtained solid compounds from these coloured solutions, and formulated these as $S(SbF_5)$, $Se(SbF_5)_2$ and $Te(SbF_5)_5$. Symons et al. (26) in further experiments showed that the species responsible for the blue colour of sulphur in SbF_5 moved to the cathode on electrolysis. This indicated that contrary to their earlier conclusions, the blue colour is in fact due to a cationic species and therefore unlikely to be S_2O_3. Gardner and Frankel (27) showed by e.s.r. measurements that the blue solutions of sulphur in oleum contained two radicals with g values of 2.016 and 2.026. Symons et al. (28) examined the e.s.r. spectra of solutions of sulphur in 25% and 65% oleum and also showed the presence of two radical species for which they obtained the g values of 2.018 and 2.032. These authors further claim that the e.s.r. spectrum is best interpreted by postulating a species of the type $X_2S\text{-}SX_2^+$, where X is a univalent group derived from the solvent. Cady and Shreeve (29) in 1961 studied the reaction of sulphur with $S_2O_6F_2$, by irradiating the mixture with ultraviolet light for an extended period. They observed a colour change from yellow to orange to white to blue and finally to green, and suggested that the colour changes may be due to surface effects. Lux and Bohm (30) recently investigated the solutions of sulphur in various oleum concentrations, using UV-visible spectroscopy, and came to the conclusion that at least four different species are formed. They designated these species as S_X (absorption maximum at 590 nm), S_I (absorption maximum at 330 nm), S_Z (absorption maximum at 400 nm) and $S_8.nSO_3$ (absorption maximum at 233 nm). Hilger (31) in 1966 investigated the coloured solutions of selenium and tellurium in detail. The relevant results of his investigation are summarised below:-

(1) The green solutions of selenium in concentrated H_2SO_4 are in a lower oxidation state than the yellow selenium solutions.

(2) Selenium reacts with SeF_4 in the presence of moisture to give a green solution, the absorption spectra of which was identical to the green solution of selenium in concentrated H_2SO_4. Magnetic data showed the green species to be diamagnetic.

(3) Selenium reacts with $SeOF_2$ to give green and yellow solutions.

(4) Tellurium dissolves in HSO_3F, HSO_3Cl, oleum, SbF_5 and concentrated H_2SO_4 to give red solutions.

More recent work from these laboratories has confirmed many of the earlier qualitative observations, and has shown that under mild oxidising conditions, the colours obtained by sulphur, selenium and tellurium, are in fact due to polyatomic cations. The details of these investigations are given in the introduction to the appropriate chapters on these elements. A number of authors have published their work on the polyatomic cations of sulphur, selenium and tellurium during the course of the present investigation. It seems more appropriate to discuss these very recent studies in the chapters devoted to the element concerned.

(b) Purpose of this work.

The object of the present work was two-fold;

(i) to determine the best preparative routes to solid derivatives of reported polyatomic cations of Group VI; many of these cations were previously known only in the liquid phase.

(ii) to synthesise compounds containing previously unknown polyatomic cations of sulphur, selenium and tellurium. It was of particular interest to isolate these materials as solids, since this might at some future date allow elucidation of the cation structure by X-ray crystallography.

CHAPTER II

Experimental Methods

1. Preparation and Purification of Materials.

Fluorosulphuric Acid

Technical fluorosulphuric acid (Baker and Adamson) was purified by double distillation in a two-stage still, as described by Milne (32). The still was rigorously dried by flaming out, and by passing a slow stream of nitrogen or dry air through it overnight. Passage of dry air through the receiver was continued during the distillation.

The initial fluorosulphuric acid contained a large excess of sulphur trioxide, which was not effectively removed by distillation. In such cases pellets of sodium bifluoride were added to the crude acid. The bulk of the acid then distilled over the range of 162 to 164°C. The purity of the final product was checked cryoscopically, and any excess of sulphur trioxide was titrated with hydrogen fluoride until the freezing point rose to -89.00°C. Addition of a 20% w/w solution of hydrogen fluoride in fluorosulphuric acid were made using an all teflon-syringe fitted with a cap made from 1 mm Kel-F tubing. A calculated quantity of the hydrogen fluoride solution was then added to the bulk stock of the solvent.

Antimony Pentafluoride

Antimony pentafluoride (Ozark Mahoning Co.) was doubly distilled in a pyrex glass still in an atmosphere of dry nitrogen. The fraction boiling between 142°C and 143°C was collected.

Arsenic Pentafluoride.

Arsenic pentafluoride (Ozark Mahoning Co.) was condensed on a glass vacuum line which had been rigorously dried by flaming with a bunsen burner.

Phosphorus Pentafluoride.

Phosphorus pentafluoride (Matheson's) was used directly from the cylinder. The manipulations were carried out on a monel vacuum line. The purity of AsF_5, and PF_5, was checked using a gas-phase infrared steel cell with AgCl windows.

Peroxydisulphuryl Difluoride.

Peroxydisulphuryl difluoride, $S_2O_6F_2$, was prepared by the method of Dudley and Cady (33), by reaction of fluorine and sulphur trioxide at 100°C over a silver fluoride catalyst. The catalyst was prepared from a copper mesh which had been coated in a silver cyanide complex bath. This silver coated catalyst was then fluorinated until no more fluorine was consumed. The flow rates of each reactant, diluted with nitrogen, were monitored by fluorolube oil bubblers. The fluorine flow rate was maintained slightly in excess of one half the sulphur trioxide flow rate and the reaction vessel was maintained at 115-120°C. The product was collected in a trap cooled with finely crushed dry ice. Final purification of the product was accomplished by pumping the product at dry ice temperature for a few hours. Prior to use the peroxydisulphuryl difluoride was distilled from dry ice on a pyrex vacuum line fitted with teflon taps.

Sulphur Trioxide.

Sulphur trioxide was distilled from Baker and Adamson 'Sulfan' in a still which was protected from moisture by a magnesium perchlorate drying tube.

Hydrogen Fluoride. Anhydrous hydrogen fluoride (Matheson's) was used directly.

Arsenic Trifluoride.

Anhydrous grade arsenic trifluoride (Research Organic Inorganic Chemical Co.) was further purified by refluxing it over sodium fluoride and fractionating it through a short column. B. Pt.57-58°C.

Sulphuric Acid.

Stock solutions of sulphuric acid with a composition very near to 100% were prepared by mixing 95.5% sulphuric acid (C.P. grade) with reagent grade fuming sulphuric acid (30% SO_3). This acid was adjusted to exactly 100% composition in a conductivity cell. The minimum specific conductance of 100% sulphuric acid has been previously reported (34) as 1.0432×10^{-2} ohm^{-1} cm^{-1} at 25°C.

Fuming Sulphuric Acid.

Oleums of known composition were obtained by distilling sulphur trioxide into a weighed amount of 100% sulphuric acid.

Sulphur. Sulphur was 99.999% grade (K & K Labs.). Finely powdered sulphur was stored over P_2O_5 in a dessicator.

Selenium and Tellurium.

Both selenium and tellurium, 99.7% (K & K Labs.) were stored in a P_2O_5 dessicator. Finely powdered elements were pumped under vacuum for a few hours before use.

2. Manipulation of Materials

All manual operations were carried out in a very good dry box containing a Mettler H6 balance. This dry box (S. Blickman Inc.) had an evacuable port which was refilled with extra dry nitrogen. The atmosphere was circulated through an external circuit in which any volatile products were removed in liquid nitrogen traps. For non-quantitative work, a second smaller dry box was used. This dry box was fitted with a similar circulating system, and had a port which was slowly flushed with extra dry nitrogen for ten to twenty minutes before entry.

Antimony pentafluoride was handled using a dry smooth-glass syringe. Solutions in fluorosulphuric acid were handled using platinum needles. The ends of the needles could be closed off with Kel-F tubing, and the syringes conveniently weighed before and after additions. Vacuum line operations were performed either on a pyrex, or on a monel vacuum line. Experiments with peroxydisulphuryl difluoride were carried out on a pyrex line which was set up inside a fume hood. This line was fitted with 4mm Fischer and Porter teflon-glass valves. Attachments were made either with 1/4" teflon Swagelok connectors, or with B10 joints using Kel-F grease (3M Co.). The monel vacuum line was fitted with Kel-F seated Whitey valves, and with a monel Bourdon gauge (Taylor Instruments Co.). Kel-F traps were connected with a teflon Swagelok to one of the four outlets. Gas cylinders were connected by a Swagelok via 1/4" teflon tubing to one of the outlets. Arsenic pentafluoride and phosphorus pentafluoride were handled on another calibrated pyrex vacuum line equipped with a mercury manometer. The line was thoroughly flamed out under vacuum before use. The gases mentioned above appear to attack mercury extremely slowly.

3. Experimental Technique.

Synthetic reactions were normally carried out in pyrex glass reaction vessels as shown in Figure 1. The large reaction vessel was used when a greater amount of the reaction product was required. A sintered glass disc of medium or fine grade was included to remove any unreacted or insoluble material. Oxidation reactions were carried out using antimony pentafluoride, arsenic pentafluoride, phosphorous pentafluoride or peroxydisulphuryl difluoride as oxidising agents. Some typical reaction procedures are described below.

Reactions with Antimony Pentafluoride.

In a dry box, a known weight of SbF_5 was introduced via a smooth glass syringe into arm R of the reaction vessel (Fig. 1). The appropriate amount of the element was then added into arm L which contained a magnetic stirring bar. This arm was connected to a Swagelok device via 1/4" o.d. glass tubing. Similarly arm R, containing SbF_5, was closed by means of a Whitey valve which was subsequently attached to the vacuum line at A'. This end of the reaction vessel was cooled in liquid nitrogen and the whole apparatus was evacuated. About 50 ml of dry sulphur dioxide was introduced into the system and the reaction vessel was sealed off at points A and A'. When the system reached room temperature the SbF_5-SO_2 mixture was allowed to pass into the arm containing the element. The reaction vessel was placed on a magnetic stirrer and the contents of the arm were stirred for 2-3 days during which time cold tap water was circulated via a rubber tubing on the upper part of the vessel. In most cases, the required product was found to be soluble in liquid SO_2, thus facilitating its extraction.

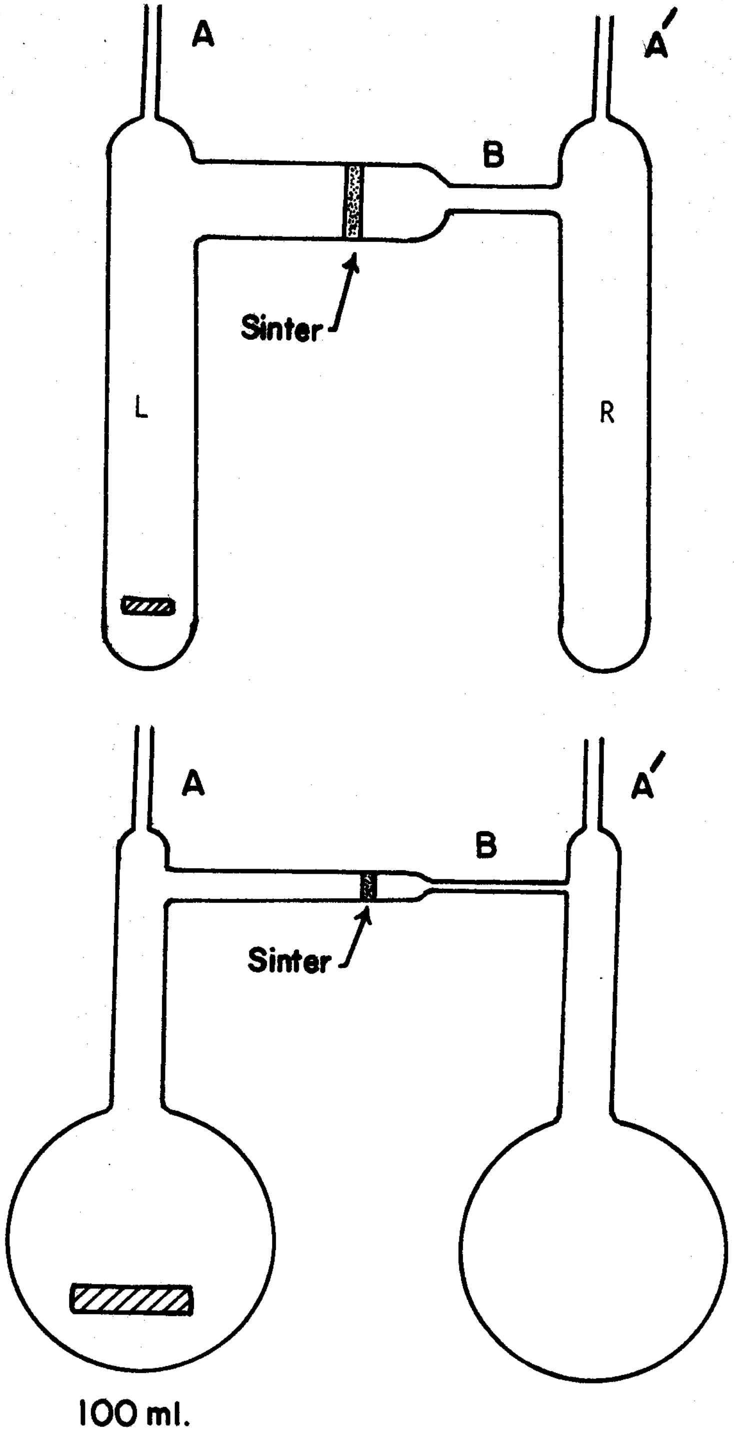


Figure 1. Reaction Vessels.

The soluble products were then filtered through the glass sinter into arm R, leaving behind a white solid which was shown to be SbF_3. The soluble compound was recovered from its solution by evaporating all volatiles into arm L. When the reaction product appeared dry, the vessel was sealed off at point B (Fig. 1).

Reactions with Arsenic Pentafluoride.

Arsenic pentafluoride oxidation reactions were more convenient than antimony pentafluoride oxidation reactions for three reasons;

(1) It was not necessary to use the dry box, as all handling of arsenic pentafluoride could be carried out on the vacuum line.

(2) The reduced product of arsenic pentafluoride, AsF_3, is volatile (B. Pt.57-58°C), and therefore easily removed under vacuum.

(3) Arsenic pentafluoride normally reacted to give a simple anion AsF_6^-, which is conveniently characterised by Raman, infrared and ^{19}F nmr.

A calibrated pyrex glass vacuum line was used to introduce the required amount of arsenic pentafluoride. The technique of carrying out a reaction was essentially the same as for the antimony pentafluoride case described above, except the reduced product, AsF_3, was removed under vacuum.

Reactions with Peroxydisulphuryl Difluoride.

Caution was exercised in handling peroxydisulphuryl-difluoride. The reactions were normally carried out in liquid SO_2 as a solvent. On many occasions, during the study of reaction between $S_2O_6F_2$ and sulphur, the reaction vessel exploded when it was allowed to warm up to room temperature. It was found necessary to allow the temperature to increase very slowly by successively replacing the liquid nitrogen dewar with a chloroform slush bath, then a carbon tetrachloride slush bath, and then allowing the reaction mixture to warm up to room temperature. Peroxydisulphuryl difluoride is a particularly convenient oxidising agent as it is reduced to the fluorosulphate anion.

$$S_2O_6F_2 + 2e \longrightarrow 2SO_3F^-$$

4. UV and Visible Absorption Spectra.

Absorption spectra were recorded from 220 to 700 nm on either a Bausch and Lomb Spectronic 505, or on a Cary model 14 spectrophotometer. One centimeter path length silica cuvettes, with quartz inserts to vary the path length down to 0.03 mm, facilitated study of concentrated solutions. Path lengths were calibrated with alkaline solutions of potassium chromate (35). The custom-made quartz cells (Hellma Ltd.) in which all four sides were optically clear were also used. These cells had the obvious advantage of giving two different path lengths when used with the quartz inserts. The cells and inserts were rigorously dried, and stored in a vacuum desicator over phosphorus pentoxide. The cells were filled in a dry box, and teflon covers were clamped on, and bound with teflon tape.

5. Magnetic Susceptibility Measurements.

Magnetic susceptibilities were determined by the Gouy method using an Alpha Scientific Laboratory Model AL 7500 electromagnet, and a Sartorius Vacuum Electrono microbalance. The sample consisted of ten cm of solid or solution sealed in a fifteen cm long 5 mm o.d. quartz tube. The sample was suspended in an atmosphere of dry nitrogen, the microbalance could be read to 1 μg. The quartz tube constant was calibrated with standard nickel(II) chloride solution (36).

The magnetic susceptibilities were calculated using the following expression:-

$$10^6\chi = \frac{\beta(F - \delta)}{w}$$

where β is the 'tube calibration constant', w is the weight of the sample in g, F is the force on the specimen, and δ is the force on the quartz tube. χ was converted to the susceptibility per-g atom of element to yield χ_g in c.g.s. units.

6. Nuclear Magnetic Resonance Spectroscopy.

Fluorine nmr spectra were measured using either a Varian DP-60 Spectrometer operating at 56.4 MHz, or a Varian HA-100 spectrometer. Low-temperature spectra were obtained using a Varian V-4540 temperature controller with the variable temperature probe.

7. Raman Spectroscopy.

Raman spectra were recorded using a Spex Industries Model 1400 spectrometer employing a double monochromator and a phototube detector with an electrometer amplifier and recorder. The exciting radiation was the green 5165-Å line a Spectra - Physics Model 140 Ar ion laser or the 6328-Å line of a Spectra-Physics Model 125 He-Ne laser. Standard samples, both solids and liquids, were sealed in 2 mm o.d. glass capillary tubes, and mounted horizontally in a brass holder. For low temperature spectra the sample tubes were mounted in a quartz tube with an evacuated jacket, silvered except for a cm band around the centre. Nitrogen was boiled off at a variable rate from a Dewar, and passed through the tube, and the temperature was recorded with a thermocouple.

8. Electron Spin Resonance Spectroscopy.

Electron spin resonance Spectra of the solids and solution were obtained on a JOELCO Model JES 3BS-X spectrometer. The g values were obtained by comparison with manganous ion.

9. Infrared Spectroscopy.

Infrared spectra were obtained on powders between silver chloride plates using a Perkin-Elmer Model 227 spectrophotometer.

10. Cryoscopy.

The apparatus and technique for making cryoscopic measurements in fluorosulphuric acid has been described in detail by Gillespie, Milne and Thompson (37).

The cryoscope, containing approximately 130 g solution, was cooled in a liquid nitrogen bath, and the pressure within its vacuum jacket was adjusted to give a cooling rate of between 0.2 and 0.4°C per minute. The temperature was measured to 0.001°C with a Leeds Northrup platinum resistance thermometer used in conjunction with a Mueller resistance bridge. The thermometer calibration was checked periodically by determining its resistance at the triple point of water using a Trans-Sonics Inc. 'Equiphase cell.'

Resistance readings were recorded at thirty second intervals starting when the solution had reached the estimated freezing point. When the solution had supercooled by approximately 2°C, freezing was initiated by dropping in a small piece of platinum cooled in liquid nitrogen. The temperature rose rapidly, after which a cooling curve was plotted with readings at one minute intervals for fifteen minutes, with occasional reversal of the 1 m amp thermometer current. The cooling curve was extrapolated back to give the freezing point, which was estimated to be accurate to $\pm$ 0.005°C (37).

Additions were made through a B 14 joint at the top of the cryoscope. At other times this joint was capped with a P_2O_5 guard tube which served as the exit for the slow stream of dry air continually sweeping the top of the cryoscope. The freezing point depression caused by the presence of the solute is given by the expression:

$$\Delta T = K_f \nu m$$

where: ΔT is the freezing point depression

m is the molality of the solute

ν is the number of particles produced per molecule of solute

k_f is the cryoscopic constant.

A value of 3.93$\pm$0.05 (32) was used for the cryoscopic constant of fluorosulphuric acid.

11. Analysis.

Selenium.

Weighed quantities of the compound were decomposed with water and dissolved in the minimum volume of warm nitric acid. The diluted solution was warmed with an excess of hydrazine hydrochloride for 1 h, and the resulting grey selenium was filtered, dried, and weighed.

Antimony.

The method was adapted from that of Johnson and Newman (38). The Sb(V) from weighed samples of the compound was reduced with phosphorus and iodine, and the Sb(III) titrated with standard iodine solution, in the presence of boric acid to eliminate interference from fluoride ion (39).

Fluoride. Weighed samples of the compound were hydrolysed with a slight excess of sodium hydroxide for 3 days at 100°C in sealed tubes. After filtering off any solid, the fluoride in the filtrate was determined by potentiometric titration with standard lanthanum nitrate, using an Orion fluoride ion activity electrode as indicator (40).

AsF_6^-.

The method of Dess et al. (41, 42) was used to determine AsF_6^-. The AsF_6^- was precipitated as tetraphenylarsonium hexafluoroarsenate from an acidic solution and weighed as such after drying at 100°C.

Tellurium.

The method for the determination of tellurium was essentially the same as that for selenium described above.

Sulphur.

Sulphur was determined gravimetrically as $BaSO_4$.

The compounds $Se_4(Sb_2F_{11})_2$, $Se_8(AsF_6)$ and "$TeSO_3$" were analysed by the methods described above. All other elemental analyses were carried out by Alfred Bernhardt Mikroanalytisches Laboratorium, 5251 Elbach über Engelskirchen, Fritz-Pregl-Strasse 14-16, West Germany.

12. Preparation of Te(I) fluorosulphate.

In a typical experiment about half of a quantity of 7.73 g of finely powdered dry tellurium was added to a solution of 6.00 g of $S_2O_6F_2$ in 35 g of HSO_3F acid at -75°C, in an apparatus shown in Fig. 2. The red solution obtained was allowed to warm up to -23°C with constant stirring. After a few hours the solution had become dark yellow in colour. Small further additions of tellurium were then made by gently tapping Section A of the apparatus, the whole quantity being added in a period of about 30 hours. The solution was kept at -23°C for a further 18 hours to ensure complete reaction. About 250 ml of liquid SO_2 was condensed in flask C containing the solution. A bright yellow compound precipitated and after this had been allowed to stand overnight to settle, a faint red solution was obtained. This red solution was carefully decanted off into bulb B which was kept cold at -63°C. The bright yellow solid was then extracted several times with SO_2 until the sulphur dioxide remained colourless. Flask B was replaced by E while flask C was under a positive pressure of dry nitrogen. The solid in C was pumped for 48 h at -63°C to remove all the SO_2. The product was a fine bright yellow powder. This solid decomposed if allowed to warm up to -23°C. A vessel G, containing 60 g of the cryoscopically adjusted HSO_3F was attached at section F under dry nitrogen atmosphere. Cold fluorosulphuric acid was added to the cold yellow solid drop by drop, until all the yellow solid had dissolved to give a deep yellow solution. This solution was kept under vacuum at -23°C for 24 h to ensure the removal of any remaining SO_2.

Samples of the yellow solution were analysed as follows: The solution was hydrolysed by adding ice that had been previously cooled in liquid nitrogen. It was then oxidised with nitric acid and evaporated to dryness with HCl several times and any insoluble silica was filtered off. The solution was then reduced with hydrazine hydrochloride and the elemental tellurium was filtered, dried and weighed.

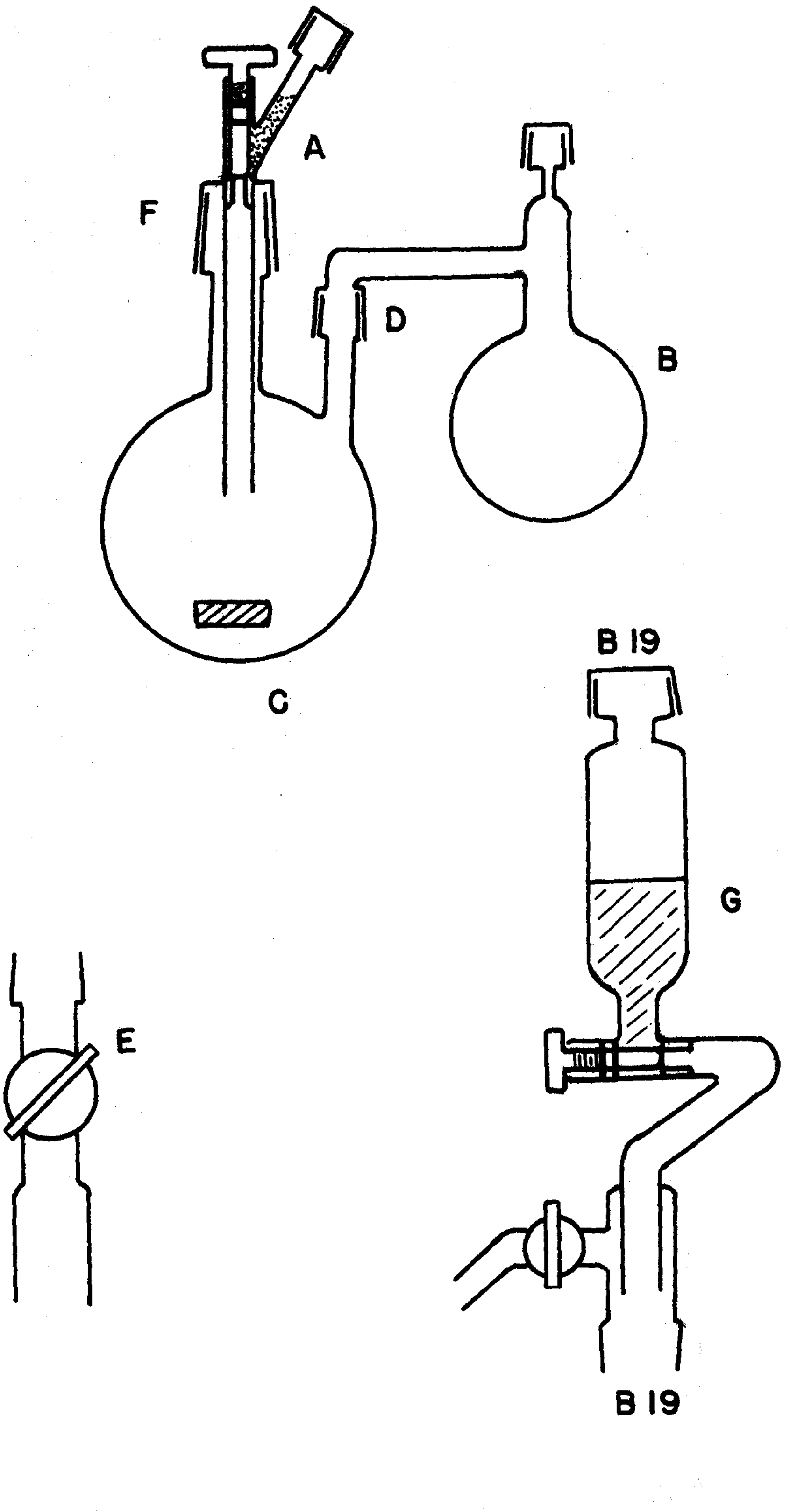


Figure 2. Apparatus for preparing Te(I) fluorosulphate

CHAPTER III

Compounds of Selenium in +1/4 and +1/2 Oxidation States

1. Introduction

Gillespie and co-workers have recently shown (43) that selenium can be oxidised by fluorosulphuric acid, 100% sulphuric acid, oleum and peroxydisulphuryl difluoride to give green and yellow species in solution. These solutions were investigated by conductometric, cryoscopic, spectrophotometric, and magnetic methods. The green and yellow species were shown to be new polyatomic cations Se_8^{2+} and Se_4^{2+} respectively. Yellow compounds of selenium, which had been formulated as $SeSO_3$ and $Se(SbF_5)_2$, had been reported (6, 25) prior to the investigation of Gillespie and co-workers. It seemed probable, that these compounds might contain the yellow Se_4^{2+} cation, and that the formulations $SeSO_3$ and $Se(SbF_5)_2$ might not be entirely correct.

This chapter reports the study of the oxidation of selenium using antimony pentafluoride and arsenic pentafluoride as oxidising agents.

2. (a) Preparation of $Se_4(Sb_2F_{11})_2$ by oxidation with SbF_5.

Powdered selenium was heated for 6 h at 100-140°C with an excess of antimony pentafluoride to give a homogeneous yellow solution and a small amount of white sublimate. On cooling the solution, a yellow crystalline solid separated. This was washed with SbF_5 and pumped dry at 140°C for 36 h to give a bright yellow powder. The yellow compound darkens rapidly on exposure to moist air, and instantly decomposes to red selenium when added to water. On heating in dry nitrogen, decomposition to black selenium with melting occurs below 200°C. The yellow compound dissolves immediately in sulphuric, disulphuric, and fluorosulphuric acids to produce yellow solutions.

Elemental analysis gave the following results: Se, 27.06, 27.02; Sb, 38.65, 38.43; F, 33.7, 34.10. Table I shows the analyses expected for various compounds that might be formed under the experimental conditions.

Table I

Calculated Analyses for Possible Compounds

Compound	Se %	Sb %	F %
$Se(SbF_5)_2$	15.40	47.52	38.08
$SeSbF_5$	26.70	41.17	32.12
Se_2SbF_6	40.12	30.93	28.96
$Se_2Sb_2F_{11}$	25.87	39.89	34.24
$SeSbF_6$	25.09	38.69	36.22

The analysis is consistent with $Se_2Sb_2F_{11}$ or $SeSbF_6$ containing selenium in the +1/2 and +1 oxidation states respectively. The absorption spectrum of the yellow compound (Fig. 3) shows the characteristic 410 nm

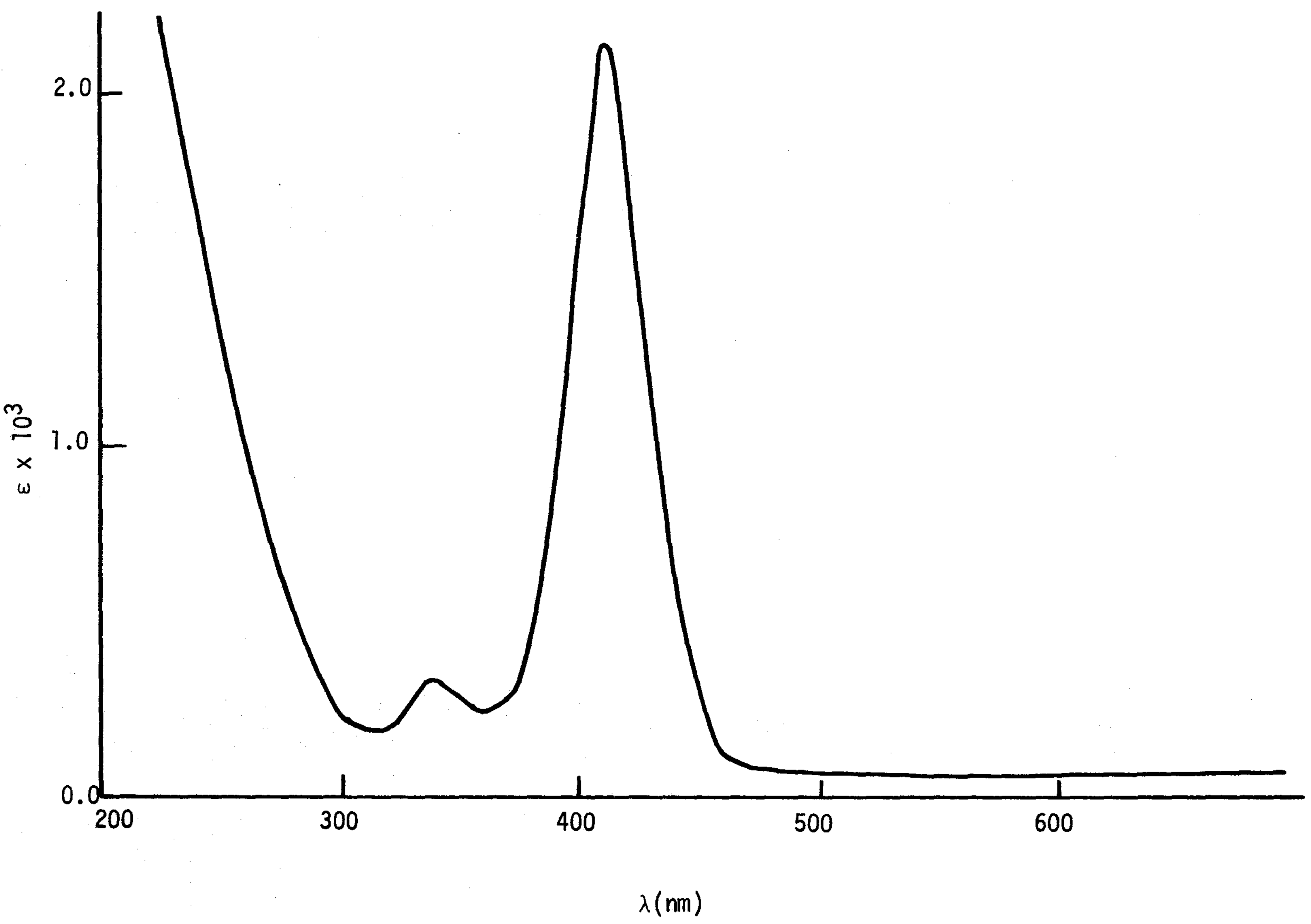
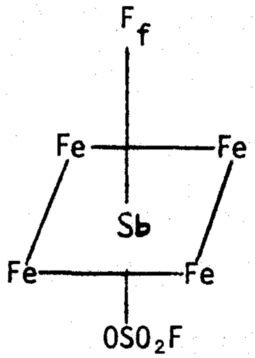


Figure 3. Absorption Spectrum of the Se_4^{2+} Cation in HSO_3F.

absorption of the Se_4^{2+}cation (43), with an extinction coefficient of 2170 l $mole^{-1}$ (Se) cm^{-1} which is in good agreement with the value of 2120 l $mole^{-1}$ (Se) cm^{-1} given for the Se_4^{2+} ion in fluorosulphuric acid (43). It is clear that the compound gives rise to Se_4^{2+} virtually quantitatively in solution. The yellow solid and solutions in HSO_3F show a strong characteristic Raman line at ca. 327 cm^{-1} (43). The solid thus contains the same selenium species, namely Se_4^{2+}, as the solution. The ^{19}F spectrum of a solution of $Se_4(Sb_2F_{11})_2$ in fluorosulphuric acid is shown in Fig. 4. It has a broad peak F_d at +162 ppm (from HSO_3F) which may be assigned to SbF_6^-, a doublet F_e at 154 ppm, and a quintet F_f at 172 ppm with a coupling constant of 100 Hz which may be assigned to the $SbF_5(SO_3F)^-$ anion (I) (44).



I

The doublet arises from the four equivalent fluorines F_e and the quintet from F_f. The relative areas of the signals from F_d and F_e were 5.9/4.0, in good agreement with the expected ratio of 6.0/4.0 for the formation of SbF_6^- and $SbF_5(SO_3F)^-$ according to the equation

$$Sb_2F_{11}^- + SO_3F^- \longrightarrow SbF_6^- + SbF_5(SO_3F)^-.$$

The ^{19}F nmr spectrum of the yellow compound in SO_2 at -90°C is that of the $Sb_2F_{11}^-$ anion, previously reported by Gillespie and Moss (45)

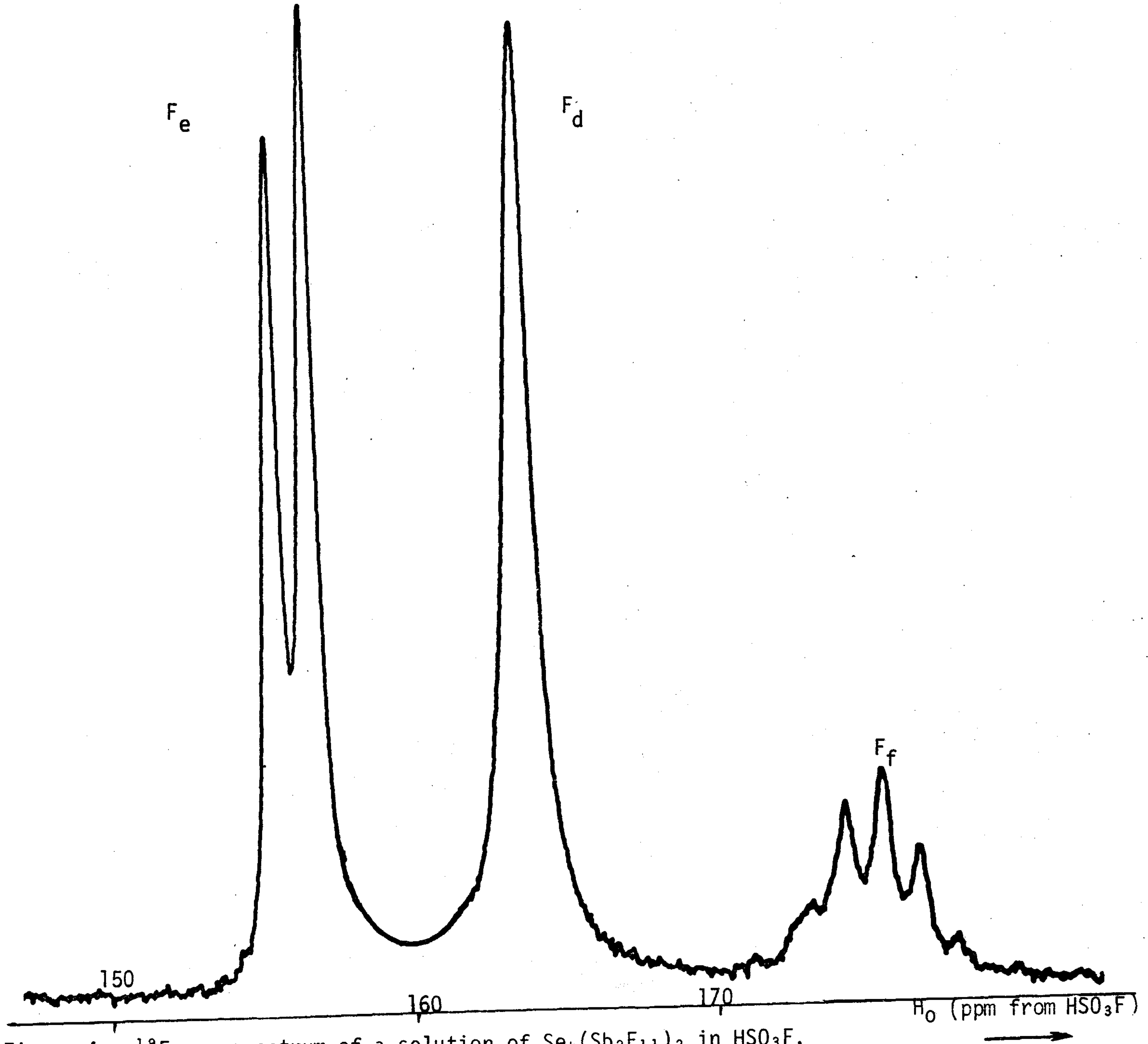
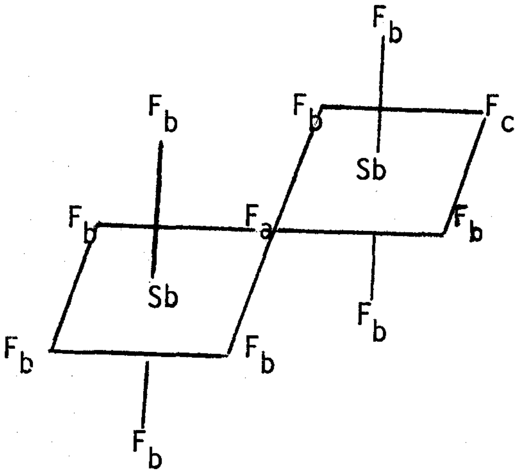


Figure 4. ^{19}F nmr spectrum of a solution of $Se_4(Sb_2F_{11})_2$ in HSO_3F.

for solutions of SbF_5 in HF. The spectrum is shown in Fig. 5. It consists of a multiplet at 92 ppm, a doublet of a doublets at 111 ppm, and a quintet at 133 ppm from external $CFCl_3$. This is essentially the same spectrum as was observed previously for a 20.9% solution of SbF_5 in hydrogen fluoride (45) and attributed to the $Sb_2F_{11}^-$ ion, II.



II

The low field multiplet is assigned to the bridging fluorine F_a, the doublet of doublets to the eight-equivalent fluorines F_b, and the quintet to the two equivalent fluorines F_c. The chemical shifts agree well with those observed previously (46) for the $Sb_2F_{11}^-$ ion in SO_2 solution: multiplet F_a 89-91 ppm, doublet of doublets, F_b 109-111 ppm, and a quintet F_c 131-135 ppm. The coupling constants J_{ab}=60 and J_{bc}=102 Hz are in good agreement with the previously observed values of J_{ab}=59 Hz and J_{bc}=102 Hz (46). Thus the ^{19}F nmr data confirms that the anion in the yellow compound is $Sb_2F_{11}^-$ and the compound therefore may be formulated as $Se_4(Sb_2F_{11})_2$.

(b) Preparation of $Se_4(AsF_6)_2$ by oxidation of selenium with AsF_5.

On treating selenium with large amounts of AsF_5 in liquid SO_2

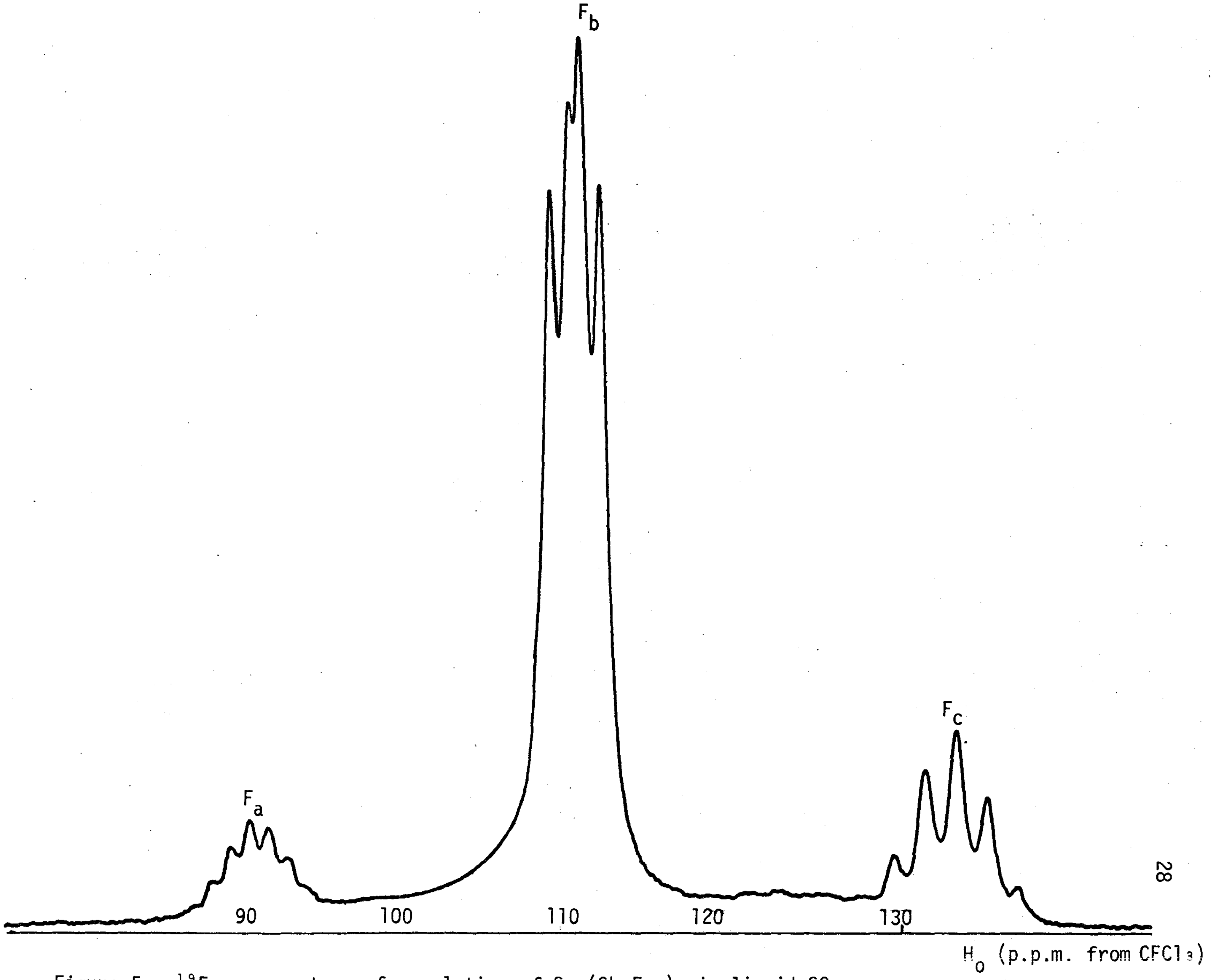


Figure 5. ^{19}F nmr spectrum of a solution of $Se_4(Sb_2F_{11})_2$ in liquid SO_2.

at room temperature, only the green species (discussed below) was obtained. However on increasing the temperature to 80°C, the green solution in liquid SO_2 gradually deposited a yellow solid.

In a typical experiment, a large excess of arsenic pentafluoride (4.00 g, 0.0235 mole) was condensed onto powdered selenium (1.00 g, 0.0127 mole) in liquid SO_2 in a reaction vessel. The reaction vessel was heated gradually to 80°C for 8 days during which time, the yellow compound precipitated from a deep green solution. The reaction was further kept at this temperature until a colourless solution with a bright yellow precipitate was obtained. On removal of the solvent and AsF_3 under vacuum, a yellow amorphous solid was obtained. The compound was very similar to $Se_4^{2+}(Sb_2F_{11}^-)_2$ in its behaviour towards moisture and on dissolution in strong acids.

Elemental analysis gave the following results: Found: Se, 44.95; AsF_6^-, 55.30. Calculated for $Se_4(AsF_6)_2$: Se, 45.53; AsF_6, 54.47. The analysis is clearly consistent with the formulation Se_2AsF_6, with selenium in the +1/2 oxidation state. The absorption spectrum of a solution in HSO_3F was identical to that of $Se_4^{2+}(Sb_2F_{11}^-)_2$ shown in Fig. 3. The Raman spectrum of the solid showed the characteristic line at ca. 328 cm^{-1}. It is concluded that both the solid and its solution in HSO_3F contain the Se_4^{2+} cation. The ^{19}F nmr spectrum of a solution of $Se_4(AsF_6)_2$ in fluorosulphuric acid had only one broad signal at $\delta_{CFCl_3} = 61.6$ ppm, in addition to the solvent peaks. The spectra remained essentially unchanged on cooling the solution to -80°C. A solution of $Bu_4N^+AsF_6^-$ in fluorosulphuric acid gave a signal at $\delta_{CFCl_3} = 63$ ppm, in addition to the solvent peak. The infrared spectrum of $Se_4(AsF_6)_2$ had a strong absorption at 700 cm^{-1}. Cesium hexafluoroarsentate has a similar strong absorption at 699 cm^{-1} (47). Thus the ^{19}F nmr and infrared confirm that the anion is AsF_6^-. The compound may therefore be formulated as $Se_4(AsF_6)_2$ and it is formed according to the equation,

$$4Se + 3AsF_5 \longrightarrow Se_4^{2+}(AsF_6)_2^- + AsF_3.$$

3. Preparation of Compounds Containing the Green Se_8^{2+} Cation.

(a) Preparation of $Se_8(Sb_2F_{11})_2$ by oxidation of selenium with SbF_5.

In the preparation of the yellow compound, $Se_4^{2+}(Sb_2F_{11}^-)_2$, it was noted that the first product was a green material which on prolonged heating at 100-140°C gave the final yellow product. This more reduced species was thus prepared by carrying out the reaction between selenium and SbF_5 dissolved in liquid SO_2 at -23°C or at room temperature.

In a typical experiment, antimony pentafluoride (3 g, 0.015 mole) was added to powdered selenium (1.974 g, 0.025 mole) in SO_2 at -63°C; the mixture was allowed to warm up to -23°C and stirred for three days. A very dark green solution containing some dark solid was obtained which gave a green solid on pumping off the sulphur dioxide. The solid was extracted with approximately 30 ml of sulphur dioxide for four times until the remaining solid residue was white. This white solid was identified as antimony trifluoride, which is insoluble in sulphur dioxide. The Raman spectrum was identical with that of an authentic sample and the oxidation state of antimony was confirmed by the Rhodamine-B test. The sulphur dioxide extract was evaporated under vacuum and a dark green microcrystalline solid was obtained (4.6 g, 0.003 mole). This green compound darkens rapidly on exposure to moist air and instantly decomposes to red selenium when added to water. It dissolves readily in 100% sulphuric acid, oleum and fluorosulphuric acid to produce green solutions. On heating in a sealed tube the compound gave a yellow melt over the range 180-190°C and finally black selenium was deposited at approximately 200°C. Presumably the $Sb_2F_{11}^-$ anion further oxidises the green species to the yellow Se_4^{2+} cation on heating.

Elemental analysis gave the following results: Found: Se, 40.40; Sb, 30.5; F, 28.70. Table II shows the analyses expected for various compounds that might be formed under the experimental conditions.

TABLE II

Calculated Analyses for Possible Compounds

Compound	Se %	Sb %	F %
$Se\ SbF_5$	26.70	41.17	32.12
Se_2SbF_6	40.12	30.93	28.96
$Se_2Sb_2F_{11}$	25.87	39.89	34.24
Se_3SbF_6	50.12	25.76	24.12
$Se_3Sb_2F_{11}$	34.36	35.25	30.31
Se_4SbF_6	57.26	22.07	20.67
$Se_4Sb_2F_{11}$	41.40	31.60	27.30

The analysis is consistent with Se_2SbF_6 or $Se_4Sb_2F_{11}$containing selenium in the +1/2 and +1/4 oxidation states respectively. The absorption spectrum of a solution of the compound (Fig. 6), in fluorosulphuric acid gave the characteristic absorption maxima at 295, 470, and 685 nm with an extinction coefficient for the 295 nm peak of 980 mole $(Se)^{-1}$ 1 cm^{-1}. The wavelength of the absorption maxima and the extinction coefficient agree well with values reported previously for the Se_8^{2+} ion (43). Thus the compound dissolves to give a quantitative yield of the Se_8^{2+} cation.

The infrared spectrum of this green compound, $Se_8(Sb_2F_{11})$ was essentially identical with that of $CsSb_2F_{11}$ over the range 450-1800 cm^{-1} and, in particular, contained a broad band at 650-770 cm^{-1} assigned to Sb-F stretching modes, and a weaker band at 476 cm^{-1} which appears to be characteristic of the Sb-F-Sb bridge of $Sb_2F_{11}^-$. This band has been observed previously at 523 cm^{-1} in $VO_2^+Sb_2F_{11}^-$ (48), at 485 cm^{-1} in $Se_4^{2+}(Sb_2F_{11})_2^-$ (49), and at 479 cm^{-1} in $Cs^+Sb_2F_{11}^-$ (50). The ^{19}F nmr spectrum of $Se\ (Sb_2F_{11})_2$ dissolved in SO_2 at -90°C was identical to that of $Se_4(Sb_2F_{11})$ shown in Fig. 5. The ^{19}F nmr and infrared spectrum confirm the anion as $Sb_2F_{11}^-$. It is concluded that the compound has an ionic structure, $Se_8^{2+}(Sb_2F_{11}^-)_2$ and that it is formed according to the equation,

$$8\ Se + 5\ SbF_5 \longrightarrow Se_8^{2+}(Sb_2F_{11}^-)_2 + SbF_3.$$

(b) <u>Preparation of $Se_8(AsF_6)_2$ by oxidation of selenium with AsF_5.</u>

In a typical experiment, arsenic pentafluoride (1.614 g, 0.0095 mole) was condensed onto powdered selenium (1.970 g, 0.025 mole) in

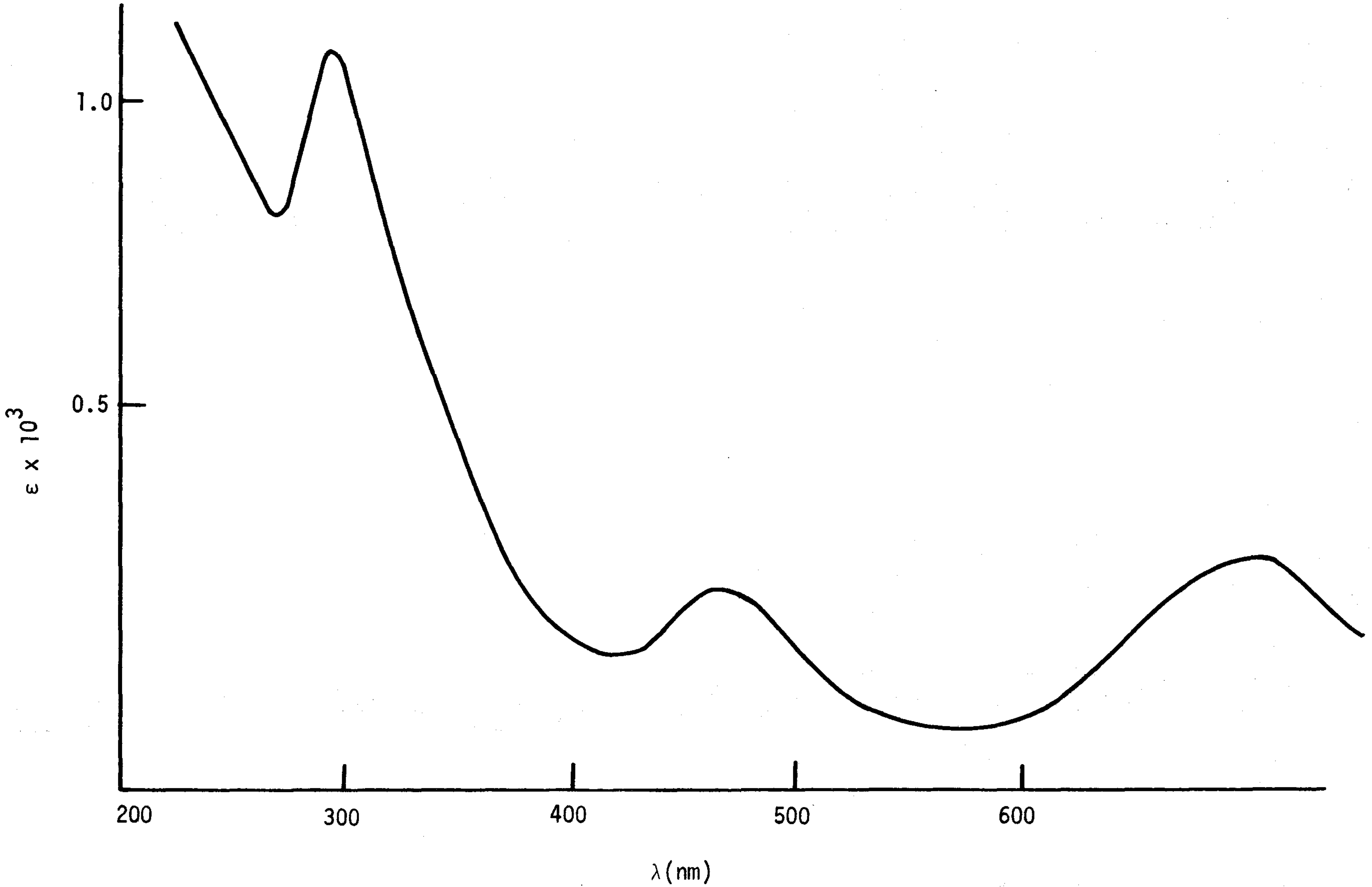


Figure 6. Absorption spectrum of the Se_8^{2+} Cation in HSO_3F.

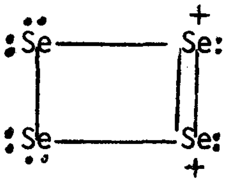
anhydrous fluoride at -78°C and the mixture was allowed to warm up to 0°C over a period of 3 days. A volatile product was condensed out in an adjoining trap. This was identified as arsenic trifluoride by means of the infrared spectrum of the vapour. On removal of the solvent under vacuum, a semicrystalline dark green solid product was obtained (3.23 g, 0.0032 mole). The compound reacts with moisture to give black selenium and dissolves in fluorosulphuric acid to give a green solution having the characteristic spectrum of Se_8^{2+} (p.33 this chapter). On heating in a sealed tube, the compound melts at 178-182°C to form a green melt and on further heating, black selenium is deposited.

Elemental analysis gave the following results: Found: Se, 63.1; AsF_6^-, 37.0. Calculated for $Se_8^{2+}(AsF_6^-)_2$: Se, 62.57; AsF_6, 37.0. The absorption maxima and extinction coefficients for a solution in HSO_3F were identical to that obtained from $Se_8^{2+}(Sb_2F_{11}^-)_2$ (p. 32). The infrared spectrum and ^{19}F nmr of the compound confirmed that the anion is AsF_6^-. (for details see p. 29). Therefore the compound can be formulated as having the ionic structure $Se_8^{2+}(AsF_6^-)_2$, and it is formed according to the equation,

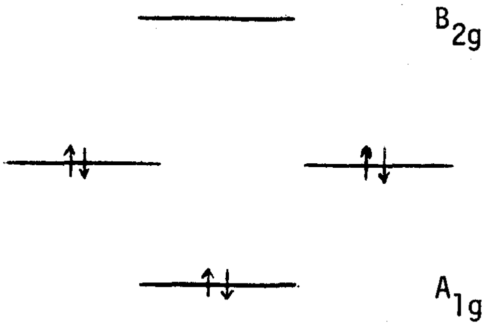
$$8\ Se + 3AsF_5 \longrightarrow Se_8^{2+}(AsF_6^-)_2 + AsF_3.$$

4. Structures

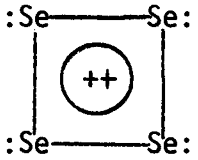
The structure of Se_4^{2+} has been shown to be square planar, both by single crystal X-ray crystallography and by vibrational spectroscopy (51, 49). The electronic structure of the Se_4^{2+} cation, with 22 electrons, may be conveniently described as a resonance hybrid of valence bond structures of the type



i.e. a delocalised π-system is present. Alternatively, the bonding in the ion may be described in terms of molecular orbital theory. Of the four π-type molecular A_{1g}, E_u, B_{2g} orbitals that can be constructed from the four p-orbitals perpendicular to the plane of the ring, the lowest three are occupied.



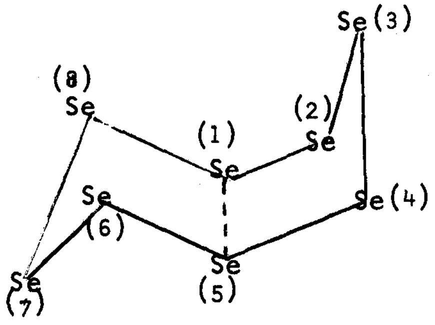
These six electrons may perhaps be regarded as constituting an aromatic sextet,



where the closed circle denotes a closed shell six π-electron system.

The Se-Se bond length in Se_4^{2+} has been found (51) to be 2.285Å as compared to the value of 2.34Å for Se-Se bond length in Se_8 (52, 53) and a normal coordinates analysis (49) yields a value of 2.2 mdynes/°A for the Se-Se stretching constant (force constant values for $^{80}Se_2$ and $(CH_3)_2Se_2$ (54) are 3.498 mdynes°A^{-1} and 1.674 mdyne °A^{-1} respectively), indicating some multiple bonding in Se_4^{2+} cation. Since the work reported here was carried out, a preliminary report of an X-ray crystallographic study of the compound $Se_8^{2+}(AlCl_4)_2^-$ has appeared (55). This compound was prepared by the reaction of selenium, selenium tetrachloride and aluminium trichloride and was shown to consist of discrete Se_8^{2+} and $AlCl_4^-$ ions. The configuration of the Se_8^{2+} ion is that of a ring with approximate m(C_s) symmetry, as shown in Fig. 7. The structure consists of two fused 5-membered rings, and is intermediate between Se_8 (52,53) and S_4N_4 (56, 57) (isoelectronic with Se_8^{4+}). It contains the first example of a branched selenium chain through the long Se_1-Se_5 bond.

average Se-Se distance around the ring = 2.32 + 0.03°A



Se_2-Se_4 = 3.36 ± 0.02°A

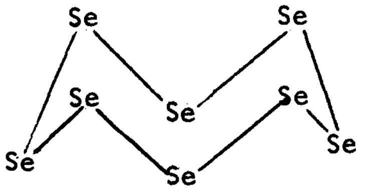
Se_1-Se_5 = 2.83 ± 0.01°A

< $Se_6Se_7Se_8$ =90°

< $Se_2Se_3Se_4$

other <Se =98°

Se_8^{2+}



bond distances = 2.34°A

bond angles = 105.7°

Se_8

Se_8

Figure 7. Structure of Se_8^{2+} Cation

CHAPTER IV

Compounds of Tellurium in +1/3, +1/2 and +1 Oxidation States

1. Introduction

Gillespie et al. recently showed (58) that elemental tellurium can be oxidised in strongly acidic media e.g. HSO_3F, oleum or 100% H_2SO_4 to a red species. The red solution in cold fluorosulphuric acid was investigated (58) by cryoscopic, conductometric, spectrophotometric and magnetic methods, and the results strongly indicated that the solution contained the Te_4^{2+} cation. During the course of the above mentioned investigations, Bjerrum et al. (59) have described the identification of Te_{2n}^{n+} (n probably equal to 2) in fused $NaAlCl_4$. The latter authors have also obtained some evidence for another tellurium species with a formal oxidation state between +1/2 and 0, but this was not identified.

Red compounds of tellurium which had been formulated as $TeSO_3$ and $Te(SbF_5)_5$ had been reported (6, 25) prior to the investigation of Gillespie and co-workers. It seemed reasonable to suppose that these compounds might contain the red Te_4^{2+} cation and that the above formulation may not be correct. Barr et al (58) also showed that tellurium can be further oxidised to a yellow species, the oxidation state of which was suggested as +1.

Selenium and sulphur have been shown to form the ions Se_8^{2+} (60) and S_8^{2+} (61) respectively, containing the element in the +1/4 oxidation state, but no evidence had been obtained for an analogous oxidation state of tellurium.

This chapter reports the study of the oxidation of tellurium using SbF_5, AsF_5, SO_3 and $S_2O_6F_2$ as oxidising agents, which had the objective of preparing new compounds of tellurium in the +1/2 and +1 oxidation states and in particular to obtain further evidence on the +1 oxidation state and if possible to obtain evidence for the +1/4 oxidation state.

2. Preparation of Compounds Containing the Te_4^{2+} Cation

(a) preparation of $Te_4(Sb_2F_{11})_2$ by oxidation of tellurium with SbF_5.

In a typical experiment antimony pentafluoride (30.1g, 0.139 mole) was added to powdered tellurium(6.0g, 0.047 mole) in liquid sulphur dioxide at -63°C and the mixture was stirred for several days at -23°C. The red solution was filtered leaving a yellow residue which was repeatedly washed with sulphur dioxide until the washings were colourless and all the red compound had therefore been removed. The red solution was evaporated to dryness and the resulting red solid was kept under vacuum to remove any remaining traces of sulphur dioxide. The characterisation of the yellow residue is described below under Section 3a.

Elemental analysis of the red compound gave the following results:- Found: Te, 35.88; Sb, 34.23; F, 32.21. The analysis expected for various compounds that might be formed under the experimental conditions are given in Table III.

Table III

Calculated analyses for various possible compounds.

Compound	% Te	% Sb	% F
$TeSbF_5$	37.06	35.36	27.59
$TeSbF_6$	35.11	33.50	31.37
$TeSb_2F_{11}$	21.99	41.98	36.03
Te_2SbF_6	51.98	24.65	23.22
$Te_2Sb_2F_{11}$	35.97	34.45	29.60

The analysis is consistent with $Te_2Sb_2F_{11}$ or $TeSbF_6$ containing tellurium in the +1/2 or +1 oxidation state respectively. The absorption spectra of solutions of the compound in fluorosulphuric and sulphur dioxide were identical with that of the red species in fluorosulphuric acid as shown in Fig 8. The molar extinction coefficient at the wavelength of maximum absorption was found to be 2200 l $mole^{-1}$ (Te)cm^{-1} which is in good agreement with the value of 2400 l $mole^{-1}$ (Te) cm^{-1} given for the Te_4^{2+} species (58) in fluorosulphuric acid. The Raman spectrum of the solid showed the same characteristic frequencies at 219 and 139 cm^{-1} as were observed for the red solution of tellurium in HSO_3F acid shown in Fig 9. These frequencies are very reasonable for Te-Te vibrations (Te-Te stretching frequency for Te_2F_{10}(62) = 168 cm^{-1}) and the spectrum is very similar to that of Se_4^{2+} (43) which has a very strong polarised line at 327 cm^{-1} and a weak line at 188 cm^{-1} except that the two lines observed for the red tellurium species are shifted, as expected to lower frequencies. The Se_4^{2+} ion has been shown to have a square planar structure (p. 35 Chapter III). The 327 cm^{-1} and 188 cm^{-1} Raman lines have been assigned to the A_{1g} and B_{2g} modes of a square planar structure (49) and the lines observed at 219 cm^{-1} and 139 cm^{-1} may reasonably be assigned to the same modes of a square planar Te_4^{2+} cation.

The Se_4^{2+} cation has an absorption spectrum that is very similar to that observed for the red tellurium species in general appearance but shifted to shorter wavelength and with a molar extinction coefficient of 2100 l $mole^{-1}$ (Se) cm^{-1} at the wavelength of maximum absorption in HSO_3F acid (410 nm). The similarity in the spectra of Se_4^{2+} and the red tellurium species has recently been pointed out by Stephens (63) who has also shown that the magnetic circular dichroism of solutions of these species are very similar. It seems very reasonable to conclude therefore that the red tellurium compound contains the Te_4^{2+} cation and that this cation has a square planar structure. The ^{19}F nmr of the red solution in sulphur dioxide showed the characteristic pattern of the $Sb_2F_{11}^-$ anion (Fig. 5.)

It is thus clear that the compound has the ionic structure $Te_4^{2+}(Sb_2F_{11}^-)_2$.

(b) <u>Preparation of $Te_4(AsF_6)_2$ by oxidation of tellurium with AsF_5</u>.

In a typical experiment arsenic pentafluoride (2.55 g, 0.015 mole) was condensed onto powdered tellurium (2.55g, 0.02 mole) in liquid SO_2 at -196°C and the mixture was allowed to warm up to room temperature. A deep red solution containing the red solid was obtained after stirring

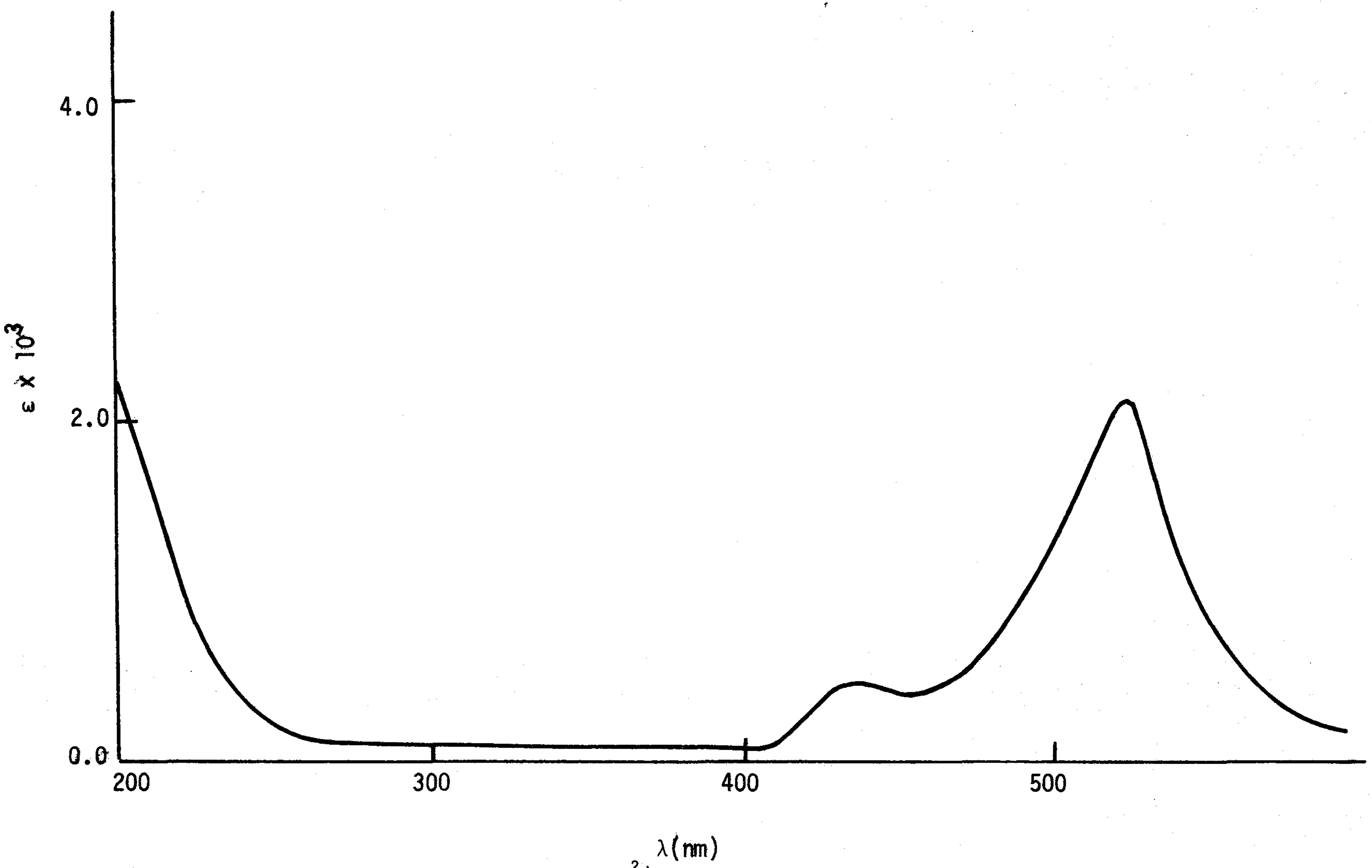


Figure 8. Absorption spectrum of the Te_4^{2+} cation in HSO_3F.

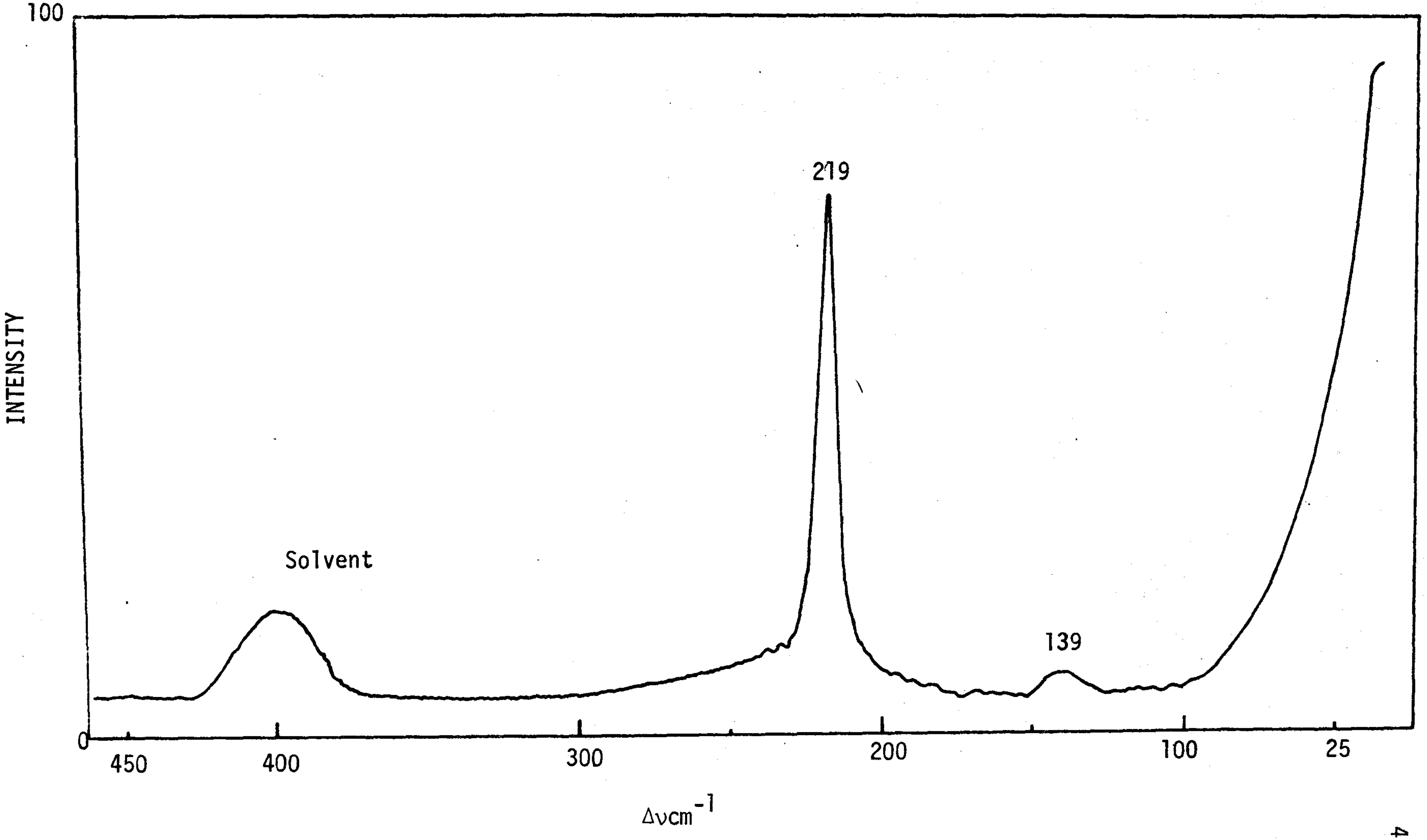


Figure 9. Raman spectrum of a 0.1m solution of Te in HSO_3F at -80°C.

for 24 hours. The red solid was isolated after removing all the volatiles under vacuum.

Elemental analysis for this red solid gave the following results: Found Te, 57.64. Calculated for $Te_4(AsF_6)_2$: Te, 57.46. The absorption spectrum in SO_2 and HSO_3F showed the characteristic peak of Te_4^{2+} at 510 nm. The Raman spectrum showed the A_{1g} and B_{2g} modes of Te_4^{2+} at 219 and 139 cm^{-1}. The infrared spectrum had a strong band at 700 cm^{-1}. $CsAsF_6$ has an absorbtion at 699 cm^{-1} (47). The ^{19}F nmr spectrum of a solution in acetone gave the 1:1:1:1 quartet of AsF_6^- $\delta CFCl_3$ 62 p.p.m., J_{As-F} 920 H [cf. aqueous solution of AsF_6^-; $\delta CFCl_3$, 60.5 p.p.m. J_{As-F} = 930 Hz (64).] It is concluded that the compound is $Te_4^{2+}(AsF_6^-)_2$.

(c) Preparation of $Te_4(SO_3F)_2$ by oxidation of tellurium with $S_2O_6F_2$.

In a typical experiment 2.00 g (0.0101 mole) of $S_2O_6F_2$ was condensed on to powdered red tellurium (3.82 g, 0.0300 mole) in SO_2 at -196°C and the mixture was allowed to warm up very slowly to -63°C over a period of a few days. The mixture was stirred for a day at -23°C. At this time the dark red solution contained a dark red solid and SO_2 and excess $S_2O_6F_2$ were then pumped off leaving 5.31 g of a red amorphous solid. This corresponded to an essentially quantitative yield of 0.0075 mole of $Te_4(SO_3F)_2$. With excess $S_2O_6F_2$ a yellow solid was obtained but this appeared to be unstable at any temperature above -20°C rapidly becoming dark in colour.

Elemental analysis gave the following results: Found: Te, 35.85. Calculated for $Te_4(SO_3F)_2$; Te, 36.03. The analysis is consistent with tellurium in +1/2 oxidation state. The absorption spectrum of the compound in HSO_3F at 0°C was identical to that shown in Fig. 8. The compound decomposes rather rapidly when exposed to 6328 Å laser radiation but at -140°C a Raman spectrum was obtained which showed' the strong 218 cm^{-1} frequency of the Te_4^{2+} cation.

The stoichiometry of the preparative reaction, the chemical analysis, and the spectroscopic results show clearly that the red compound is $Te_4^{2+}(SO_3F^-)_2$.

(d) <u>Attempted preparation of a compound containing the Te_4^{2+} cation, by oxidation of tellurium with SO_3.</u>

Kapoor (65) had previously investigated the reaction of elemental tellurium with liquid sulphur trioxide and isolated a red compound. On the basis of absorbtion spectroscopy in 100% H_2SO_4, he concluded that the red compound was a mixture of tne red Te_4^{2+} ion and the yellow Te_n^{n+} ion. It appears that at room temperature 100% H_2SO_4 and HSO_3F initially oxidises elemental tellurium predominantly to a yellow species which is not stable in this solvent, and disproportionates to Te_4^{2+} and Te(+4). The pure Te_4^{2+} species was however shown (58) to be stable in fluorosulphuric acid at 0°C, where further oxidation to the yellow species is not observed, and therefore it is clear that absorption spectra studies should be carried out in this solvent.

The reaction of elemental tellurium with sulphur trioxide was reinvestigated in order to establish whether the red compound was a pure species or a mixture of a red and a yellow compound, and to attempt to isolate the pure compounds. About 5 g of finely powdered tellurium was allowed to react with 10 g of freshly distilled sulphur trioxide at room temperature with constant stirring. After a few minutes the black tellurium had reacted to give a red amorphous powder. The reaction was allowed to proceed for a further few hours, until all the tellurium had reacted. Excess sulphur trioxide was removed by pumping to a constant weight at room temperature. The product was a bright red amorphous solid which darkened on exposure to moist air and instantaneously decomposed to elemental tellurium when added to water. The red solid dissolved in 100% H_2SO_4 and HSO_3F to give a red solution. Elemental analysis gave the following results: Te, 55.10, 55.00; S, 18.08, 18.04. Table IV shows the analyses expected for various compounds might be formed under the experimental conditions.

Table IV

Calculated analyses for various possible compounds

Compound	Te %	S %
$TeSO_3$	61.46	15.41
$Te_4S_3O_{10}$	66.59	12.53
$Te_4S_4O_{13}$	60.30	15.12
$Te_4S_2O_7$	74.36	9.32
$Te_2(HS_2O_7)$	59.05	14.81
$Te_2S_4O_{13}$	43.17	21.65
$Te_2S_3O_{10}$	49.92	18.77
$Te(HS_2O_7)_2$	41.89	21.01

The analysis is not consistent with any of the compounds listed in Table IV. The absorption spectrum of its solution in cold HSO_3F acid is reproduced in Fig 10, showing that the compound contained both the yellow Te_n^{n+}, and the red Te_4^{2+} species in solution. It has been pointed out previously (This chapter p. 45) that the red Te_4^{2+} ion is not further oxidised to the yellow Te_n^{n+} in cold fluorosulphuric acid and this must mean that the red compound is in fact a mixture of Te_4^{2+} and Te_n^{n+} compounds (the red compound obtained from the reaction of tellurium with SbF_5 has been previously shown (p. 39) to contain both Te_4^{2+} and Te_n^{n+} species). A further confirmation of this was obtained from the Raman spectrum (Fig. 11), which showed the characteristic stretching modes of Te_4^{2+} and 219 and 139 cm^{-1} and at 199 cm^{-1} for the Te_n^{n+} cation. An attempt was made to separate these species by treating the red compound with liquid SO_2, but both species were found to be insoluble in this solvent.

It is concluded that the red compound is a mixture, containing both the Te_4^{2+} and Te_n^{n+} species.

3. Preparation of Compounds containing the yellow Te_n^{n+} cation.

(a) Preparation of $Te_n^{n+}(SbF_6^-)_n$ by oxidation of tellurium with SbF_5

The yellow residue, insolbule in sulphur dioxide, that was obtained in the reaction of antimony pentafluoride with tellurium was heated at 100°C for 6 h and a white solid sublimate was obtained. This was identified as SbF_3 by comparison of its Raman spectrum with an authentic sample. The remaining yellow material was involatile and appeared to be quite stable up to 120°C.

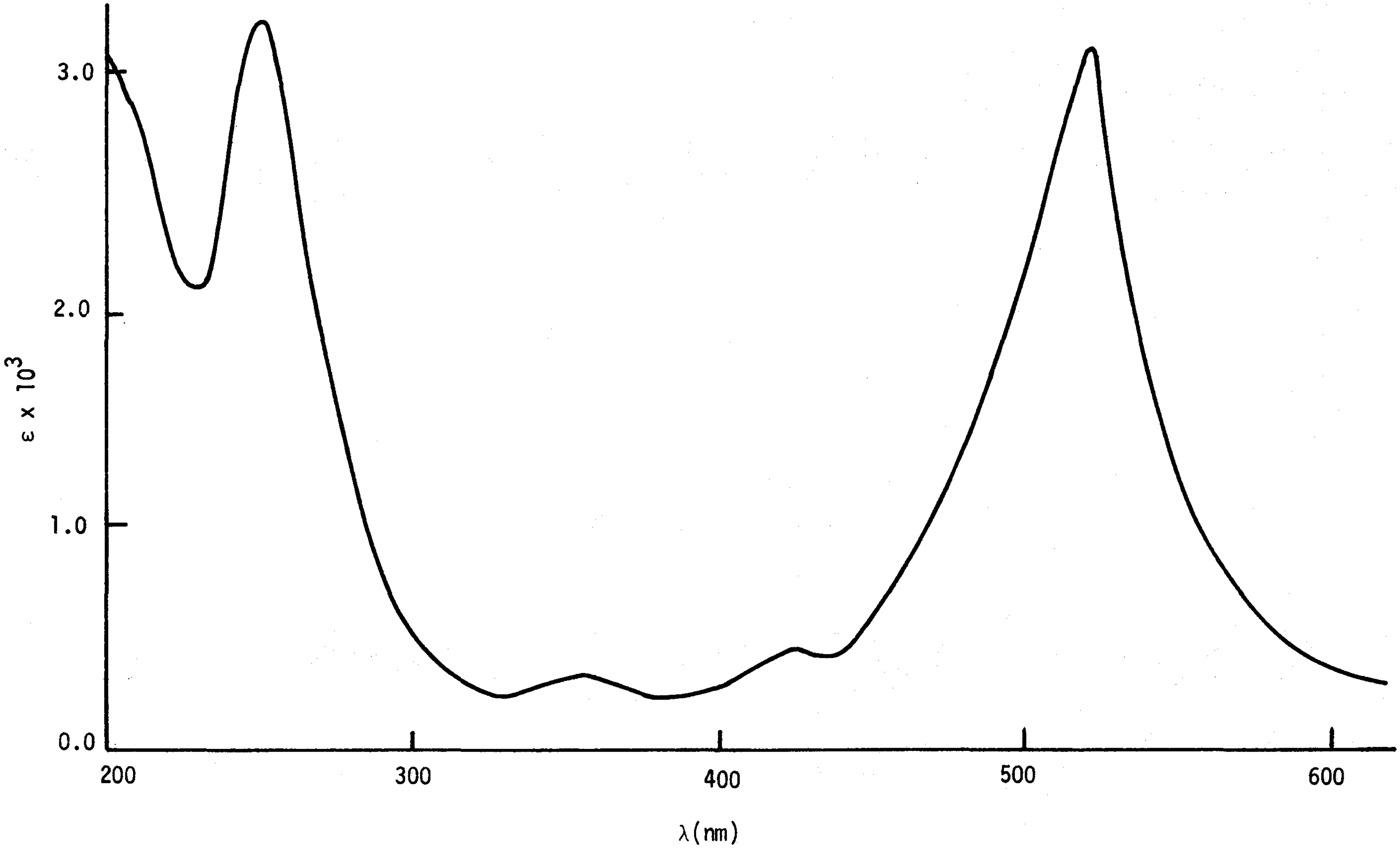


Figure 10. Absorption Spectrum of a HSO_3F Solution of the product obtained from the reaction between tellurium and SO_3.

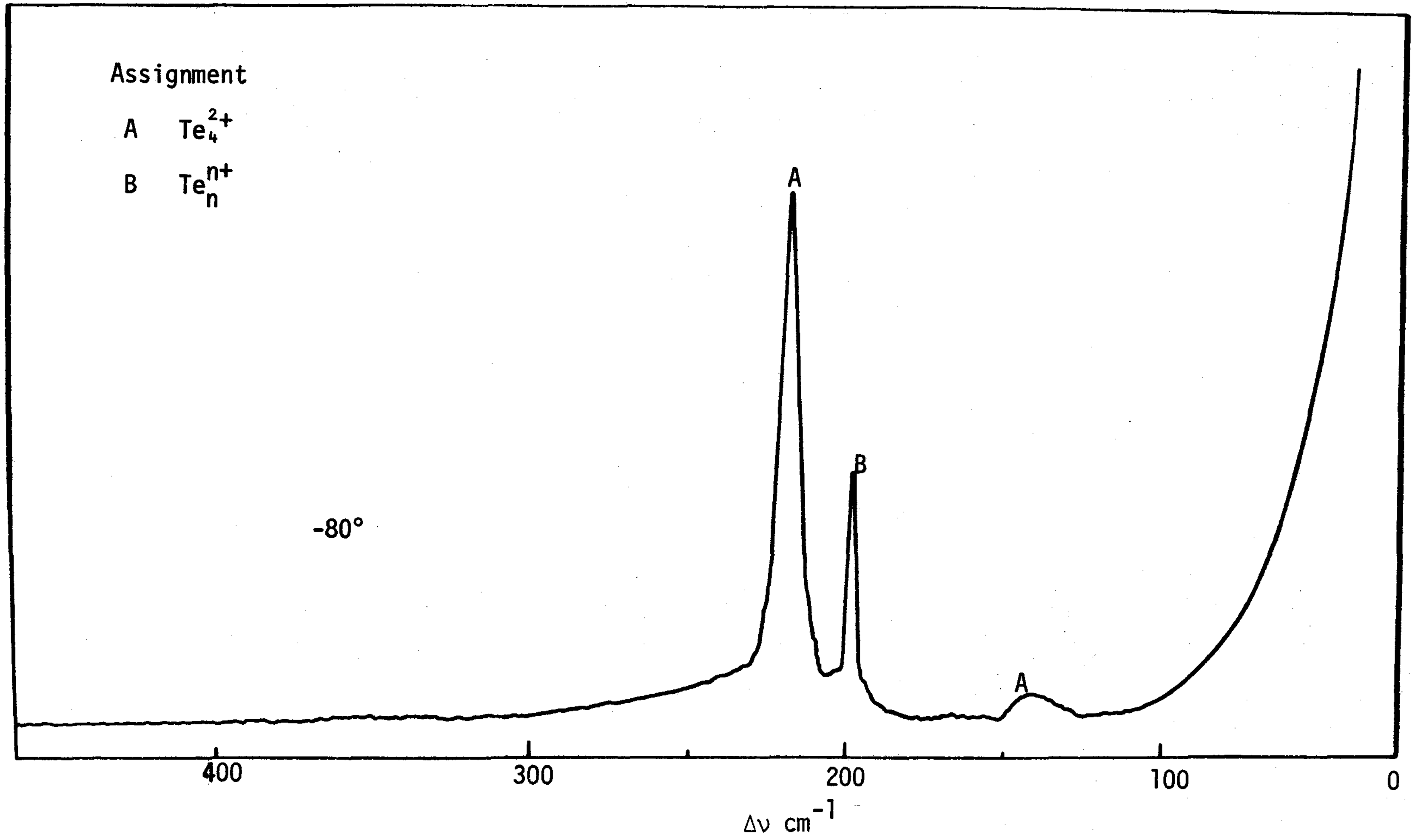


Figure 11. Raman Spectrum of the product obtained from the reaction between tellurium and SO_3

Elemental analysis gave the following results: Te, 35.42; Sb, 33.45; F, 31.13. Calculated for $TeSbF_6$: Te, 35.11; Sb, 33.50, F, 31.17. The infrared spectrum of the solid had the characteristic strong broad band of SbF_6^- at 699 cm^{-1} (47). The compound was not stable in HSO_3F as it gave a red solution containing the Te_4^{2+} cation which is presumably formed by a disproportionation reaction, which must also give tellurium in a higher oxidation state, probably the +4 state. A stable yellow solution was however obtained in HSO_3F/SbF_5 mixture which has a higher acidity than HSO_3F. The absorption spectrum in this mixture is shown in Fig 12. The extinction coefficient was found to be 6300 l $mole^{-1}$ (Te) cm^{-1} at the maximum at 250 nm. The extinction coefficient agrees well with the value of 6400 l $mole^{-1}$ (Te) cm^{-1} reported previously (66) for the yellow solution obtained by reacting 1 mole tellurium in HSO_3F with 2 moles $S_2O_6F_2$. The magnetic data shown in Table V gave a value of -21×10^{-6} c.g.s. units for the magnetic susceptibility per g atom of tellurium, after making ligand corrections (67). The cation is clearly diamagnetic. The Raman spectra of $TeSbF_6$ and its solution in HSO_3F at low temperature showed the same characteristic line at 199 cm^{-1}, shown in Fig 13, as is observed for the yellow solution of $Te/S_2O_6F_2$ in HSO_3F.

The composition of $TeSbF_6$ confirms that the yellow species contain tellurium in the +1 oxidation state. The vibration frequency at 199 cm^{-1} in the Raman spectrum is very reasonable for a Te-Te stretch. (The Te-Te stretching mode appears at 219 cm^{-1} in Te_4^{2+} cation and at 168 cm^{-1} in Te_2F_{10}(62).) The yellow compound presumably contains a

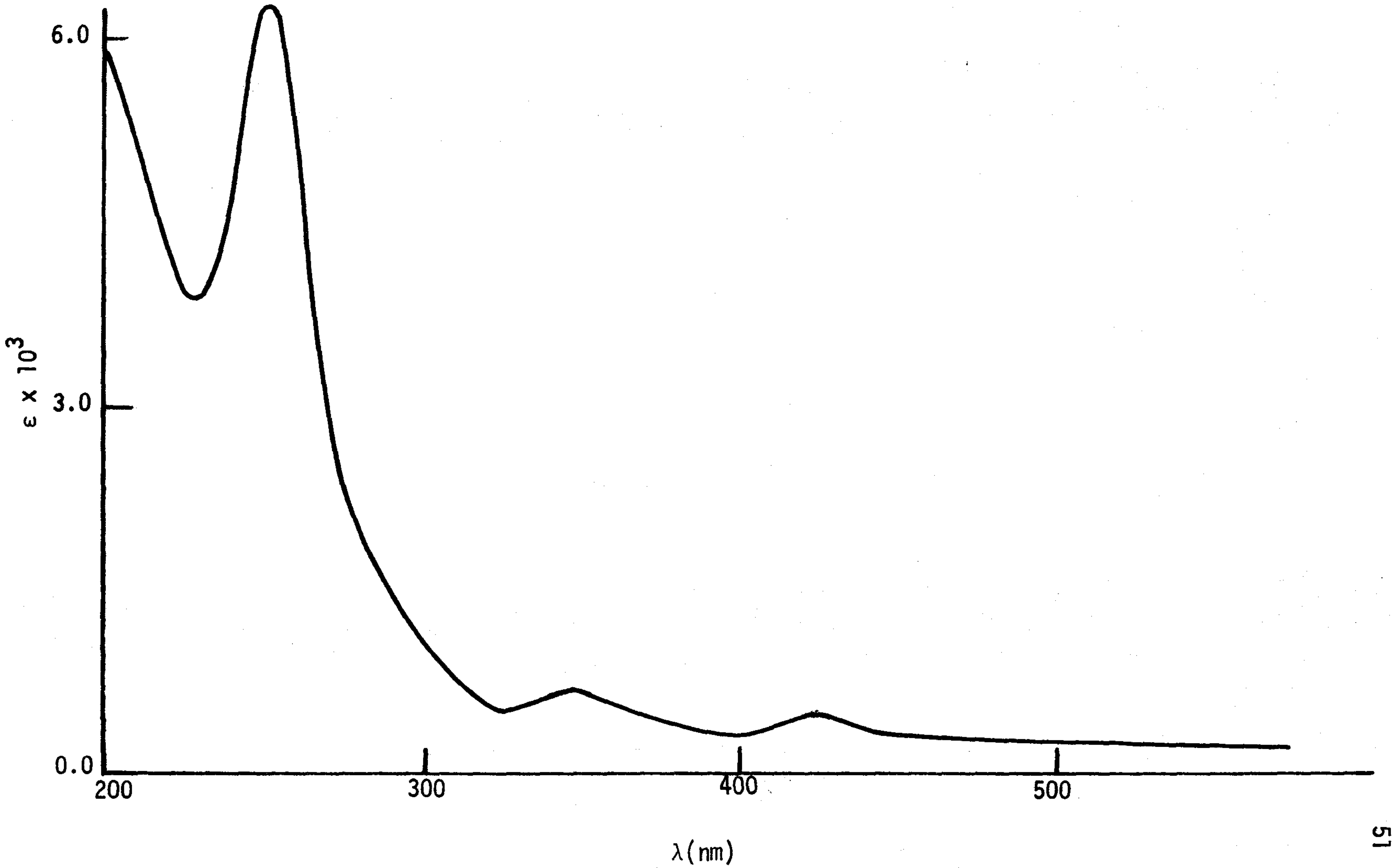


Figure 12. Absorption spectrum of the Te_n^{n+} cation in HSO_3F-SbF_5.

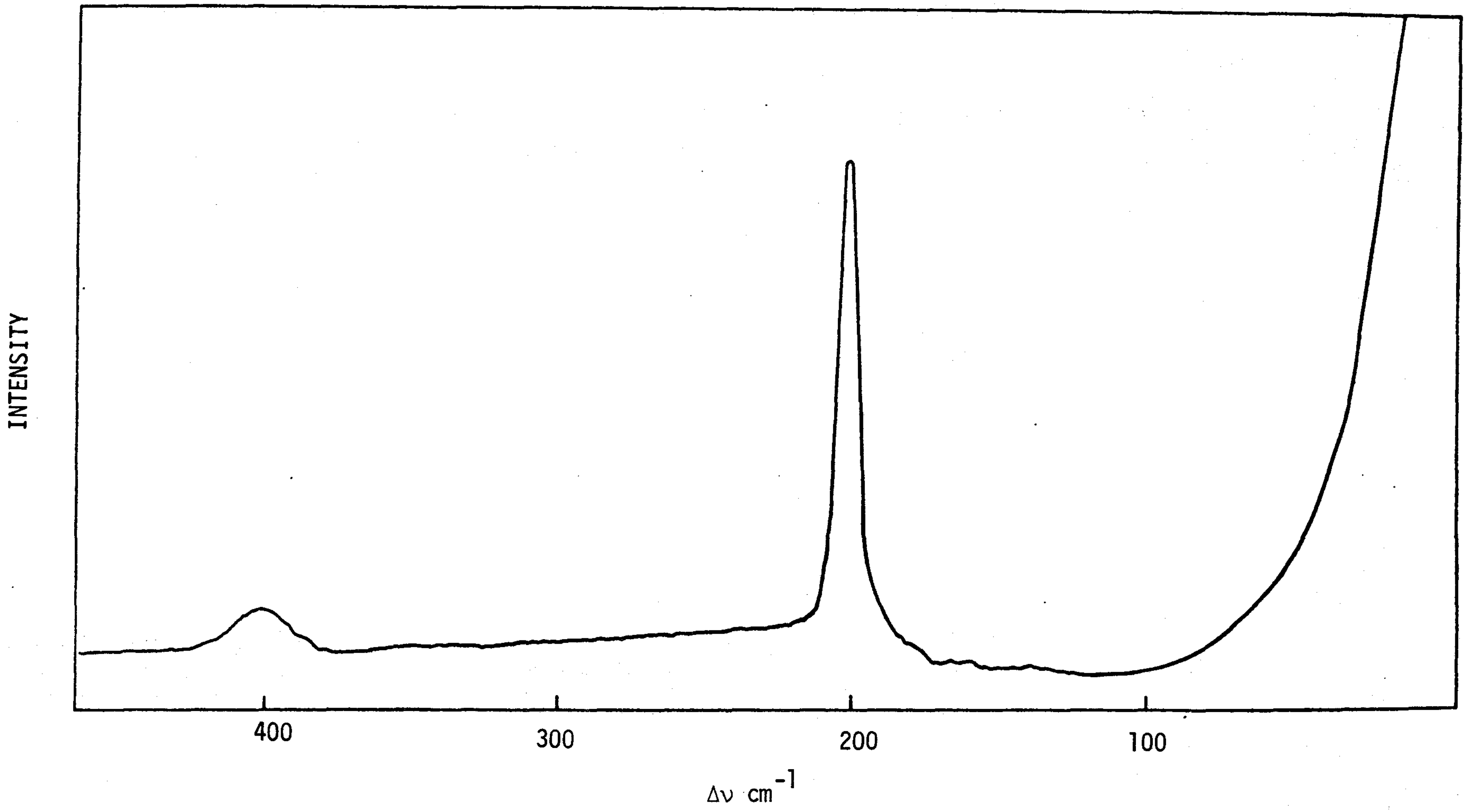


Figure 13. Raman spectrum of $Te_n^{n+}(SbF_6)_n^-$ at -90°C.

polyatomic cation of tellurium i.e. Te_n^{n+}. It was not possible to determine the degree of polymerisation of the cation in $Te_n^{n+}(SbF_6^-)_n$ by cryoscopy in HSO_3F or liquid SO_2 as the compound had a very limited solubility in these solvents. Cryoscopic measurements were also not possible in HF as the yellow compound disproportionated to give black elemental tellurium and presumably a higher oxidation state of tellurium, probably the +4 state.

(b) Preparation of $Te_n^{n+}(S_3O_{10}^{2-})_{n/2}$ by oxidation of tellurium with SO_3.

About 5 g of finely powdered tellurium was dissolved in 20 g of freshly distilled sulphur trioxide at room temperature with constant stirring. After a few minutes a red solid separated, which on further stirring, at room temperature for 5 days gave a bright yellow product. Excess sulphur trioxide was then removed by pumping at room temperature. The final product was a yellow amorphous powder which darkened rapidly on exposure to the atmosphere and instantly decomposed to give black tellurium when added to water.

Elemental analysis gave the following results: Found: Te, 48.89. The exact nature of the anion is not known; but tellurium analysis was consistent with the formulation, $Te_n^{n+}(S_3O_{10}^{2-})_{n/2}$ for which the calculated % tellurium is 49.92. A solution of this compound in 30% oleum gave an identical spectrum to that shown in Fig 12. The Raman spectrum of the solid had a characteristic frequency at 199 cm^{-1}. The composition confirms that the tellurium in the compound is in the +1 oxidation state. The magnetic susceptibility per g-atom of tellurium, after making the ligand corrections (67), was found to be -37×10^{-6} c.g.s. units. The cation is clearly diamagnetic, presumably therefore

Table V

Magnetic data* for the yellow $Te_n^{n+}(SbF_6^-)_n$ compound.

Temperature	$-\Delta W$	wt. of compound
°C	μg	= 0.45g
22	240	
0	240	$\chi_g = 77.5 \times 10^{-6}$
-42	240	(uncorrected for ligands)
-67	240	
-100	240	χ_g (corrected for ligands) $= 21 \times 10^{-6}$

*Quartz tube constant 1.44, diamagnetic correction for ligands taken from reference (67).

defined as c.g.s. units per 127.6 g tellurium.

odd electron species such as Te^{+} and Te_3^{3+} can be ruled out and the most likely possibilities would appear to be Te_2^{2+}, Te_4^{4+}, Te_6^{6+} or Te_8^{8+}.

(c) Preparation of $Te_n^{n+}(SO_3F^-)_n$ by oxidation of tellurium with $S_2O_6F_2$.

In an attempt to find the value of n for the yellow Te_n^{n+} cation, it was found that Te(1) fluorosulphate could be obtained as a stable solution in fluorosulphuric acid if it was kept at all times below -23°C. The details of preparation of this fluorosulphate together with its analysis are given in Chapter II. (page 19) The Raman spectrum of the concentrated yellow solution showed the characteristic frequency of Te_n^{n+} at 199 cm^{-1} (p. 43 Fig 9). Magnetic susceptibility data is recorded in Table VI. The susceptibility per g-atom of tellurium, after making diamagnetic corrections for the solvent and ligands, was found to be -36.6×10^{-6} c.g.s. units. The cation is clearly diamagnetic, therefore any odd electron species such as Te^{+}, Te_3^{3+} can be ruled out. Freezing point depression measurements on solutions in HSO_3F were made, in colloboration with O. C. Vaidya (66), by adding small amounts of the concentrated fluorosulphuric acid solution to fluorosulphuric acid in a cryoscope. The measured freezing points are given in Table VII and the results are shown in Fig 14 together with theoretical curves for the various possible species Te_2^{2+}, Te_4^{4+}, Te_8^{8+} and Te_n^{n+} where n approaches infinity. The results clearly indicate that the cation is not Te_2^{2+} but because of the considerable experimental difficulties in making these measurements the results are not sufficiently accurate to distinguish clearly between Te_4^{4+} and the higher polymers Te_6^{6+} and Te_8^{8+}.

Table VI

Magnetic data for the yellow Te_n^{n+} species in HSO_3F.

Temperature	$-\Delta W$	
°C	μg	
-100	770	$\chi_g^* = -36.6 \times 10^{-6}$ c.g.s.
-67	770	
-42	-776	
-16°C	-760	

Quartz tube correction 2.30, diamagnetic correction for the solvent 720 μg, diamagnetic correction for the ligands (67) 40.1 μg.

*Corrected value in g-atom of tellurium.

Table VII

Freezing point depression for yellow solution of tellurium in HSO_3F.

Concentration mole (Te)Kg^{-1}	θ, °C
0.0398	0.16
0.07567	0.31
0.0993	0.41
0.1336	0.55
0.1698	0.71

θ = freezing point depression

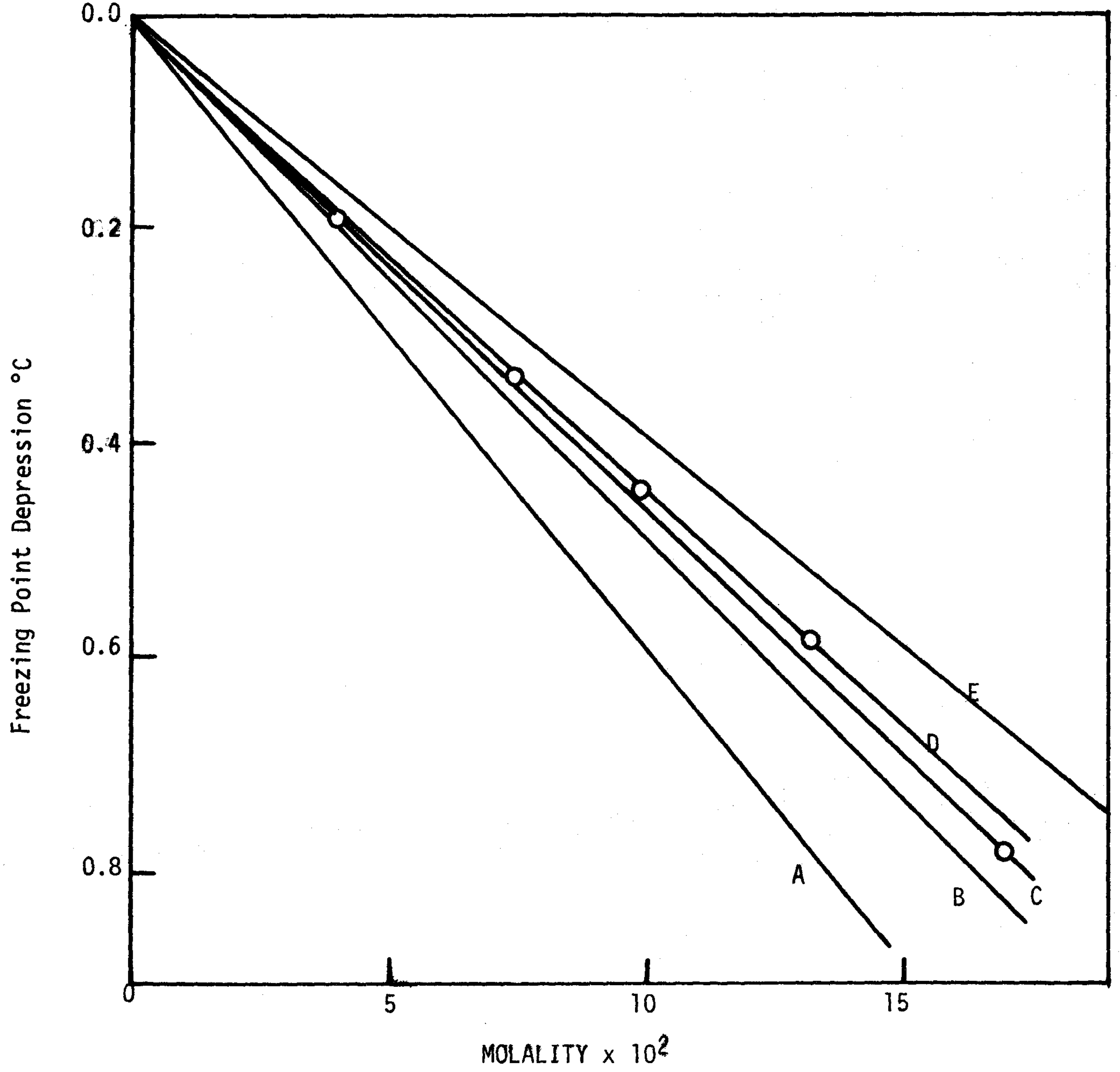


Figure 14. Freezing point depressions for solution of $TeSO_3F$ in HSO_3F. The straight lines are calculated freezing point curves for A, Te_2^{2+}; B, Te_4^{4+}; C, Te_6^{6+}; D, Te_8^{8+}; E, $Te_\infty^{\infty+}$.

4. Preparation of compounds containing the Te_{3n}^{n+} cation

(a) Preparation of $Te_{3n}^{n+}(AsF_6^-)_n$ by oxidation of tellurium with AsF_5.

In the work described in the preceding sections no evidence was obtained for a Te_8^{2+} species which might have been expected by analogy with S_8^{2+} (61) and Se_8^{2+} (60). We therefore further investigated the oxidation of tellurium with the rather mild oxidising agent AsF_5 in sulphur dioxide solution and using excess tellurium in an attempt to identify this lower oxidation state. However in experiments using 3 moles of AsF_5 for 8 moles of tellurium according to the equation

$$8\ Te + 3\ AsF_5 \longrightarrow Te_8AsF_6 + AsF_3$$

unreacted tellurium remained even after very long reaction times. Therefore further experiments were carried out using somewhat larger amounts of AsF_5.

In a typical experiment, arsenic pentafluoride (0.076 g, 0.0045 mole) was condensed on to the powdered tellurium (0.995g, 0.0078 mole) in sulphur dioxide at -196° and the mixture was allowed to warm up to room temperature. The solution acquired a deep red colouration after stirring for 3 hours at room temperature, but this colouration diminished considerably on standing for a further 24 h and a voluminous grey solid remained which proved to be insoluble in sulphur dioxide. The product was extracted several times with liquid sulphur dioxide to remove the soluble Te_4^{2+} species and then all the volatiles were removed under vacuum leaving a grey amorphous powder.

Elemental analysis gave the following results: Found Te, 67.41; As, 13.40; F, 19.20. Table VIII lists the analyses for various compounds that might be formed under the experimental conditions.

Table VIII

Calculated Analyses for Possible Compounds

Compound	% Te	% As	% F
Te_4AsF_6	72.99	10.71	16.30
Te_3AsF_6	66.96	13.10	19.94
Te_2AsF_6	57.46	16.87	25.67

The analysis is consistent with Te_3AsF_6 containing tellurium in +1/3 (Te_{3n}^{n+}) oxidation state. Magnetic susceptibility data is shown in Table IX. The magnetic susceptibility per-g atom of tellurium is found to be 7 x 10^{-6} c.g.s. units i.e. the cation is slightly paramagnetic. This paramagnetism is however much too small for an odd electron species such as Te_3^+ or Te_9^{3+} which can therefore be ruled out.

The infrared spectrum of the solid had a strong absorption at 700 cm^{-1} which showed the presence of AsF_6^- ion, ($CsAsF_6$[47], 699 cm^{-1}). It was not possible to obtain a Raman spectrum, presumably the dark compound absorbs most of the incident light. The ^{19}F n.m.r. spectrum of a solution in acetone gave a 1:1:1:1 quartet of AsF_6^-(δ_{CFCl_3}62 p.p.m., J_{As-F} = 920 Hz) cf.aqueous solution of $AsF_6^-$$\delta_{CFCl_3}$, 60.5 p.p.m., J_{As-F}= 930 Hz[64]). No suitable solvent for absorption spectra measurements was found as the compound is insoluble in liquid SO_2, reacts with BCl_3 and AsF_3 and is rapidly oxidised to Te_4^{2+} in 100% H_2SO_4 and in HSO_3F. A reflectance spectrum of the grey compound is shown in Fig. 15, only one broad peak centered at 485 nm^{-1} was observed.

Table IX

Magnetic* susceptibility data for $Te_{3n}^{n+}(AsF_6^-)_n$.

T	$-\Delta W$
°C	µg
22	230
0	235
-80	230
-120	230

wt. of compound = 0.29g

χ_g* (corrected for ligands)
= -65×10^{-6} c.g.s. units

---

*Quartz tube constant 1.44, diamagnetic correction for ligands (67) -72×10^{-6} c.g.s. units.

Since the cation is diamagnetic the most probable formulae are Te_6^{2+} or Te_{12}^{4+}. Assuming that the cation is Te_6^{2+} its formation from tellurium and AsF_5 is described by the equation

$$6Te + 3AsF_5 \longrightarrow Te_6^{2+}(AsF_6^-)_2 + AsF_3.$$

This +1/3 oxidation state is presumably the lower oxidation state reported by Divers and Shimose (p. 2 Chapter I) and by Bjerrum et al. (p. 38) although there is some discrepancy in colour between our material and that reported by Divers and Shimose (6). The later authors described the colour of their compound as dark brown, whereas our compound is grey. It is likely that the brown colour may have been caused by some red Te_4^{2+} as an impurity, because no mention is made of any attempt to purify the compound.

(b) Attempted preparation of $Te_{3n}^{n+}(SbF_6^-)_n$ by oxidation of tellurium with SbF_5.

An attempt was also made to prepare the Te_{3n}^{n+} cation from the reaction of elemental tellurium and antimony pentafluoride. In a typical reaction elemental tellurium(1.00g, 0.0078 mole) was reacted with SbF_5(0.737 g, 0.0034 mole) in liquid SO_2 at room temperature. The solution acquired a deep red colouration after stirring for 2 hours at room temperature, but this colour disappeared on stirring for a further 24 h and a voluminous grey solid remained which proved to be insoluble in liquid SO_2. A grey amorphous powder was obtained after removing all the volatiles. It is interesting to note that the same sequence of reactions has been observed for the oxidation of tellurium with AsF_5 (p. 59 this chapter). Evidently the same Te_{3n}^{n+} cation is

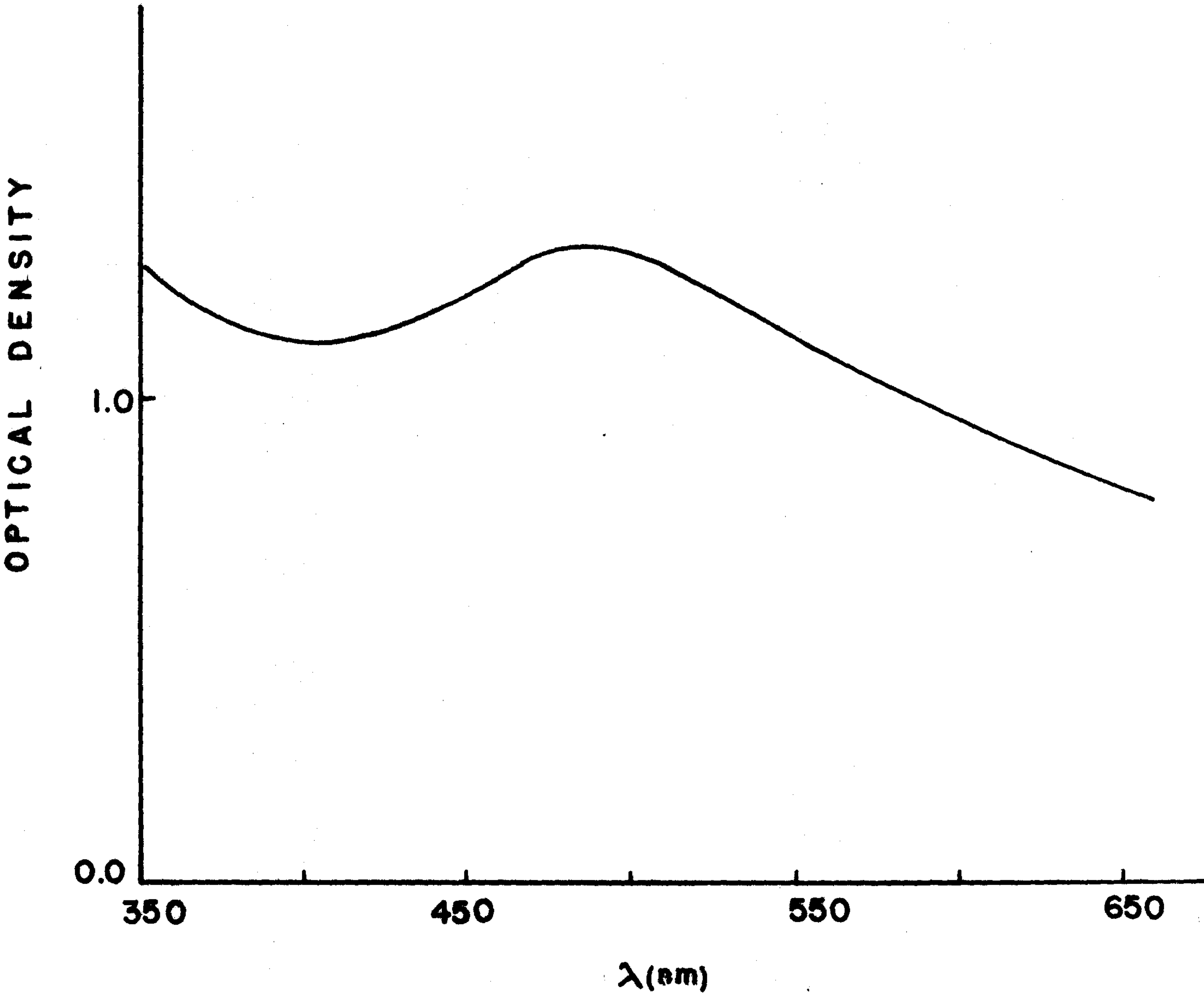


Figure 15. Reflectance spectrum of $Te_{3n}^{n+}(AsF_6^-)_n$.

produced by oxidation of tellurium with SbF_5, but mainly because of the difficulties involved in removing SbF_3 from the reaction product, it was not further investigated.

In the investigations of the polyatomic cations of selenium and sulphur we have found no analogous cations to the Te_{3n}^{n+} species. It may be significant that tellurium initially reacts with AsF_5 or SbF_5 to give the red Te_4^{2+} cation which subsequently reacts further with elemental tellurium to give the Te_{3n}^{n+} cation. This behaviour is in contrast to the stepwise oxidation of Se_8 or S_8 and suggests that the oxidation of Te_6^{2+} to Te_4^{2+} is more rapid than either the oxidation of tellurium to Te_6^{2+}, or the reduction of Te_4^{2+} by elemental tellurium.

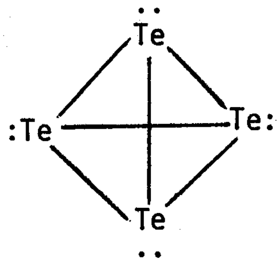
5. Structures.

From spectrophotometric and Raman evidence, it is concluded that the species Te_4^{2+} has a square planar structure analogous to the square planar Se_4^{2+} cation. Professor Corbett (68) very recently informed us that they have isolated two compounds, $Te_4(AlCl_4)_2$ and $Te_4(Al_2Cl_7)_2$ containing the Te_4^{2+} cation and have determined their crystal structures by X-ray diffraction studies. The structure of the Te_4^{2+} cation is indeed square planar. The Te-Te bond distance is 2.662 (5)°A.

The structure of the Te_n^{n+} and Te_{3n}^{n+} ions are clearly of great interest. The cryoscopic evidence for Te_n^{n+} rules out Te_2^{2+} but other species such as Te_4^{4+}, Te_6^{6+}, and possibly Te_8^{8+} might be expected to have the structures I, II or III and IV respectively shown in Fig. 16. Te_4^{4+} is isoelectronic with P_4 which is known to have a tetrahedral structure.

Te_6^{6+} could have either benzene-like or trigonal prism structure and Te_8^{8+} would be expected to have a cubic structure.

A plausible structure for Te_6^{2+} (Fig. 17) would be V and related resonance structures which are similar to that proposed for the "isoelectronic" S_4N_2 (69) molecule. This might also be called an "aromatic" 10π electron system and is clearly closely related to the hexagonal ring structure (6π electron system) proposed as a possible structure for Te_6^{6+}. Another possible structure would be VI; a bicyclic structure which is reminiscent of bicyclo (2, 2, 0) hexane.



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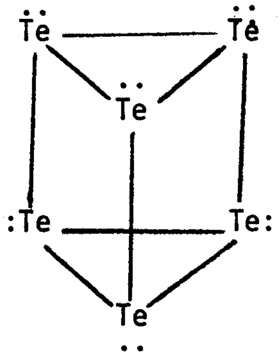

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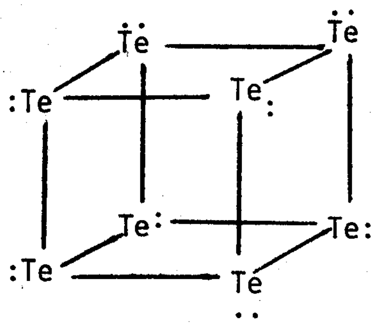

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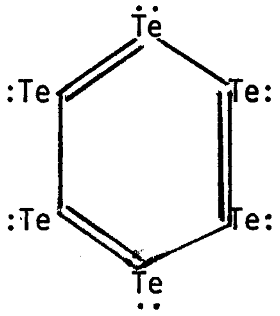
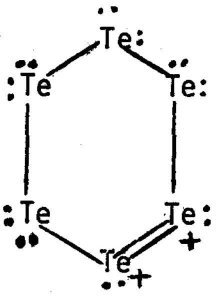
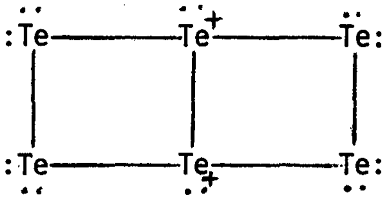


III

Figure 16. Possible structures for Te_n^{n+} cation.





VI

Figure 17. Possible Structures for Te_6^{2+} cation.

CHAPTER V

Section A

Compounds of sulphur in the +1/8, +1/4 and +1/2 oxidation states.

1. Introduction

In a preliminary investigation Barr et al. (70) showed that sulphur can be oxidised with $S_2O_6F_2$ in fluorosulphuric acid to give yellow, blue and almost colourless species which are in increasing order of oxidation state. Gillespie and Passmore (61) have recently studied the oxidation of sulphur with arsenic pentafluoride and isolated two compounds containing the red S_{16}^{2+} and the blue S_8^{2+} cations in the form of $S_{16}^{2+}(AsF_6^-)_2$ and $S_8^{2+}(AsF_6^-)_2$ respectively. Cryoscopic and conductometric measurements have given further confirmation that the red species is S_{16}^{2+} (71).

This chapter reports the results of an investigation of the oxidation of sulphur using antimony pentafluoride and peroxydisulphuryl difluoride as oxidising agents, which had the objective of preparing new compounds of S_{16}^{2+} and S_8^{2+} and in particular of identifying and obtaining compounds of the higher oxidation state for which preliminary evidence was obtained by Barr in these laboratories.

2. Preparation of $S_{16}(SbF_6)_2$ by the oxidation of sulphur with SbF_5.

In a typical experiment, sulphur (2.0g, 0.0078 mole) was stirred with antimony pentafluoride (2.54g, 0.0117 mole) in anhydrous HF at room temperature for three days. On removing the solvent under vacuum, a red solid was obtained. This was extracted several times with liquid

SO_2 leaving a white residue which was shown to be SbF_3. On evaporating the SO_2 extract under vacuum, a red solid was obtained (3.79g, 0.0077 mole).

Elemental analysis gave the following results: S, 51.75; Sb, 24.05; F, 23.95. Calculated for S_8 SbF_6: S, 52.06; Sb, 24.76; F, 23.18. The elemental analysis is consistent with S_8 SbF_6 containing sulphur in the +1/8 oxidation state. The absorption spectrum of the compound in HSO_3F was identical with that of the solution of $S_8/S_2O_6F_2$ at mole ratio of 16:1 in HSO_3F as shown in Fig. 18. The infrared spectrum of the solid had the characteristic strong band of SbF_6^- at 699 cm^{-1}.

The ^{19}F nmr spectrum of a solution of the red compound in HSO_3F had in addition to the solvent resonance, a strong resonance at 166 p.p.m. from HSO_3F which may be assigned to SbF_6^- and a weak spectrum characteristic of $SbF_5(SO_3F)^-$ resulting from solvolysis of SbF_6^- (44). The ^{19}F nmr of a solution, of the red compound, in SO_2 at -90°C had only one broad signal at $\delta_{CFCl_3} = 105.5$ ppm. The chemical shift of this broad resonance agree well with that observed previously for the SbF_6^-, in the compound $C_6H_5N(CH_3)_3^+SbF_6^-$ at $\delta_{CFCl_3} = 104.8$ ppm.

It is concluded that the red compound may be formulated as $S_{16}^{2+}(SbF_6^-)_2$ and is formed according to the equation,

$$2S_8 + 3SbF_5 \longrightarrow S_{16}^{2+}(SbF_6^-)_2 + SbF_3.$$

The e.s.r. spectrum of the red solution of $S_{16}(SbF_6)_2$ in liquid SO_2 was identical with that shown in Fig. 30b. There is a very strong resonance at g = 2.031, a very weak resonance at g = 2.018. The discussion on the e.s.r. spectrum is deferred until Chapter V, Section B.

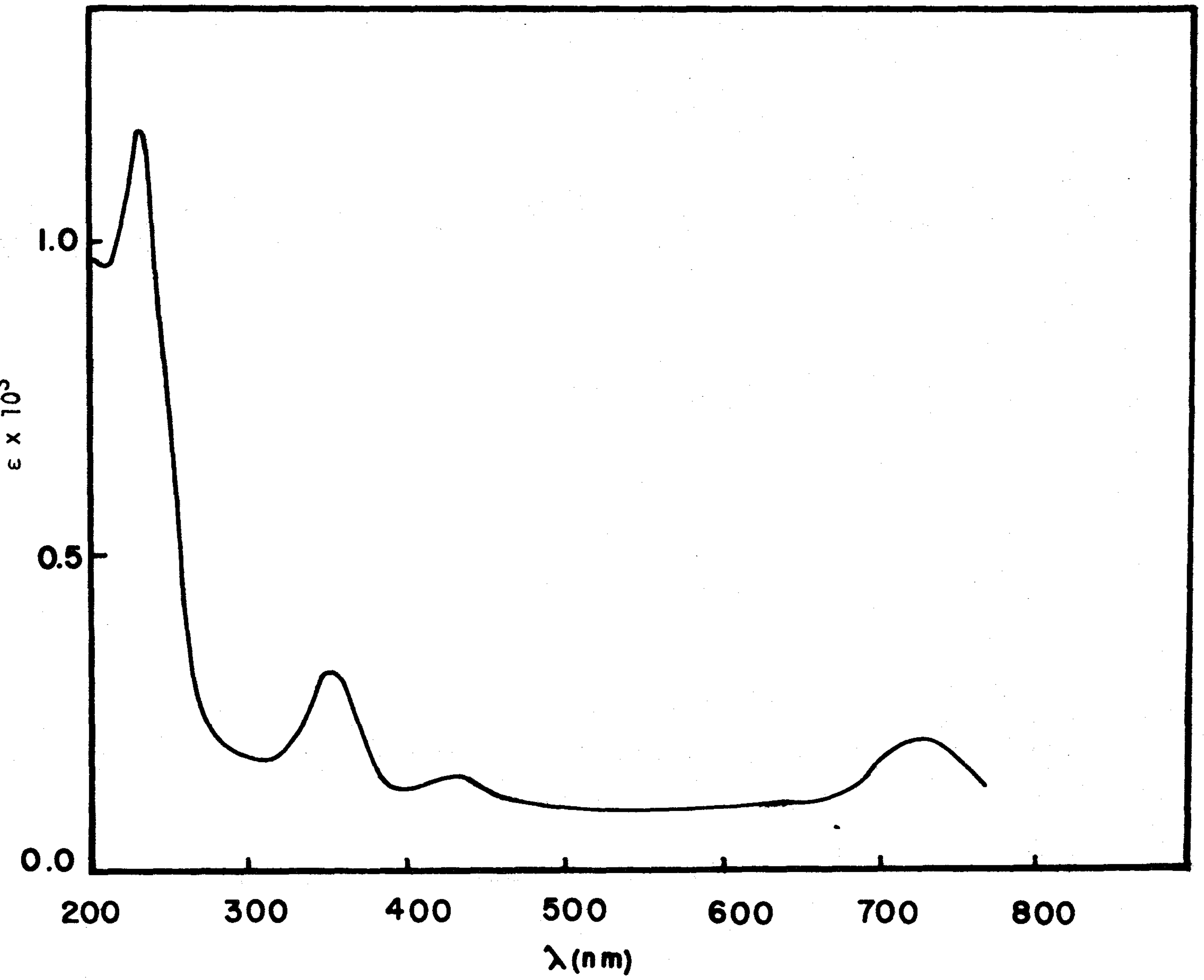


Figure 18. Absorption spectrum of the S_{16}^{2+} cation in HSO_3F.

3. Preparation of $S_8(Sb_2F_{11})_2$ by the oxidation of sulphur with SbF_5.

In a typical experiment antimony pentafluoride (10.4g, 0.048 mole) was added to powdered sulphur (2.09g, 0.00816 mole) in liquid SO_2 at -63°C and the mixture was allowed to warm to room temperature and then stirred for a few days. A very dark blue solution containing some dark solid was obtained. The blue solid was extracted four times with 50 ml of SO_2 until the remaining solid residue was white. This white solid was identified as antimony trifluoride. The SO_2 extract was evaporated under vacuum and a dark blue crystalline solid was obtained (7.33g, 0.0081 mole).

Elemental analysis gave the following results: S, 21.21; Sb, 40.71; F, 37.74. Calculated for $S_4(Sb_2F_{11})$: S, 22.03, Sb, 41.60; F, 36.00. The analysis is consistent with $S_4(Sb_2F_{11})$ containing sulphur in the +1/4 oxidation state. This material gave blue solutions in oleum and fluorosulphuric acid. The absorption spectrum of the solution in fluorosulphuric acid is shown in Fig. 19. The spectrum was identical with that reported (61) for $S_8(AsF_6)_2$ with an absorption maxima at 590 nm and an extinction coefficient of 2.32×10^3 mole (S) kg. cm^{-1}. (c.f. the extinction coefficient for the wavelength of maxima absorption of $S_8(AsF^-)_6$, 2.5×10^3 mole (S) kg. cm^{-1}). The infrared spectrum was essentially the same as that for $Se_4^{2+}(Sb_2F_{11}^-)_2$ discussed in Chapter III, Section 3(a). It contained a broad band at 650-770 cm^{-1} assigned to Sb-F stretching modes and a weaker band at 478 cm^{-1} which appears to be a stretching mode associated with the Sb-F-Sb bridge in $Sb_2F_{11}^-$. The ^{19}F nmr spectrum in liquid SO_2 at -90°C consisted of a multiplet at 92 ppm and a doublet of doublets at 111 ppm and a quintet at

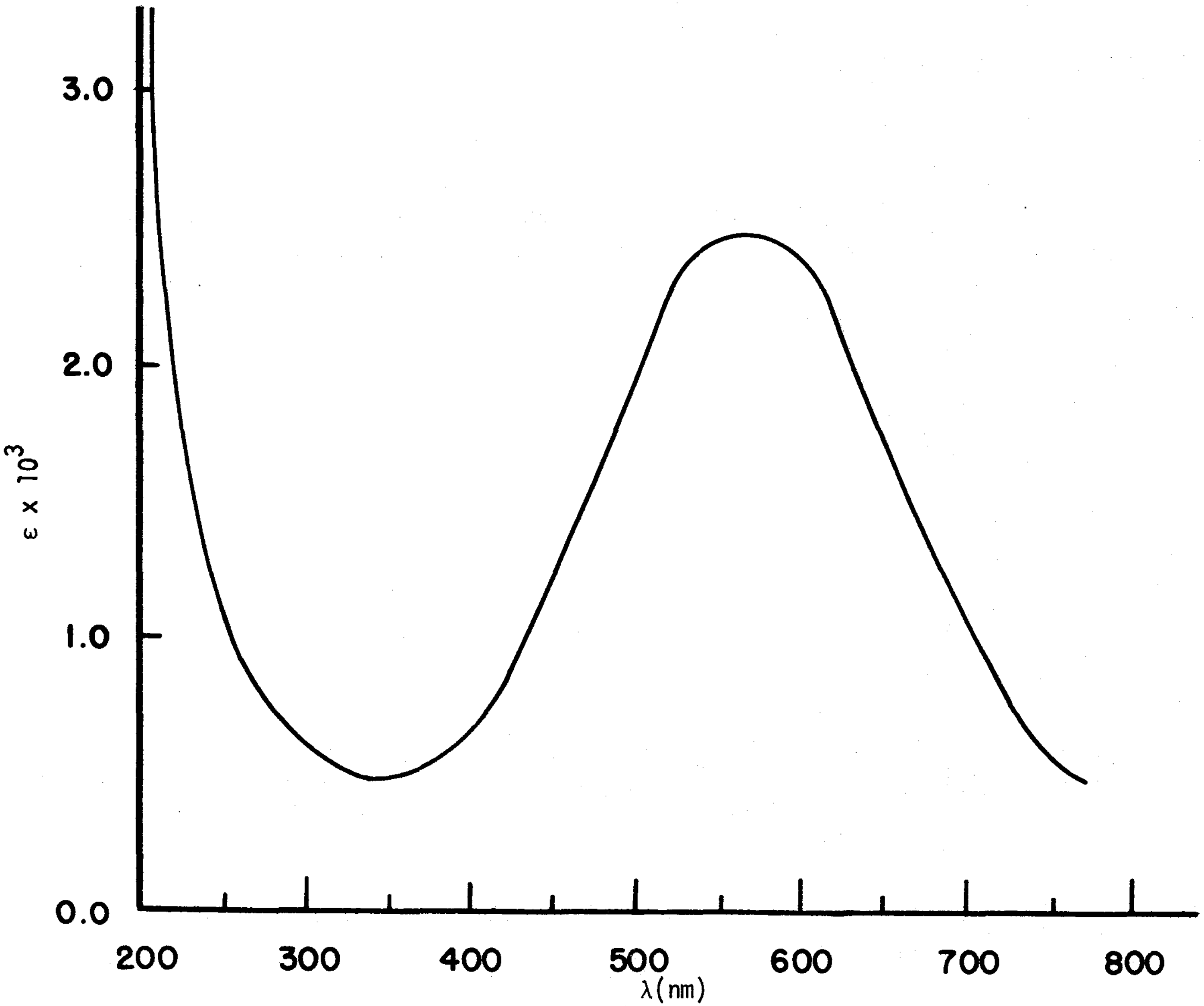


Figure 19. Absorption spectrum of the S_8^{2+} cation in HSO_3F.

133 p.p.m. from external $CFCl_3$ with coupling constants of 59 and 102 Hz. The spectrum was identical with that shown in Fig 5, and the chemical shifts and coupling constants agree well with those observed previously for $Sb_2F_{11}^-$ (46). The ^{19}F nmr spectrum of a solution in HSO_3F was identical to that shown in Fig. 4, it consisted of a single broad peak at 166 p.p.m. (from HSO_3F) which may be assigned to SbF_6^-, a doublet at 155 p.p.m. and a quintet at 183 p.p.m. with a coupling constant of 100 Hz which may be assigned to the $SbF_5SO_3F^-$ anion. The areas of the peaks were consistent with the formation of equal amounts of SbF_6^- and $SbF_5(SO_3F)^-$ according to the equation,

$$Sb_2F_{11}^- + SO_3F^- \longrightarrow SbF_6^- + SbF_5(SO_3F)^-.$$

It is concluded that the compound may be formulated as $S_8^{2+}(Sb_2F_{11}^-)_2$ and that it is formed according to the equation

$$S_8 + 5\ SbF_5 \longrightarrow S_8(Sb_2F_{11})_2 + SbF_3.$$

The e.s.r. spectrum of the blue solution of $S_8(Sb_2F_{11})_2$ in HSO_3F was identical with that shown in Fig. 30a. A strong resonance at g = 2.018 is observed. The discussion on e.s.r. spectroscopy is deferred to section B of this chapter.

4. Preparation of $S_4(SO_3F)_2$ by oxidation of sulphur with $S_2O_6F_2$.

In a typical experiment an excess of $S_2O_6F_2$ (10g, 0.05 mole) was condensed onto powdered sulphur (2g, 0.0078 mole) in liquid SO_2 at -196°C and the mixture was then allowed to warm up to -23°C through intermediate temperatures over a period of several days. An interesting sequence of colour changes was observed. At -63°C sulphur reacted very slowly to give the red species, however at -23°C a greenish blue solution was obtained. The reaction vessel was left at -23°C for a further few days until a deep greenish blue solution was obtained. At this point the reaction vessel was left at room temperature and the solution further stirred until a white crystalline product was obtained. Any excess $S_2O_6F_2$ and SO_2 were pumped off under vacuum leaving a white product. Careful temperature control was necessary as any rapid increase in the temperature resulted in an explosion. The white product was extremely hygroscopic, reacted with moist air to give the red species, and instantaneously decomposed to elemental sulphur when added to water.

Elemental analysis gave the following results: S, 57.93; F, 11.15; O, (by difference) 30.92. Table X shows the analyses expected for various compounds that might be formed under the experimental condition.

TABLE X

Calculated Analyses For Possible Compounds

Compound	S %	F %	O %
$S(SO_3F)_2$	41.74	16.52	41.74
$S(SO_3F)$	48.85	14.50	36.65
$S_2(SO_3F)$	58.8	11.62	29.50
$S_3(SO_3F)$	65.64	9.74	24.62

The analysis is clearly consistent with S_2SO_3F containing sulphur in +1/2 oxidation state. The solid was found to be dimagnetic with a g-atom susceptibility of -24×10^{-6} c.g.s. units. By analogy with the previously reported Se_4^{2+} and Te_4^{2+} cations (43, 58) it is reasonable to formulate this compound as $S_4(SO_3F)_2$. It did not give a stable

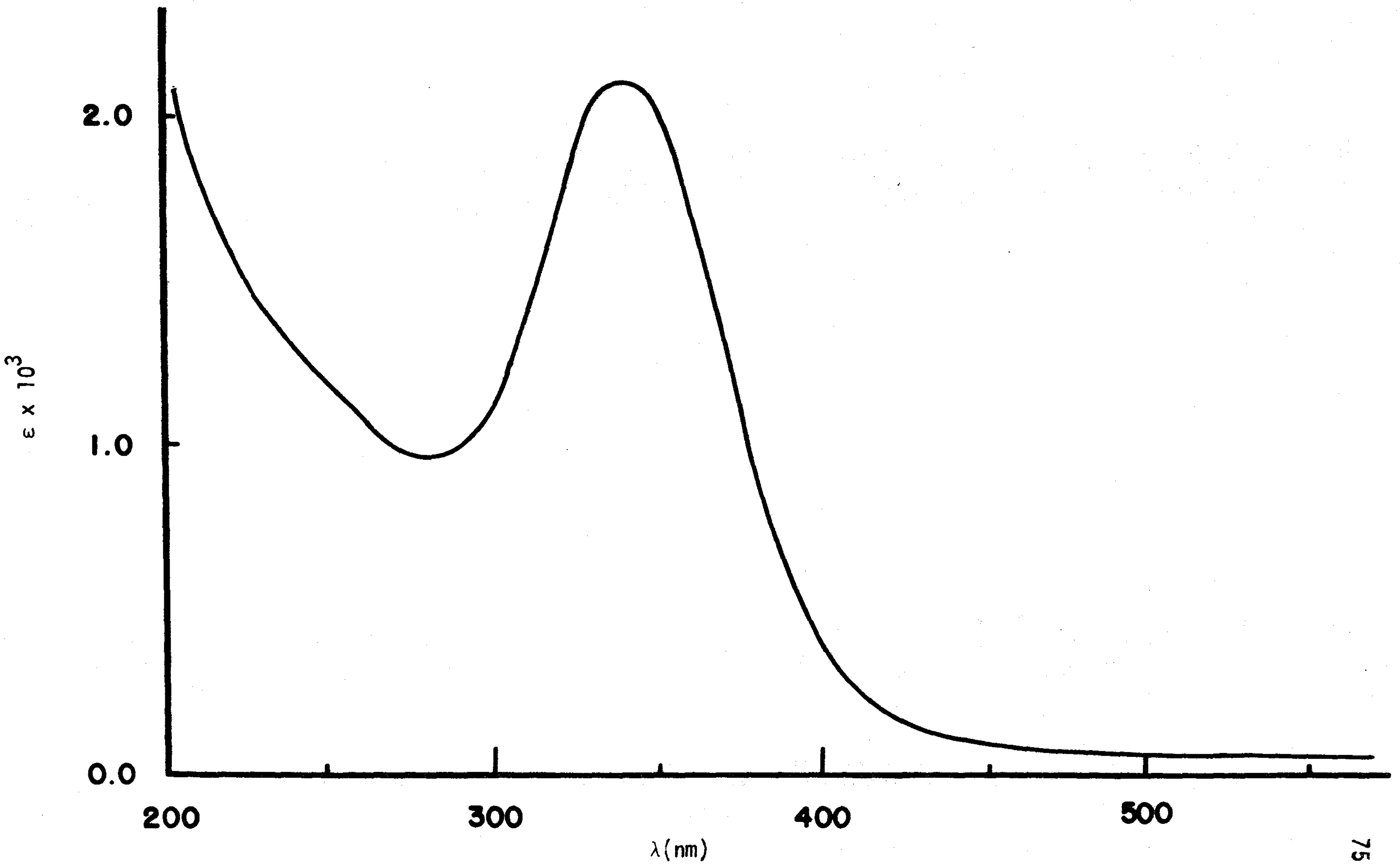


Figure 20. Absorption spectrum of the S_4^{2+} cation in HSO_3F-SbF_5.

solution in HSO_3F as the characteristic peak of the blue S_8^{2+} cation appeared and increased in intensity with time. However a stable colourless solution was obtained in HSO_3F - SbF_5 which had the absorption spectrum shown in Fig. 20, with a strong peak at 330 nm and a weak poorly resolved peak at 280 nm.

The absorption spectra of Te_4^{2+}, Se_4^{2+} and S_4^{2+} are very similar in shape, each having a strong peak at longer wavelengths and a weak peak at shorter wavelengths, the λ_{max} decreases steadily in the series Te_4^{2+}, Se_4^{2+} and S_4^{2+} as shown in Table XI. This similarity lends further support to the identification of the S_4^{2+} ion. The Raman frequencies of $S_4(SO_3F)_2$ are given in Table XII together with the assignments made on the basis of a predominantly ionic model i.e. $S_4^{2+}(SO_3F)_2^-$ containing a square planar cation similar to the cations Se_4^{2+} (49) and Te_4^{2+} (68). The anion vibrations are assigned using previously published assignments for SO_3F^- (73, 74, 75). The frequency 584 cm^{-1} assigned to the A_{1g} mode of the square planar S_4^{2+} cation is slightly higher than the frequency of the S-S stretch in S_2Cl_2 76,77 (540 cm^{-1}) which presumably contain a single bond between the sulphur atoms, just as the frequency (327 cm^{-1}) assigned to the A_{1g} mode of Se_4^{2+} is a little higher than the Se-Se stretching frequency (290 cm^{-1}). The frequencies530 and 330 cm^{-1} assigned to the B_{1g} and B_{2g} respectively are reasonable since they bear approximately the same relationship to the A_{1g} mode of the S_4^{2+}, as do the similar frequencies of the Se_4^{2+} cation (B_{1g} 309; B_{2g}, 188 cm^{-1}) to the A_{1g} vibration of that cation. The weak band observed at 460 cm^{-1} is not easily assignable to an anion frequency. It may be the E_u mode of the cation, which though Raman inactive

TABLE XI

Comparison of the Absorption Spectra of Te_4^{2+}, Se_4^{2+} and S_4^{2+} Cations

Cation	$\lambda_{max.}$ (nm)	
	Strong	Weak
Te_4^{2+}	510	420
Se_4^{2+}	410	320
S_4^{2+}	330	∿280

TABLE XII

Raman Frequencies of $S_4^{2+}(SO_3F^-)_2$

Relative* Intensity	Frequency Shift (cm^{-1})	Assignment S_4^{2+}	SO_3F^-
2	300	Lattice Vib.	
2	313		
16	330	$\nu_3(B_{2g})$	
15	382		$\nu_6(e)$
5	460	$\nu_4(E_u)$	
10	530	$\nu_2(B_{1g})$	
50	564		$\nu_3(a_1)$
100	584	$\nu_1(A_{1g})$	
75	591		$\nu_5(e)$
5	635		
13	709		
13	866		$\nu_2(a_1)$
39	1070		$\nu_1(a_1)$
35	1230		$\nu_4(e)$
40	1240		
10	1303		
6	1434	?	

---

*Peak height

in an isolated (centrosymetric) M_4^{2+} cation could become weakly allowed in the Raman if the symmetry of the cation is lowered by the site symmetry in the solid. The E_u mode of $Se_4^{2+}(SO_3F^-)_2$ is observed weakly in the Raman (49).

5. Attempted Preparation of $S_4(SbF_6)_2$ by Oxidation of Sulphur with SbF_5.

In a typical experiment a large excess of SbF_5 (120g, 0.55 mole) was reacted with elemental sulphur (3g, 0.012 mole) at 140° for several days during which time the dark blue had become colourless. After removal of the excess SbF_5 by heating to 100° under vacuum, a white solid was obtained, which turned blue when exposed to moist air and decomposed to elemental sulphur when reacted with water.

The white product was insoluble in liquid SO_2 and decomposed to the blue species on prolonged heating at 100° under vacuum. The reduced product which was presumably the compound $SbF_5.SbF_3$ cannot be separated from the white sulphur compound by either SO_2 extraction or sublimation. The elemental analysis of the white compound in such a case would have no significance. It is perhaps worth mentioning that the white compound which Ruff et al. (24) and Peacock et al. (25) obtained from the reaction of sulphur and excess SbF_5 is presumably a mixture. The compound had slight solubility in HSO_3F to give the characteristic absorption of S_4^{2+} at 330 nm as shown in Fig. 20. Mainly because of the difficulties involved in separating $SbF_5.SbF_3$ from the reaction product, it was not further investigated.

6. Attempted Preparation of $S_4(AsF_6^-)_2$ by Oxidation of Sulphur with AsF_5.

A large excess of AsF_5 (20.4g, 0.12 moles) was condensed onto finely powdered sulphur(3.0 g, 0.012 mole) in a thick walled pyrex glass tube in liquid SO_2 at -196°C. The reaction was allowed to stir at room temperature for a few days. A deep blue solution containing blue solid was obtained. On further heating this solution at 80°C for two weeks, there was no apparent change in the blue colour. It is clear that the S_4^{2+} ion cannot be obtained using AsF_5 as an oxidising agent; presumably AsF_5 is not as strong an oxidising agent as SbF_5.

7. Structures

(a) S_4^{2+} cation.

On the basis of the similarity of the absorption spectra and Raman spectra of the S_4^{2+} cation to those of Te_4^{2+} and Se_4^{2+}, it seems very probable that S_4^{2+} has a square planar structure. Recently Stephens (63) has pointed out the similarities of the magnetic circular dichroism of S_4^{2+} with those of the square planar Se_4^{2+} (51) and Te_4^{2+} (68) cations. He concluded, as we do, that S_4^{2+} has a square planar structure.

(b) S_8^{2+} cation.

The crystal structure of $S_8^{2+}(AsF_6^-)_2$ has been recently determined by Davies et al. (80) by X-ray diffraction. The configuration of the S_8^{2+} is that of a ring with approximate m symmetry and is similar to that of the Se_8^{2+} described in Chapter III (p. 37). The structure of S_8^{2+} is shown in Fig. 21, together with a list of bond lengths and bond angles. The most significant difference between the Se_8^{2+} structure and the S_8^{2+} structure is that the only short cross-ring distance in Se_8^{2+} is Se (1) - Se (5) which has a bond length of 2.83°A comparable to the S(1) - S(5) in S_8^{2+}. However in S_8^{2+} there are a number of other S-S distances (listed average S-S bond length around the ring = 2.037°A

$<S_2S_3S_4$ = $<S_6S_7S_8$ = 93°

all other angles = 102°

S_1S_5 = 2.86°A

S_8S_6 = 3.00°A

S_2S_4 = 2.94°A

S_1S_7 = 3.07°A

S_5S_7 = 3.09°A

S_3S_1 = 3.14°A

S_3S_5 = 3.17°A

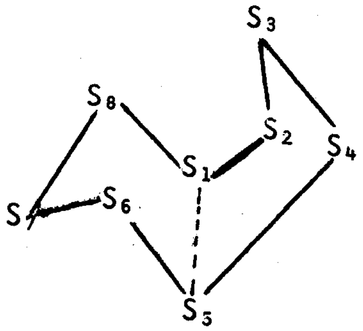
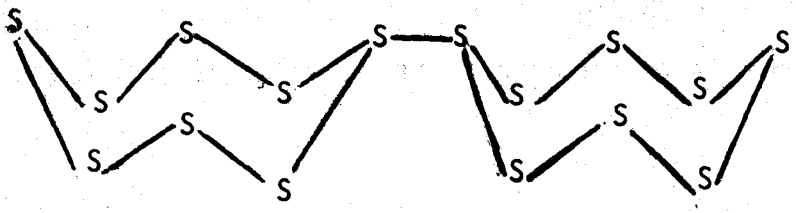


Fig. 21. Structure of S_8^{2+} cation.

in Fig. 21) smaller than the Van der waal's non-bonding interaction of 3.3°A, and presumably therefore there is some interaction between these sulphur atoms.

(c) S_{16}^{2+} cation.

Structural data on the S_{16}^{2+} ion is as yet not available. A plausible structure might be two S_8 rings joined by a single S-S bond.



CHAPTER V

Section B

Solutions of Sulphur in Oleum: UV-Visible Absorption and electron-spin resonance spectra of solutions of sulphur in oleum.

1. Introduction

A detailed historical introduction to the coloured solutions of sulphur in oleum is given in Chapter I (P. 2). The nature of the coloured solutions obtained in sulphur trioxide had remained unsolved ever since their discovery by Buchloz in 1804. Brown, greenish-blue and deep blue solutions have been observed in various concentration of oleum. The species responsible for the blue colour have been variously identified as S_2O_3 (5, 20), S_2(8), the radical ion $[X_2S\ \text{-}SX_2]^+$ (26), and a species designated as S_x (30).

This chapter reports the study of the species formed in solutions of sulphur in sulphuric acid and oleum having the composition in the range, 95% H_2SO_4 to 100% SO_3. The solutions were also investigated for radical species by e.s.r. spectroscopy.

2. Results

(a) Solutions of Sulphur in 95 to 100% H_2SO_4.

A saturated solution of sulphur in 95 to 100% H_2SO_4 at room temperature was found to be colloidal as evident by the observed Tyndall effect. The colloidal solution gave an absorption spectrum (Fig. 22b) which consisted of three bands at 225 nm, 260 nm and 320 nm. On heating elemental sulphur in this solvent for 12 hours at 75°C, the clear solution gave a spectrum which was identical to the spectrum of sulphur dissolved in hexane. The spectra are shown in Fig. 23.

(b) Solution of Sulphur in 1-2% Oleum.

A saturated colourless solution of sulphur in 1-2% w/w oleum at room temperature gave an absorption which consists of three bands at 235 nm, 260 nm and 320 nm. (Fig. 22a). The solutions were still colloidal, but a new peak at 235 nm appeared in place of the 225 nm peak of the S_8 molecule.

(c) Solutions of Sulphur in 5% oleum.

After 6 h at room temperature a 1.2×10^{-4} M solution of sulphur in 5% w/w oleum gave a very pale yellow solution. The spectrum (Fig. 24 (a)) of the freshly prepared solution had absorptions at 235, 350, 430 and 720 nm. The intensity of these peaks slowly decreased with time, with a corresponding increase in that of the SO_2 band at 280 nm. The results are summarised in Fig. 24. A new weak peak at 590 nm appeared after 6 hours.

(d) Solutions of Sulphur in 10% oleum.

A freshly prepared 9×10^{-5}M solution of sulphur in 10% w/w oleum had a greenish colour which with time changed to a light blue colour. The intensity of the absorption band at 235, 330, 430 and 590 nm decreased, with a corresponding increase in the SO_2 peak at 280 nm. The results of the changes of the spectra with time are summarised in Fig. 25.

(e) Solutions of Sulphur in 15% oleum.

A freshly prepared 4 x 10^{-5}M solution of sulphur in 15% w/w oleum yielded a blue solution in an hour at room temperature. The absorption bands of the freshly prepared solution were at 330, 280 and 590 nm (Fig. 25a). The intensity of the 330 nm band decreased rapidly with an initial increase of the 590 nm band. The results of the changes of the spectra with time are summarised in Fig. 25. After a period of 5 weeks the blue solution had become colourless and only the SO_2 peak at 280 nm could be observed.

(f) Solutions of Sulphur in 30% oleum.

A freshly prepared 2.3 x 10^{-5}M solution of sulphur in 30% w/w oleum gave a blue solution which had absorption bands at 330 nm, 590 nm and a relatively weak peak of SO_2 at 280 nm. (Fig. 27a). The 330 nm peak rose in intensity at the expense of the 590 nm peak. After about 5 weeks the blue solution became colourless only showing the 330 nm peak and the SO_2 peak at 280 nm. The results of the changes of the spectra with time are recorded in Fig. 27.

(g) Solutions of Sulphur in 45% oleum.

A freshly prepared 1.4 x 10^{-4}M solution of sulphur in 45% w/w oleum gave a blue solution which had the absorption bands at 330 nm and 590 nm and a relatively weak peak of SO_2 at 280 nm (Fig. 28a). The intensity of the 330 nm band increased, withacorresponding decrease in intensity of the 590 nm peak. After about 2 weeks the blue solution had become colourless, showing only the 330 nm peak and the SO_2 peak at 280 nm. The spectral changes with time are given in Fig. 28.

(h) Solution of sulphur in 65% oleum.

A freshly prepared 1.25 x 10^{-5}M solution of sulphur in 65% w/w oleum gave a blue solution which had absorptions at 330 nm and 590 nm

(Fig. 29a). The intensity of the 590 nm peak gradually decreased, with a corresponding increase of the 330 nm peak, and a new peak of SO_2 at 280 nm developed slowly. After a few days, the solution appeared colourless. The spectral changes with time are summarised in Fig. 29.

(i) Reaction of Sulphur with Liquid Sulphur Trioxide.

In a typical experiment, liquid SO_3 (20g, 0.25 mole) was distilled onto powdered sulphur (1g, 0.031 mole) 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 in contact with sulphur, the latter turned bright red which 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 and any attempt to remove the last traces of SO_3 under vacuum resulted in a complete decomposition of the product to elemental sulphur. The SO_3 moist product was dissolved in 65% w/w oleum and the absorption spectrum of this solution was recorded as fast as possible. The resulting spectrum was identical to that shown in Fig. 29a.

3. Electron-Spin Resonance of Solution of Sulphur in Oleum.

A large amount of sulphur was dissolved in 30% oleum to give a red solution which had two signals, a very strong signal at $g = 2.031$, a very weak signal at $g = 2.018$. The red solution was then further reacted with 30% oleum to give a green solution which had two e.s.r. absorptions, at $g = 2.018$ and $g = 2.031$. The intensities of these signals were proportional to the concentrations of the blue and the red species respectively. In a third experiment, sulphur was allowed to react with 30% oleum until the solution was blue. This solution had only one e.s.r. signal at g = 2.018. The blue solutions of sulphur in 65% w/w oleum gave an identical e.s.r. signal at g = 2.018 (Fig. 30a).

DISCUSSION

The absorption spectrum of the saturated colourless solutions of sulphur in 95-100% H_2SO_4 after heating at 75°C for 12 h was identical with that of the sulphur dissolved in hexane, (Fig. 23), evidently sulphur is present as S_8 molecules in 95-100% H_2SO_4. The spectra in 1-2% w/w oleum at room temperature were still colloidal (Fig. 22a), but a new strong peak at 235 nm was observed. A clear pale yellow solution obtained from sulphur in 5% w/w oleum had the absorption bands shown in Table XIII. This table also compares these absorption peaks with those of the S_{16}^{2+} cation (This chapter, p. 70). It is clear that the species present in 5% w/w oleum is the S_{16}^{2+} cation, which must be formed by the oxidation of sulphur by SO_3. It is evident that oxidation is taking place from the observation of the SO_2 peak at 280 nm. Lux and Bohm (30) had previously observed a peak at 233 nm in 5% w/w oleum which they attributed to the compound $S_8.nSO_3$. The spectral changes are shown in Figure 24. The intensity of the 235 nm peak decreased with time, with a corresponding increase in the 590 nm and 280 nm (SO_2) peaks. The absorption peak at 590 nm may be assigned to the S_8^{2+} cation which is produced by further oxidation of S_{16}^{2+}.

The solution of sulphur in 10% w/w oleum showed the presence of the S_{16}^{2+} cation and had other weak absorptions at 590 nm and 330 nm (Fig. 25). These bands have been assigned to the S_8^{2+} and S_4^{2+} ions

TABLE XIII

Comparison of the absorption spectra of the pale yellow solutions of sulphur in 5% oleum and that of the S_{16}^{2+} cation.

Solution	Absorption bands (nm)			
pale yellow solution of sulphur in 5% oleum	235(s)	350(w)	430(w)	720(m)
*yellow solution of S_{16}^{2+} in HSO_3F	235(s)	350(w)	430(w)	720(m)
*yellow solution of $S_8/S_2O_6F_2$ in HSO_3F	235(s)	350(w)	430(w)	720(m)

*Concentrated solutions are orange-red in colour.

respectively [see Chapter V, Section A (P.72,75)].The spectral changes with time may be qualitatively explained as follows:

$$\begin{tikzcd}
S_{16}^{2+} \arrow[r, dash, "v. fast"] & S_8^{2+} \arrow[r, "fast"] & S_4^{2+} \arrow[d, "fast"] \\
 & & S_8^{2+} + SO_2
\end{tikzcd}$$

The S_{16}^{2+} cation is oxidised to S_8^{2+} cation, which is further oxidised to the S_4^{2+} cation. The latter is however not stable in 10% oleum and disproportionates to S_8^{2+} and SO_2.

The spectrum of the freshly prepared blue solution of sulphur in 15% w/w oleum had only peaks corresponding to the S_8^{2+} and S_4^{2+} cations. The intensity of the S_4^{2+} peak decreased considerably faster than that of the S_8^{2+} peak, and the intensity of the SO_2 peak increased gradually with time as shown in Fig. 26. It is clear that the S_4^{2+} cation is not stable in 15% oleum and disproportionates to give S_8^{2+} and SO_2.

The spectra given in Fig. 27 show that in 30% w/w oleum only S_4^{2+} and S_8^{2+} are present initially. The intensity of the S_4^{2+} peak increases with time at the expense of the S_8^{2+} peak. In this medium S_4^{2+} appears to be much more stable with respect to disproportionation. A weak SO_2 peak appears after approximately 12 h and very slowly increases in intensity, with a corresponding decrease in the S_4^{2+} intensity. As no other new peaks appear in the spectrum, it seems that S_4^{2+} is slowly oxidised to SO_2.

The absorption spectra given in Figs. 28 and 29 show that both S_4^{2+} and S_8^{2+} are formed in 45% and 65% oleum composition. The blue solutions became colourless after a few days and the SO_2 peak appeared at 280 nm. The spectral changes that occur with time may be described qualitatively by the following scheme:-

$$\begin{tikzcd}
S_8 \arrow[r, "\text{v.v. fast}"] & S_{16}^{2+} \arrow[r, "\text{v. fast}"] & S_8^{2+} \arrow[r, "\text{fast}"] & S_4^{2+} \arrow[d, "\text{v. slow}"] \\
 & & & SO_2
\end{tikzcd}$$

A solution of the greenish-blue compound "S_2O_3" that was formed by the reaction of liquid SO_3 and sulphur, in 65% oleum gave an absorption spectrum which consisted of bands at 330 nm and 590 nm. The absorptions at 330 nm and 590 nm are characteristic of the S_4^{2+} and S_8^{2+} cations respectively. The spectrum was identical with that shown in Fig. 29a. It is clear that the compound, which had been previously formulated (5, 20) as "S_2O_3", is a mixture containing S_4^{2+} and S_8^{2+} cations. The common anion may be $HS_2O_7^-$.

The e.s.r. results are shown in Fig. 30. The red solution of sulphur obtained by reacting excess sulphur with 30% oleum gave a strong absorption at g=2.031, and a very weak absorption at g = 2.018. The blue solutions of sulphur obtained by dissolving sulphur in a large amount of 30% oleum had a strong absorption at g = 2.018. On adding some of the red solution to this blue solution the signal at g = 2.018 decreased in intensity and that at g = 2.031 increased in intensity. Since one absorption band increases when the other decreases they must be caused by two different radicals. It seems clear that the g = 2.031 absorption can be attributed to a radical species arising from S_{16}^{2+} and the absorption at g = 2.018 can be attributed to a radical species arising from the S_8^{2+} cation. Both S_{16}^{2+} and S_8^{2+} cations were found to be very slightly paramagnetic, however the paramagnetism was very much less than would be expected for radical species such as S_8^+ or S_4^+ respectively. It seems reasonable to suppose that only small amounts of the radicals S_8^+ and S_4^+ are present which are presumably in equilibrium with S_{16}^{2+} and S_8^{2+} respectively,

$$S_{16}^{2+} \rightleftharpoons 2S_8^+ \quad \text{and} \quad S_8^{2+} \rightleftharpoons 2S_4^+$$

It seems likely that the first stage of oxidation of S_8 involves the loss of one electron to give the S_8^+ radical ion which then dimerises extensively leaving only a small equilibrium concentration of S_8^+. On further oxidation S_8^+ presumably loses another electron to become S_8^{2+} which appears to have a slight tendency to dissociate into S_4^+ radical ions. On further oxidation S_4^+ presumably loses another electron to become S_4^{2+} which appears to have no tendency to dissociate into radical ions.

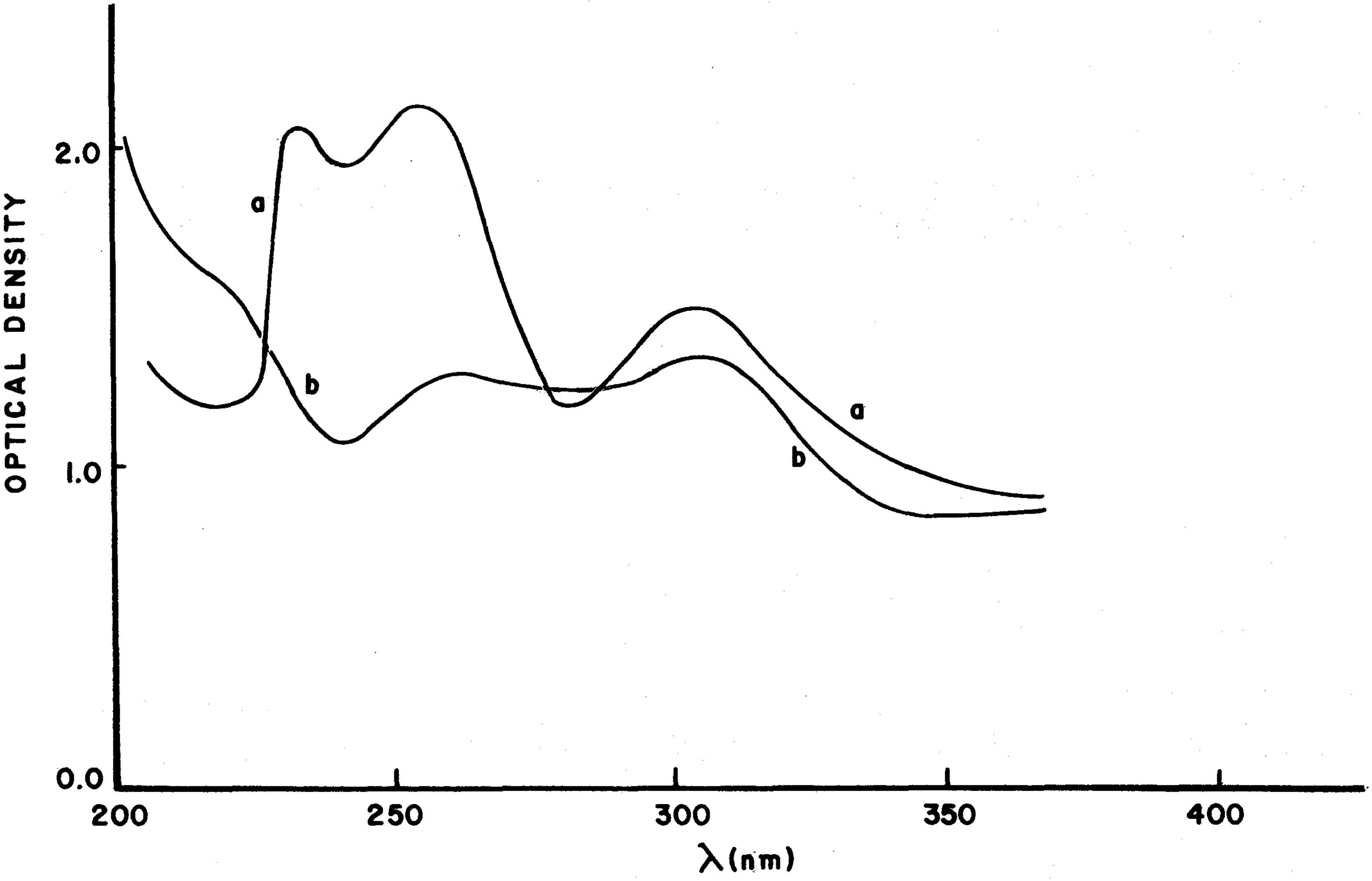


Figure 22. Absorption spectra of saturated solutions of sulphur in (a) 95 to 100% H_2SO_4 and (b) 1 to 2% w/w oleum.

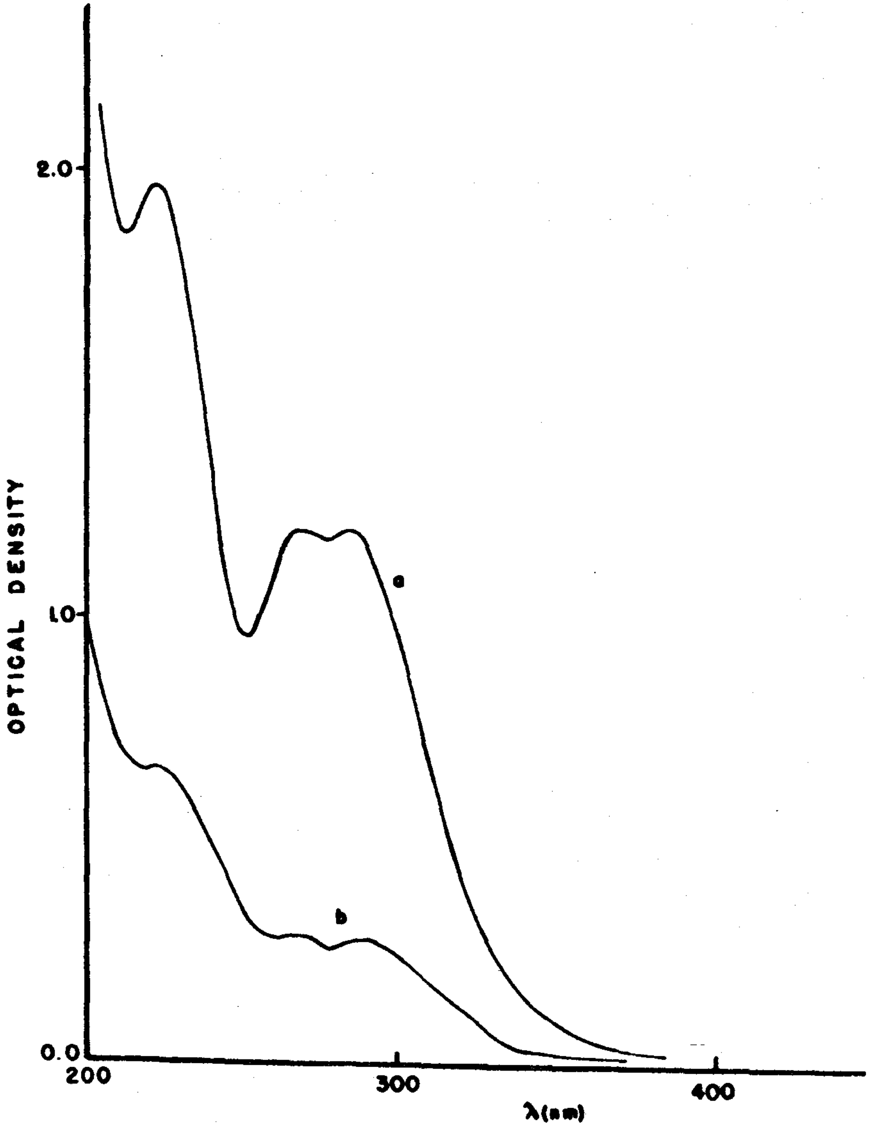


Figure 23. Absorption spectra of solutions of sulphur (S_8) in (a) hexane (b) 95 to 100% H_2SO_4 after heating at 75°C for 12 hours.

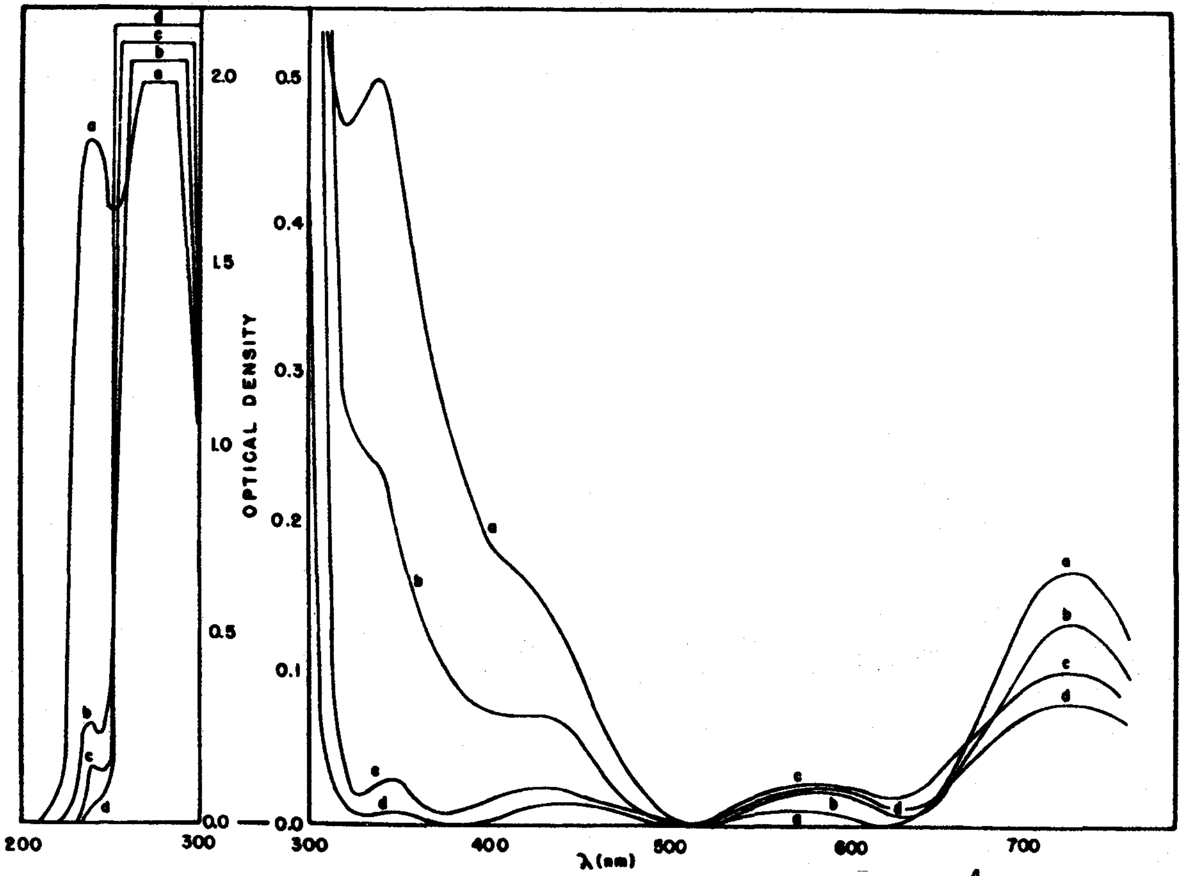


Figure 24. Time dependent absorption spectra of a 1.2 x 10^{-4} M solution of sulphur in 50% w/w oleum. Time from preparation: a) 1/2 h, b) 6 h, c) 17 h, d) 23 h.

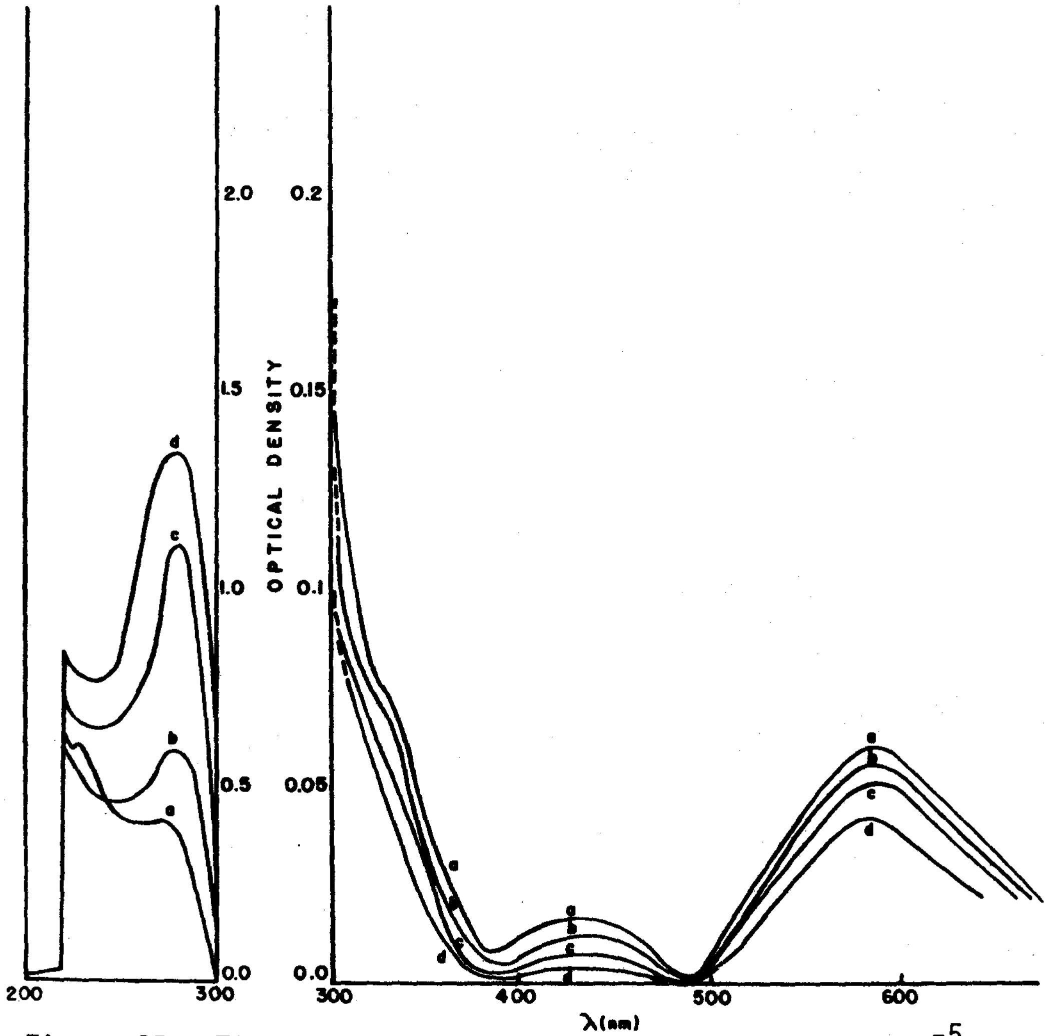


Figure 25. Time dependent absorption spectra of a 9 x 10^{-5}M solution of sulphur in 10% w/w oleum. Time from preparation: a) 1/2 h, b) 7 h, c) 17 h, d) 28 h.

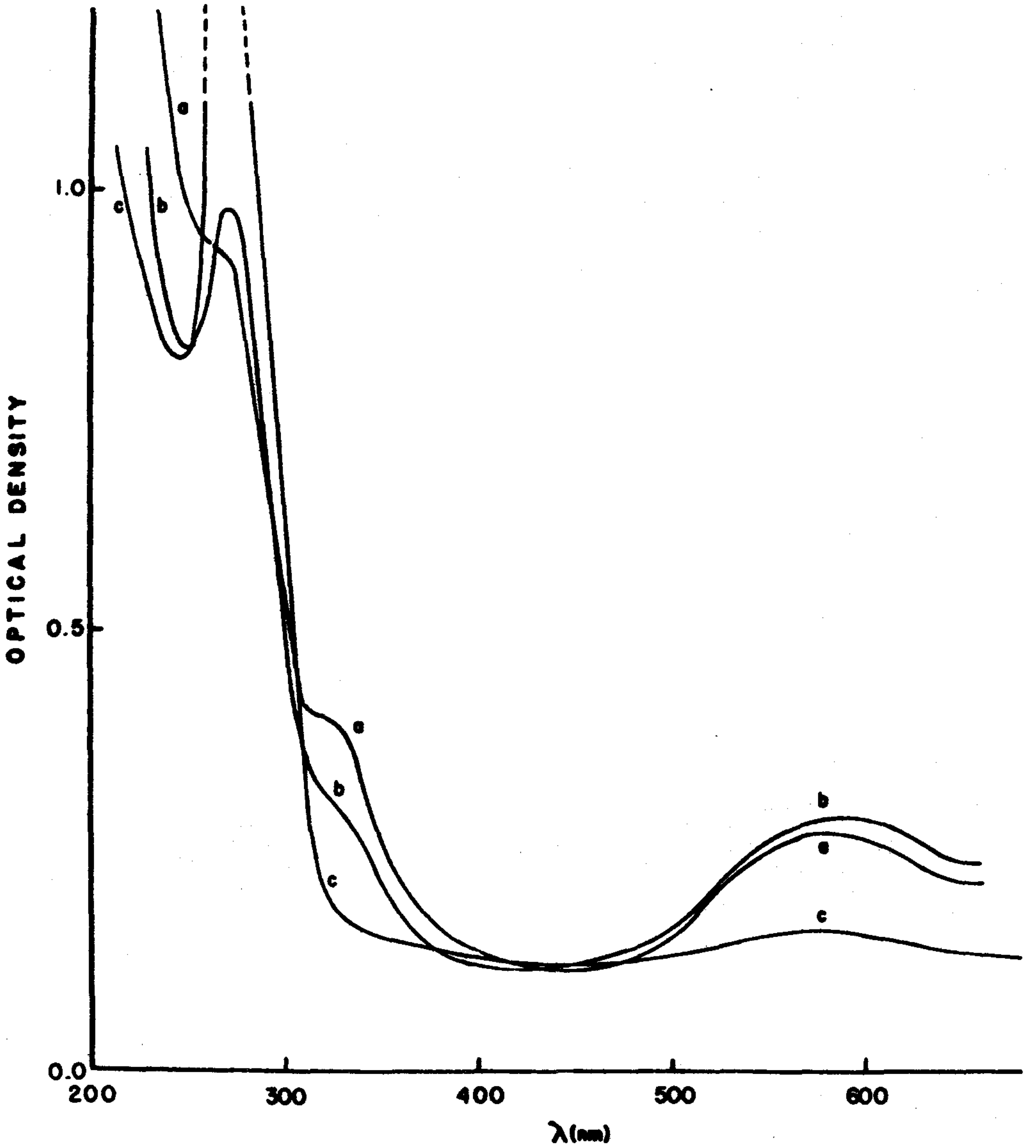


Figure 26. Time dependent absorption spectra of a 4 x 10^{-5}M solution of sulphur in 15% w/w oleum. Time from preparation: a) 1/2 h, b) 12 h, c) 55 h.

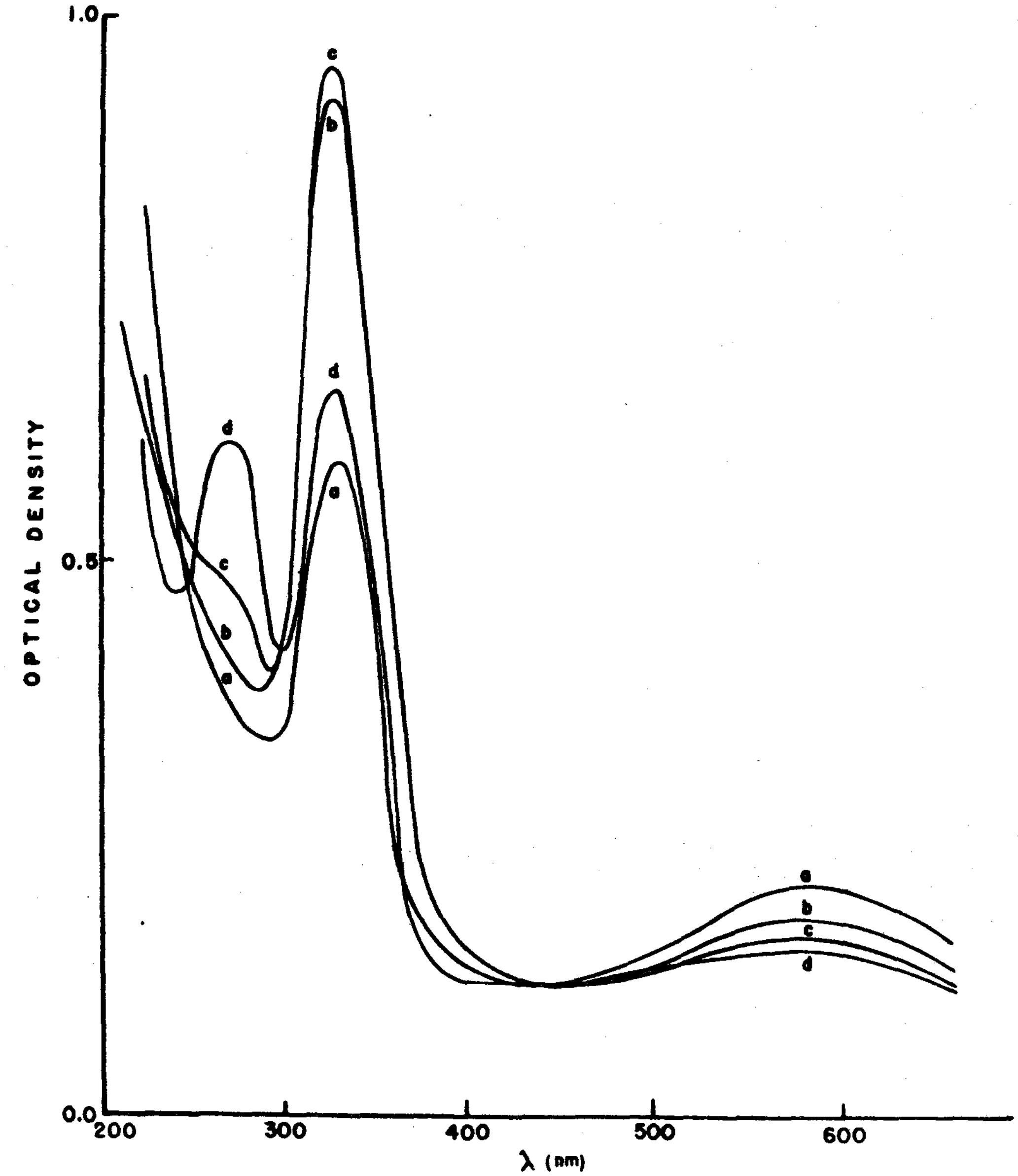


Figure 27. Time dependent absorption spectra of a 2.3 x 10^{-5}M solution of sulphur in 30% w/w oleum. Time from preparation: a) 1/2 h, b) 6 h, c) 17 h, d) 23 h.

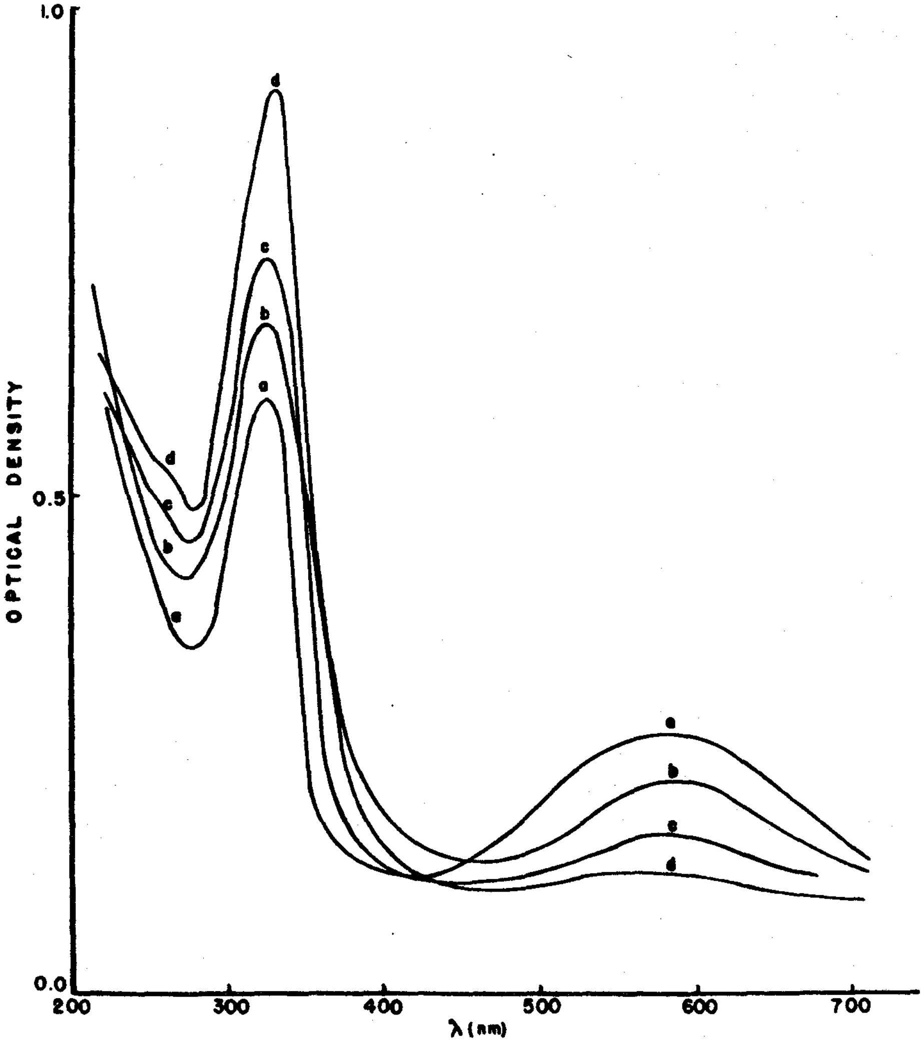


Figure 28. Time dependent absorption spectra of a 1.4×10^{-4}M solution of sulphur in 45% w/w oleum. Time from preparation: a) 1/2 h, b) 20 h, c) 72 h, d) 100 h.

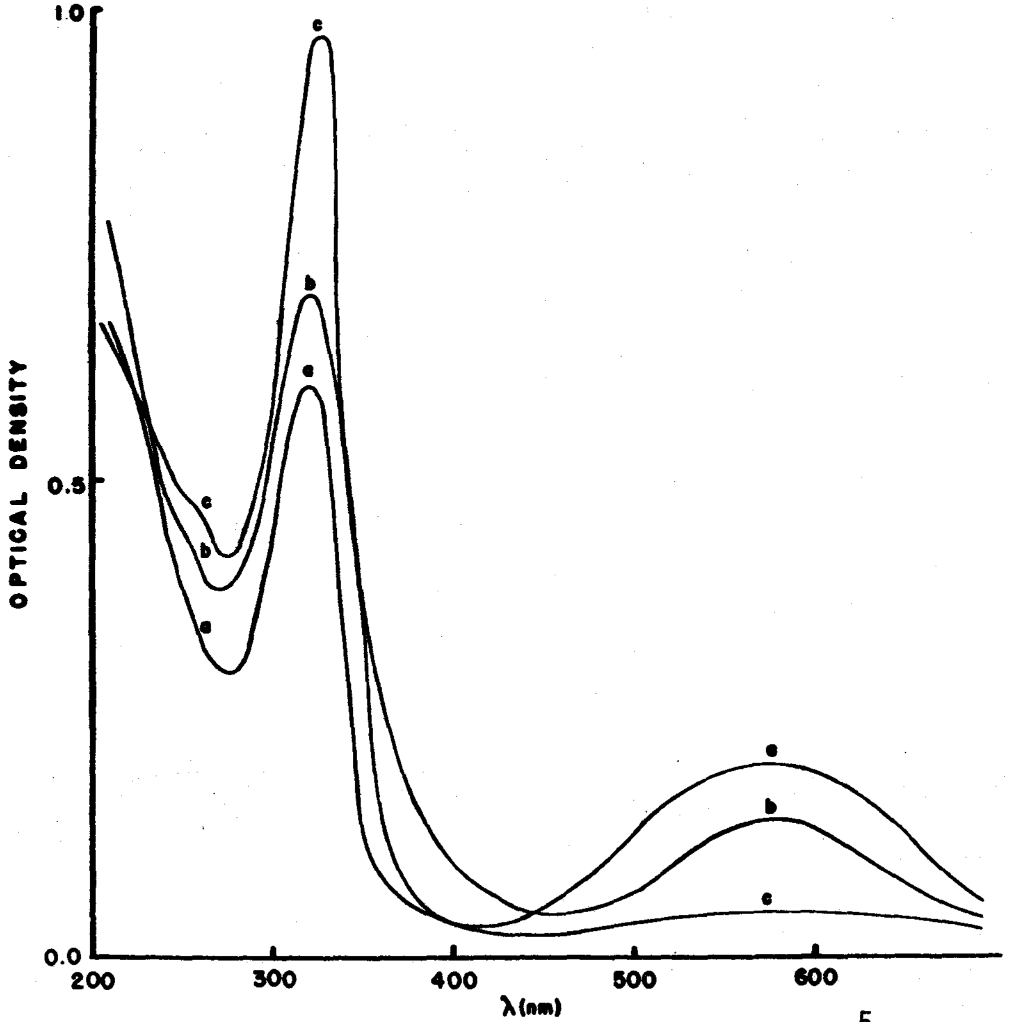


Figure 29. Time dependent absorption spectra of a 1.25 x 10^{-5}M solution of sulphur in 65% w/w oleum. Time from preparation: a) 1/2 h, b) 24 h, c) 90 h.

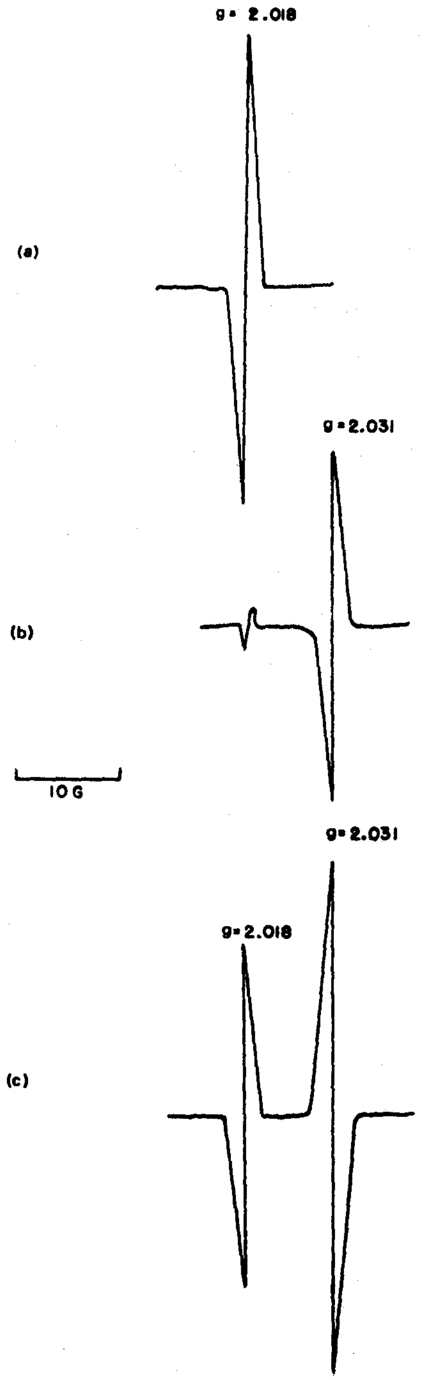


Figure 30. The e.s.r. spectra of solutions of sulphur (S_8) in 30% w/w oleum. (a) blue solution, (b) red solution, (c) mixture of blue and red solutions.

CHAPTER VI

CONCLUSIONS.

It has long been recognised that metals readily form cations but the evidence for cation formation by non-metals has only been obtained very recently. Metals, with few exceptions, have been generally found to form monoatomic cations e.g. Na^+, Mg^{2+}, etc. The only well known polyatomic cations are Hg_2^{2+} and Cd_2^{2+}. In contrast no monoatomic cations of the non-metals are known; earlier evidence for the I^+ cation (81) has been shown to be incorrect. The non-metals do, however, appear to form a variety of polyatomic cations, the first such cation to be recognised was I_2^+ (82). Recent investigations in this laboratory have given evidence for the formation of various polyatomic cations of sulphur, selenium and tellurium in solution in highly acidic solvents. The present investigation has further shown that polyatomic cations of sulphur, selenium and tellurium can be isolated as stable salts by using suitable oxidising agents such as SbF_5, AsF_5, $S_2O_6F_2$ and SO_3 in media of very low basicity. A list of the presently known cations of sulphur, selenium and tellurium is given in Table XIV together with the known stable salts of these cations. As these cations are strong Lewis Acids, we can expect them to be stable only under weakly basic conditions. They have been observed in solvents such as 100% H_2SO_4, HSO_3F, oleum and HSO_3F/SbF_5* in which the most basic species is the solvent anion. The solid compounds that have been isolated

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*The acidity of HSO_3F can be increased by the addition of SbF_5 a weak acid of this solvent. On adding SO_3 to this solution the acidity increases still further until the SbF_5:SO_3 ratio of 1:3 is reached. The resulting solutions are the most highly acidic media known at the present time. These media have been frequently referred to as super acid system.

TABLE XIV

Compounds Containing Polyatomic Cations of Sulphur, Selenium and Tellurium*

$S_{16}^{2+}(SbF_6^-)_2$		
$S_{16}^{2+}(AsF_6^-)_2$[61]		
$S_8^{2+}(Sb_2F_{11}^-)_2$	$Se_8^{2+}(Sb_2F_{11}^-)_2$	
$S_8^{2+}(AsF_6^-)_2$[61]	$Se_8^{2+}(AsF_6^-)_2$	
	$Se_8^{2+}(AlCl_4^-)_2$[55]	
		$Te_6^{2+}(AsF_6^-)_2$
$S_4^{2+}(SO_3F^-)_2$	$Se_4^{2+}(Sb_2F_{11}^-)_2$	$Te_4^{2+}(Sb_2F_{11}^-)_2$
	$Se_4^{2+}(AsF_6^-)_2$	$Te_4^{2+}(AsF_6^-)_2$
	$Se_4^{2+}(HSO_7^-)_2$[51]	$Te_4^{2+}(SO_3F^-)_2$
		$Te_n^{n+}(SbF_6^-)_n$
		$Te_n^{n+}(SO_3F)_n$

*Except where reference is indicated, the compounds listed above were isolated and characterised during the present investigation.

contain anions such as SbF_6^-, $Sb_2F_{11}^-$, or AsF_6^- which are only weakly basic, i.e. they are the anions of extremely strong acids. Table XV summarises the cationic stability with respect to disproportionation in media of increasing acidity. It is evident from an examination of Table XV that the highest oxidation state of any particular element is stabilised in less basic media than the lower oxidation states. An example which illustrates this point is that the S_4^{2+} cation is stable in HSO_3F/SbF_5 only. In HSO_3F it disproportionates to give the blue S_8^{2+} cation and SO_2. The S_{16}^{2+} cation is however stable in HSO_3F.

A long known empirical generalisation is that the electropositive character of the elements increases on descending a group in the periodic table. The observation, that tellurium readily oxidises in 100% H_2SO_4, at room temperature, to Te_4^{2+} and Te_n^{n+} cations whereas sulphur does not react with 100% H_2SO_4 even on heating for a long time, is consistent with this generalisation. It is also clear that the lower oxidation states are relatively easier to oxidise in the order Te>Se>S.

The lower oxidation states Se_{16}^{2+}, Te_{16}^{2+} and Te_8^{2+} were not observed under our experimental conditions. This does not, however, rule out the possibility of their existence under some other experimental conditions. For example, it might be possible to obtain the above mentioned cations from the elements by using very mild oxidising agents such as PF_5, $SeCl_4$ or $TeCl_4$.

There is no precedent or clear analogy for the Te_6^{2+} ion. The analogous S_6^{2+} cation might possibly by synthesised by oxidising S_{12} or

TABLE XV

Cationic Stability with Respect to Disproportionation.

Cation.	Acidic media in increasing acidity.		
	100% H_2SO_4.	100% HSO_3F.	HSO_3F/SbF_5.
S_{16}^{2+}	disproportionates to give S_8 and SO_2	stable	oxidises to S_8^{2+} and S_4^{2+} ions.
S_8^{2+}	disproportionates to give S_8 and SO_2	stable for few hours	oxidises to S_4^{2+}
S_4^{2+}	disproportionates to give S_8 and SO_2	disproportionates to give S_8^{2+} and SO_2	stable
Se_8^{2+}	stable	stable	presumably oxidises to Se_4^{2+}
Se_4^{2+}	stable	stable	stable
Te_6^{2+}	oxidises to Te_4^{2+}	oxidises to Te_4^{2+}	oxidises to Te_4^{2+} and Te_n^{n+}
Te_4^{2+}	slowly oxidises to Te_n^{n+}	stable only in cold HSO_3F otherwise oxidises to Te_n^{n+}	oxidises to Te_n^{n+}
Te_n^{n+}	disproportionates to Te_4^{2+} and Te(IV)	disproportionates to Te_4^{2+} and presumably Te(IV)	stable

S_6 which are known.

$$\begin{tikzcd}
S_{12} + AsF_5(\text{and/or } SbF_5) \arrow[r, "\text{liquid}", "SO_2"'] & S_{12}^{2+} \arrow[d, "\text{further oxidation}"] \\
S_6 + AsF_5 \text{ (or } SbF_5) \arrow[r, "\text{liquid } SO_2", "\text{as solvent}"'] & S_6^{2+}
\end{tikzcd}$$

In Group VII, cations such as I_2^+, I_4^{2+}, Br_3^+, Br_2^+ and Cl_3^+ have been observed. Evidence for these ions, and such information as is available on the structures has been reviewed by Gillespie and Morton (83). As in the group VI cations, similar stability relationships have been noted for the halogen cations. For example I_3^+ was found to be stable in the acidity of 100% H_2SO_4, whereas I_2^+ almost completely disproportionates to I_3^+ and I(III) in this media. The I_2^+ cation however required the higher acidity of HSO_3F to stabilize it. The bromine cations are still less stable. The Br_2^+ cation is completely stable in $HSO_3F/SbF_5/SO_3$ system. However, Br_2^+, substantially disproportionates to Br_3^+ and Br(I) even in the very weakly basic medium so that under the most favourable conditions investigated some 25% of the bromine in solution was present as the Br_2^+ cation (84). An extension of the observations on the stability of the halogen cations suggests that Cl_2^+ or Cl_3^+ cations might not be expected to be stable even in the most acidic media. The Cl_3^+ cation has however been identified in the compound $Cl_3^+AsF_6^-$ which was stable at -78°C, but not at higher temperatures (85), and no evidence was obtained for its existence was obtained for its existence as a stable species even in $HSO_3F/SbF_5/SO_3$. Recently Edwards et. al. (86) have isolated a stable compound $Br_2^+Sb_3F_{11}^-$ containing the Br_2^+ cation.

In this context it is perhaps worth stating a long known empirical generalisation that the stability of the lowest halides with respect to disproportionation usually increases with increasing size of the anion. This relationship further suggests that an even larger and less basic anion should be better for the stabilisation of large cations containing the element in a low oxidation state. In accordance with this relationship a stable compound $Cd_2^{2+}(AlCl_4^-)_2$ has been isolated (87), whereas the $Cd_2^{2+}Cl_2^-$ salt readily disproportionated. From a qualitative viewpoint, the stability of Br_2^+ in the compound $Br_2Sb_3F_{16}$ may be attributed to the large size and very weak basicity of $Sb_3F_{16}^-$. The basicity of the anions $Sb_nF_{5n+1}^-$ is expected to decrease in the order,

$$SbF_6^- > Sb_2F_{11}^- > Sb_3F_{16}^- \text{ etc.}$$

In Group V, Bismuth forms various cluster compounds. The material thought to be "BiCl" has been shown by X-ray crystallographic study to contain the Bi_9^{5+} cluster in addition to $BiCl_5^{2-}$ and $Bi_2Cl_8^{2-}$ (88). The Bi_5^{3+}, Bi_8^{2+}, and Bi^+ cations have been identified (89,90) in NaCl-$AlCl_3$ melts by a spectrophotometric study. The tetrachloroaluminate salts of $Bi_5^{3+}$and Bi_8^{2+} have been obtained (91) from reactions of bismuth metal with the salt mixture $BiCl_3 + 3AlCl_3$. The structure of Bi_9^{5+} is well established as a tricapped trigonal prism, no structural information is available for the Bi_5^{3+} or Bi_8^{2+} ions. Gillespie (92) has predicted a trigonal bipyramidal structure for the Bi_5^{3+} ion on the basis of his Valence-Shell-Electron-Pair Repulsion theory (VSEPR). Paul et al (93) have recently reported the study of the oxidation of the element, antimony by potassium persulphate and peroxydisulphurldifluoride in fluorosulphuric acid. It is claimed that cations such as Sb_8^{2+} and Sb_4^{2+} are formed. The results presented by these authors however could not be reproduced in these laboratories. Gillespie and Dean (94) have isolated a compound $SbAsF_6$ containing the Sb_n^{n+} cation. Evidence has also been found for an antimony cation in a higher oxidation state than +1. A detailed investigation is presently in progress. A summary of the presently known polyatomic cations, of group VII, VI and V, is given in Table XVI.

TABLE XVI

Presently Known Polyatomic Cations of Group VII, VI and V.

Gp. V		Gp. VI			Gp. VII		
		S_{16}^{2+}	-	-			
					-	-	I_5^+
Sb_8^{2+}?	Bi_8^{2+}	S_8^{2+}	Se_8^{2+}				
	Bi_3^+?			Te_6^{2+}	Cl_3^+	Br_3^+	I_3^+
-	Bi_9^{5+}						
-	Bi_5^{3+}						
Sb_4^{2+}?	-	S_4^{2+}	Se_4^{2+}	Te_4^{2+}	-	Br_2^+	$I_2^+(I_4^{2+})$
Sb_n^{n+}	-	-	-	Te_n^{n+}			

It would appear that the pattern of polyatomic cation formation follows a general group trend. The tendency to form a cation with highest positive charge per atom of the element, increases from right to left in Table XVI. For instance, iodine forms I_2^+ (+1/2), tellurium forms Te_n^{n+} (+1) and antimony forms Sb_n^{n+} (+1) and another species with an oxidation state greater than +1 and less than +3, a reflection of increasing metallic character. The expanding array of compounds containing homopolyatomic cations, of sulphur, selenium and tellurium, described herein, suggests that a general class of polyatomic cations exists in a previously unsuspected region of the periodic table. Although the comparisons and generalisations made in this chapter are necessarily somewhat speculative, they are nevertheless useful in providing a background for a general understanding of polyatomic cation formation by the non-metallic elements, and for indicating paths for future exploration.

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