

by reaction of a 10:1 mole ratio of  $\text{NH}_3$  to  $\text{CF}_3\text{S}(\text{O})\text{F}$  at  $-40^\circ$  for 2 hr and then allowing the vessel to warm slowly to room temperature. The product was purified by fractional condensation.

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## Polyatomic Cations of Tellurium. I. The $+1/3$ , $+1/2$ , and $+1$ Oxidation States of Tellurium

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Tellurium dissolves in 45% oleum to give a yellow solution and in cold  $\text{H}_2\text{SO}_4$  or  $\text{HSO}_3\text{F}$  to give red solutions which become orange-yellow on warming. It is shown that the red species is  $\text{Te}_4^{2+}$ . Tellurium can be oxidized with  $\text{SbF}_5$ ,  $\text{S}_2\text{O}_8\text{F}_2$ , and  $\text{AsF}_5$  to give the red compounds  $\text{Te}_4(\text{Sb}_2\text{F}_{11})_2$ ,  $\text{Te}_4(\text{SO}_3\text{F})_2$ , and  $\text{Te}_4(\text{AsF}_6)_2$  which were also shown to contain  $\text{Te}_4^{2+}$ . With larger amounts of the appropriate oxidizing agents tellurium can be oxidized to the  $+1$  oxidation state and the yellow compounds  $\text{TeSO}_3\text{F}$  and  $\text{TeSbF}_6$  have been prepared and characterized. It is shown that these tellurium(I) compounds and the yellow acid solutions contain a polyatomic cation  $\text{Te}_n^{n+}$  which is thought to be  $\text{Te}_4^{4+}$ . Using arsenic pentafluoride as an oxidizing agent, it was also possible to obtain tellurium in the  $+1/3$  oxidation state in the form of the compound  $\text{Te}_3\text{AsF}_6$  which is believed to contain the  $\text{Te}_3^{2+}$  cation.

In recent papers it has been shown that selenium forms the colored species  $\text{Se}_4^{2+}$  and  $\text{Se}_3^{2+}$  in strong acid solutions<sup>1</sup> and several compounds of these new cations have been described.<sup>2-3</sup> It has also been shown that sulfur can be oxidized to the colored cations  $\text{S}_{16}^{2+}$ ,  $\text{S}_8^{2+}$ , and  $\text{S}_4^{2+}$ .<sup>4,5</sup> Tellurium also forms orange or red solutions in sulfuric acid, oleum, or sulfur trioxide,<sup>6,7</sup> and a red compound "TeSO<sub>3</sub>" has been described.<sup>7-9</sup> Indeed the reaction of tellurium with concentrated sulfuric acid to produce a red color was one of the first recorded properties of tellurium. The same red color has also been obtained by passing  $\text{H}_2\text{Te}$  through a saturated solution of  $\text{TeO}_2$  in concentrated sulfuric acid and on continued passing of  $\text{H}_2\text{Te}$  it was reported that an insoluble brown substance was produced which did not appear to be elemental tellurium.<sup>10</sup> It seemed probable that these colored solutions of tellurium contain one or more polyatomic cations, analogous to those of selenium and sulfur, and this paper reports an investigation of solutions of tellurium in fluorosulfuric acid, sulfuric acid, and oleum and of the reaction of tellurium with the oxidizing agents  $\text{S}_2\text{O}_8\text{F}_2$ ,  $\text{SO}_3$ ,  $\text{SbF}_5$ , and  $\text{AsF}_5$ . Very recently Bjerrum and Smith<sup>11</sup> have shown that in  $\text{AlCl}_3\text{-NaCl}$

eutectic a red tellurium species is formed in maximum amount from Te and  $\text{TeCl}_4$  at a mole ratio of 7. They concluded that the species contains tellurium in the  $+1/2$  oxidation state and they formulated it as a polymeric cation  $\text{Te}_{2n}^{n+}$  formed according to the equation  $7\text{Te} + \text{Te}^{4+} \rightarrow (4/n)\text{Te}_{2n}^{n+}$ . They also obtained some evidence for another tellurium species with a formal oxidation state between  $+1/2$  and 0, but this was not identified. Awad<sup>12</sup> has also postulated the existence of low-valency states of tellurium, *i.e.*,  $\text{Te}_2^+$  and  $\text{Te}^+$ , in order to explain his results on the anodic dissolution of tellurium in nonoxidizing acids. Some of our results have been described in two preliminary publications.<sup>13,14</sup>

### Results and Discussion

Tellurium dissolves slowly in cold sulfuric acid or fluorosulfuric acid to produce a red solution. With 45% oleum (disulfuric acid) the reaction is more rapid, and on warming the red oleum solution, a change to orange and finally to yellow occurs. A yellow-orange color is also produced on adding peroxy sulfate to the red sulfuric acid solution or peroxydisulfuryl difluoride to the fluorosulfuric acid solution. On adding a large excess of these oxidizing agents, colorless solutions are produced, with precipitation of  $\text{TeO}_2$  in the case of the sulfuric acid solutions. In the reaction of tellurium with sulfuric, fluorosulfuric, and disulfuric acids, sulfur dioxide is produced in all three cases. The colored tellurium species are, therefore, positive oxidation states of tellurium, the yellow species being in a higher oxidation

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(9) J. J. Doolan and J. R. Partington, *ibid.*, **125**, 1402 (1924).

(10) E. Divers and M. Shimose, *ibid.*, **43**, 329 (1883).

(11) J. Bjerrum and G. P. Smith, *J. Amer. Chem. Soc.*, **90**, 4472 (1968).

(12) S. A. Awad, *Spectrochim. Acta*, **13**, 925 (1968).

(13) J. Barr, R. J. Gillespie, R. Kapoor, and G. P. Pez, *J. Amer. Chem. Soc.*, **90**, 6865 (1968).

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state than the red. The absorption spectrum of a fluorosulfuric acid solution of the red species obtained by dissolving tellurium in cold fluorosulfuric acid is shown in Figure 1 (curve A). This species has an in-

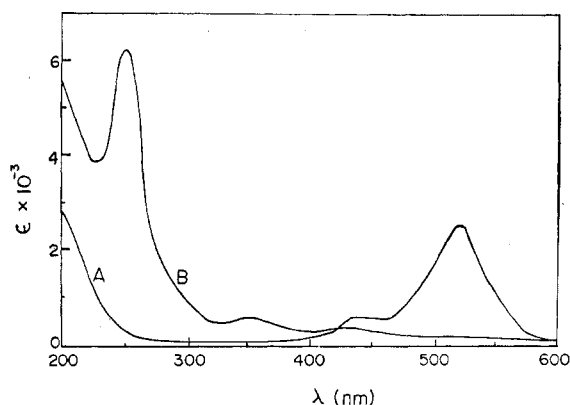


Figure 1.—Absorption spectra of  $\text{HSO}_3\text{F}$  solutions of the red species A and the yellow species B.

tense absorption maximum at 510 nm and a weak absorption at 430 nm. A similar spectrum was reported by Bjerrum and Smith for the red species although they reported the maximum absorption at 560 nm. The absorption spectrum of a fluorosulfuric acid solution of the yellow species, obtained by oxidizing tellurium with  $\text{S}_2\text{O}_6\text{F}_2$ , is also shown in Figure 1 (curve B). This has an intense absorption at 250 nm with two weak maxima at 360 and 420 nm. Quite generally it was found to be very difficult to obtain a solution of one of these species completely free from the other. For example, when tellurium is dissolved in sulfuric acid at room temperature, the solution always contains a mixture of the red and yellow species. Oxidation of tellurium with antimony pentafluoride or with sulfur trioxide was also found to give both red and yellow products.

**The Red Species.**—Stable solutions of the red species containing no more than a trace of the yellow species could be obtained by dissolving tellurium in ice-cold fluorosulfuric acid. These were investigated by means of cryoscopic and conductometric measurements. The experimental results are given in Table I. Values of

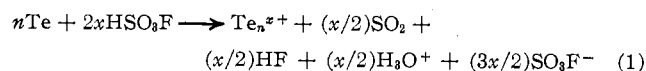
TABLE I  
CONDUCTIVITIES AND FREEZING POINT DEPRESSIONS  
FOR RED SOLUTIONS OF TELLURIUM IN  $\text{HSO}_3\text{F}$

Concn, g-atom of Te/kg	—10% $\kappa$ , ohm $^{-1}$ cm $^{-1}$ —		Concn, g-atom of Te/kg	$\theta$ , °C
	25°	−86.4°		
0.0000	1.09	0.008	0.0269	0.164
0.0098	19.82	1.632	0.0523	0.357
0.0270	49.06	3.571	0.1464	0.949
0.0582	98.99	7.193	0.1894	1.283
0.0788	130.37	9.518	0.2482	1.636
0.1250	196.78	14.094	0.3116	2.074
0.1369	200.72	14.178		
0.1580	228.99	15.909		
0.1837	263.80	18.049		
0.2166	304.76	20.542		

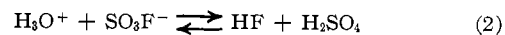
$\gamma$ , the number of moles of fluorosulfate ions produced by 1 g-atom of tellurium atoms, were calculated by comparison of the conductivities at 25 and at  $-86.4^\circ$  with those of

solutions of potassium fluorosulfate. At both temperatures  $\gamma$  was almost constant over the concentration range investigated and had values  $0.69 \pm 0.02$  at  $25^\circ$  and  $0.73 \pm 0.01$  at  $-86.4^\circ$ .

For the formation of polyatomic cations of the general formula  $\text{Te}_n^{x+}$  the reaction is



The equilibrium



which affects the value of  $\gamma$  must be allowed for. The equilibrium constant  $K$  has previously been found<sup>15</sup> to have the value of 0.12 at  $25^\circ$  and values obtained at lower temperatures<sup>15</sup> may be extrapolated to give the value of 0.030 at  $-86.4^\circ$ . When equilibrium 2 is allowed for, the relation among  $x$ ,  $n$ , and  $\gamma$  is given by the expression

$$\gamma = \frac{x}{2n(K-1)} \{K - 3.5 + (K + 5K + 0.25)^{1/2}\} \quad (3)$$

Using the above values of  $K$ ,  $\gamma = 1.39x/n$  at  $25^\circ$  and  $\gamma = 1.47x/n$  at  $-86.4^\circ$ . The experimental  $\gamma$  values then give  $x/n = 0.495 \pm 0.015$  at  $25^\circ$  and  $x/n = 0.497 \pm 0.007$  at  $-86.4^\circ$ . It is thus clear that  $n = 2x$  showing that tellurium in the red species is in the  $+1/2$  oxidation state as also found by Bjerrum and Smith.<sup>11</sup> Presumably therefore the red species is an ion of the type  $\text{Te}_{2n}^{n+}$ . An attempt was made to determine the value of  $n$ , *i.e.*, the degree of polymerization, by means of freezing point depression measurements. The measured freezing points are given in Table I and the results are shown in Figure 2 together with theoretical curves

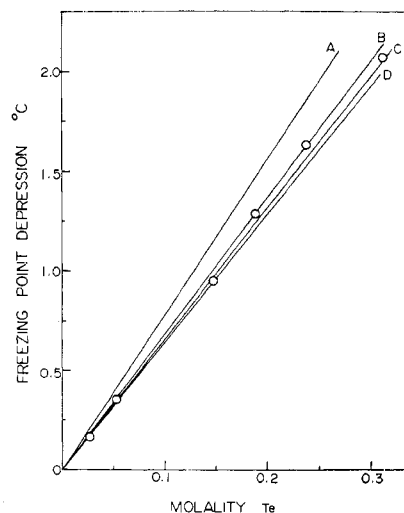


Figure 2.—Freezing point depressions for solutions of tellurium in  $\text{HSO}_3\text{F}$ . The straight lines are freezing point curves for the formation of (A)  $\text{Te}_2^+$ , (B)  $\text{Te}_4^{2+}$ , (C)  $\text{Te}_6^{3+}$ , and (D)  $\text{Te}_8^{4+}$ .

for the various possible species  $\text{Te}_2^+$ ,  $\text{Te}_4^{2+}$ ,  $\text{Te}_6^{3+}$ , etc. The results clearly rule out  $\text{Te}_2^+$  but they are not sufficiently accurate to distinguish clearly between  $\text{Te}_4^{2+}$  and the higher polymers such as  $\text{Te}_6^{3+}$  and  $\text{Te}_8^{4+}$ .

(15) R. J. Gillespie, J. B. Milne, and J. B. Senior, *Inorg. Chem.*, **5**, 1233 (1966).

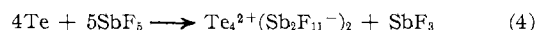
However measurements of the magnetic susceptibility of solutions in fluorosulfuric acid showed the solute to be diamagnetic with a susceptibility of  $-27 \times 10^{-6}$  cgsu (g-atom of Te) $^{-1}$  thus ruling out odd-electron species such as  $\text{Te}_6^{3+}$ .

The Raman spectra of red solutions of tellurium in sulfuric acid, fluorosulfuric acid, and oleum all showed two characteristic lines in addition to those due to the solvent: a very strong polarized line at  $219 \text{ cm}^{-1}$  and a very weak line at  $139 \text{ cm}^{-1}$ . These frequencies are very reasonable for tellurium-tellurium vibrations and the spectrum is very similar to that of  $\text{Se}_4^{2+}$ ,<sup>16</sup> which has a very strong polarized line at  $327 \text{ cm}^{-1}$  and a very weak line at  $188 \text{ cm}^{-1}$  except that the two lines observed for the red Te species are shifted, as expected, to lower frequencies. An X-ray crystallographic investigation of the  $\text{Se}_4^{2+}$  cation in the compound  $\text{Se}_4(\text{HS}_2\text{O}_7)_2$  has shown that the  $\text{Se}_4^{2+}$  ion has a square-planar structure.<sup>17</sup> The  $327\text{-}$  and  $188\text{-cm}^{-1}$  Raman lines have been assigned to the  $A_{1g}$  and  $B_{2g}$  modes of a square-planar structure and the lines observed at  $219$  and  $139 \text{ cm}^{-1}$  may reasonably be assigned to the same modes of a square-planar  $\text{Te}_4^{2+}$  cation. From the absorption spectrum of the solution of  $\text{Te}_4^{2+}$  in fluorosulfuric acid the molar extinction coefficient was found to be  $2400 \text{ l. (g-atom of Te)}^{-1} \text{ cm}^{-1}$  or  $9600 \text{ l. (mol of Te}_4^{2+})^{-1} \text{ cm}^{-1}$ . The  $\text{Se}_4^{2+}$  cation has an absorption spectrum that is very similar in general appearance but shifted to shorter wavelength and a molar extinction coefficient of  $2100 \text{ l. (g-atom of Se)}^{-1} \text{ cm}^{-1}$  at the wavelength of maximum absorption in fluorosulfuric acid ( $410 \text{ nm}$ ). The similarity in the spectra of  $\text{Se}_4^{2+}$  and the red tellurium species has recently been pointed out by Stephens,<sup>18</sup> who has also shown that the magnetic circular dichroisms of solutions of these species are also very similar. He therefore concludes, as we do, that the red tellurium species is very probably  $\text{Te}_4^{2+}$  and that it has a square-planar structure.

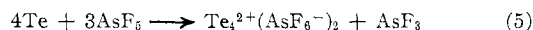
By reaction of tellurium with  $\text{S}_2\text{O}_6\text{F}_2$  in solution in sulfur dioxide at a temperature not higher than  $-23^\circ$  a red amorphous solid was obtained the weight of which corresponded to quantitative formation of  $\text{Te}_4(\text{SO}_3\text{F})_2$  and the result of analysis for tellurium was consistent with this formulation. The spectrum of a solution of the compound in  $\text{HSO}_3\text{F}$  at  $0^\circ$  was identical with that of A in Figure 1. The substance decomposed rather rapidly when exposed to  $6328\text{-\AA}$  laser radiation but at  $-140^\circ$  a Raman spectrum was obtained which showed the strong  $219\text{-cm}^{-1}$  frequency of the  $\text{Te}_4^{2+}$  cation.

By stirring tellurium with an excess of antimony pentafluoride at  $-23^\circ$  for 3 days a red solid was obtained after excess  $\text{SbF}_5$  had been removed under vacuum. On treatment of the solid with sulfur dioxide most of it dissolved readily to give a red solution leaving a small residue of an insoluble yellow compound. By successive treatments with sulfur dioxide a small amount of the yellow compound was separated and the red solution

was finally evaporated under vacuum to yield a red solid. The yellow solid is further discussed below. The  $^{19}\text{F}$  nmr spectrum of the red sulfur dioxide solution consisted simply of the spectrum of the  $\text{Sb}_2\text{F}_{11}^-$  anion.<sup>19</sup> Elemental analysis of the red solid was consistent with the composition  $\text{Te}_4(\text{Sb}_2\text{F}_{11})_2$ . The absorption spectra of solutions of the compound in  $\text{HSO}_3\text{F}$  and  $\text{SO}_2$  were identical with the spectrum of the red solution shown in Figure 1. The Raman spectrum of the solid showed the same characteristic frequencies at  $219$  and  $139 \text{ cm}^{-1}$  as were observed for the red solution of tellurium in fluorosulfuric acid. We conclude that the compound is  $\text{Te}_4^{2+}(\text{Sb}_2\text{F}_{11}^-)_2$  and that it is formed by the reaction



By treating tellurium with excess arsenic pentafluoride in solution in  $\text{SO}_2$  at temperatures below  $0^\circ$  a red solid was obtained which had a tellurium analysis consistent with the formulation  $\text{Te}_2\text{AsF}_6$ . In solution in cold sulfuric acid it gave an absorption spectrum identical with A in Figure 1. The presence of the  $\text{AsF}_6^-$  ion was confirmed by infrared and  $^{19}\text{F}$  nuclear magnetic resonance spectroscopy. We conclude that the compound is  $\text{Te}_4^{2+}(\text{AsF}_6^-)_2$  and that it is formed according to the equation



**The Yellow Species.**—The red  $\text{Te}_4^{2+}$  cation can be further oxidized to a yellow species with the absorption spectrum B shown in Figure 1. This was first investigated in fluorosulfuric acid solution using  $\text{S}_2\text{O}_6\text{F}_2$  as an oxidizing agent. The spectra of a number of solutions containing various ratios of Te to  $\text{S}_2\text{O}_6\text{F}_2$  were measured and the results are shown in Figure 3 in which the

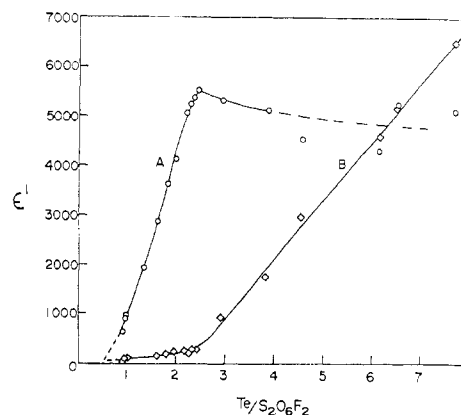


Figure 3.—Plot of  $\epsilon' = \text{OD}/2M_{\text{S}_2\text{O}_6\text{F}_2}$  against the mole ratio  $\text{Te}:\text{S}_2\text{O}_6\text{F}_2$ : A, 250-nm peak of the yellow species; B, 510-nm peak of  $\text{Te}_4^{2+}$ .

ratios of the optical densities of the 250- and 510-nm peaks to the number of equivalents of oxidizing agent per liter, *i.e.*,  $\epsilon' = \text{OD}/2M_{\text{S}_2\text{O}_6\text{F}_2}$ , are plotted against the  $\text{Te}:\text{S}_2\text{O}_6\text{F}_2$  ratio. The intensity of the 250-nm peak increases rapidly with increasing amount of tellurium, reaches a maximum value at the ratio  $\text{Te}:\text{S}_2\text{O}_6\text{F}_2 = 2.4$ , and then decreases slowly. The intensity of the 510-nm peak

(16) R. J. Gillespie and G. P. Pez, *Inorg. Chem.*, **8**, 1229 (1969).

(17) I. D. Brown, D. B. Crump, R. J. Gillespie, and D. P. Santry, *Chem. Commun.*, 853 (1968); I. D. Brown, C. Calvo, D. B. Crump, and R. J. Gillespie, to be submitted for publication.

(18) P. J. Stephens, *Symp. Faraday Soc.*, **3**, 40 (1969).

(19) R. J. Gillespie and K. C. Moss, *J. Chem. Soc.*, 1170 (1966).

increases very slowly up to the ratio  $\text{Te}:\text{S}_2\text{O}_6\text{F}_2 = 2.4$  and then increases rapidly and linearly with increasing tellurium concentration. We interpret these results in the following manner. At the ratio  $\text{Te}:\text{S}_2\text{O}_6\text{F}_2 = 0.5$  tellurium is completely converted to some  $\text{Te}(\text{IV})$  species whose exact nature is uncertain. At higher values of the  $\text{Te}:\text{S}_2\text{O}_6\text{F}_2$  ratio the yellow species and  $\text{Te}_4^{2+}$  giving rise to the characteristic 250- and 510-nm absorptions, respectively, are formed in increasing amounts. At first the predominant species is the yellow species with the 250-nm absorption. After the maximum intensity of the 250-nm peak is reached, increasing the amount of tellurium does not cause any appreciable decrease in the intensity of the 250-nm peak and therefore in the amount of the yellow species. It appears that  $\text{S}_2\text{O}_6\text{F}_2$  always reacts rather rapidly with  $\text{Te}$  at room temperature to produce the yellow species even in the presence of excess tellurium. The excess tellurium reacts relatively slowly with the solvent to form the red  $\text{Te}_4^{2+}$  ion. However, even in the presence of excess  $\text{S}_2\text{O}_6\text{F}_2$ , unless this is very large, a small amount of tellurium always reacts with the solvent to give  $\text{Te}_4^{2+}$  before the reaction between tellurium and the  $\text{S}_2\text{O}_6\text{F}_2$  is complete. Simultaneously a small amount of the yellow species is presumably oxidized to  $\text{Te}(\text{IV})$ . The optical density of the 510-nm peak due to  $\text{Te}_4^{2+}$  increases linearly with increasing  $\text{Te}$  concentration and gives a value of 2400/g-atom of  $\text{Te}$  or 9600/mol of  $\text{Te}_4^{2+}$  for the extinction coefficient of  $\text{Te}_4^{2+}$  in good agreement with the values given above. From the optical density of the 510-nm peak of 300 at  $\text{Te}:\text{S}_2\text{O}_6\text{F}_2 = 2.4$  we conclude that at this composition one-eighth of the tellurium was oxidized to  $\text{Te}_4^{2+}$  by the solvent leaving only seven-eighths to be oxidized by the  $\text{S}_2\text{O}_6\text{F}_2$ . Thus  $2.4 \times 7/8 = 2.1$  g-atoms of  $\text{Te}$  is oxidized to the yellow species by 1 mol of  $\text{S}_2\text{O}_6\text{F}_2$ . This is sufficiently close to 2 g-atoms to allow us to conclude with reasonable certainty that the yellow species contains tellurium in the +1 oxidation state. We can also conclude that the extinction coefficient of the yellow species is  $5500 \times 8/7 = 6300$  l. (g-atom of  $\text{Te})^{-1} \text{cm}^{-1}$ .

Since the spectra of the yellow +1 oxidation state species are identical in  $\text{HSO}_3\text{F}$ ,  $\text{H}_2\text{SO}_4$ , and  $\text{H}_2\text{S}_2\text{O}_7$  it seems reasonable to conclude that exactly the same species is present in all three solvents. The only reasonable possibilities would appear to be the oxide  $\text{Te}_2\text{O}$  or polyatomic cations such as  $\text{Te}_3^{2+}$ ,  $\text{Te}_4^{4+}$ , etc.

By carrying out the reaction between tellurium and  $\text{S}_2\text{O}_6\text{F}_2$  in fluorosulfuric acid at  $-23^\circ$  it was found possible to prevent the reaction with the solvent. Under these conditions 1 mol of  $\text{S}_2\text{O}_6\text{F}_2$  reacted completely with 2 g-atoms of tellurium to give a dark yellow-brown solution in about 48 hr. When a large excess of sulfur dioxide was added to this solution at  $-78^\circ$ , a bright yellow solid of composition  $\text{TeSO}_3\text{F}$  was precipitated. This solid is stable only at  $-75^\circ$  and below. It was washed with sulfur dioxide and redissolved in fluorosulfuric acid. Magnetic measurements on the fluorosulfuric acid solutions showed that the solute was diamagnetic. Hence odd-electron polyatomic ions such as  $\text{Te}^+$  and  $\text{Te}_3^{3+}$

are unlikely. The most plausible formulation would seem to be  $\text{Te}_2^{2+}$  or  $\text{Te}_4^{4+}$ . In order to attempt to distinguish between these possibilities some freezing point depression measurements were made by adding small amounts of the concentrated fluorosulfuric acid solution to fluorosulfuric acid in a cryoscope. The results are given in Figure 4 together with theoretical curves for the

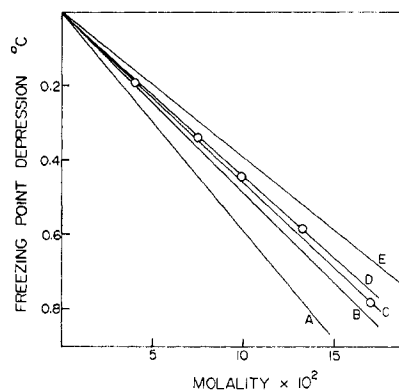
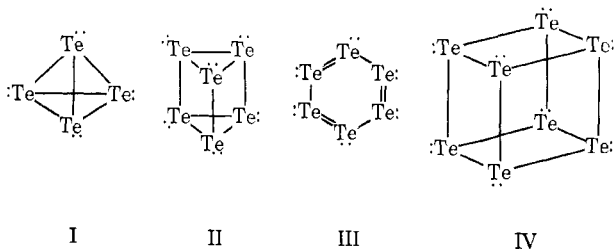


Figure 4.—Freezing point depressions for solutions of  $\text{TeSO}_3\text{F}$  in  $\text{HSO}_3\text{F}$ . The straight lines are calculated freezing point curves for (A)  $\text{Te}_2^{2+}$ , (B)  $\text{Te}_4^{4+}$ , (C)  $\text{Te}_6^{6+}$ , (D)  $\text{Te}_8^{8+}$ , and (E)  $\text{Te}_\infty^{\infty+}$ .

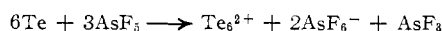
formation of  $\text{Te}_2^{2+}$ ,  $\text{Te}_4^{4+}$ ,  $\text{Te}_8^{8+}$ , and  $\text{Te}_n^{n+}$  where  $n$  approaches infinity. The results clearly indicate that the cation is not  $\text{Te}_2^{2+}$ , but because of the considerable experimental difficulties in making these measurements, the results are not sufficiently accurate to distinguish clearly between  $\text{Te}_4^{4+}$  and the higher polymers  $\text{Te}_6^{6+}$  and  $\text{Te}_8^{8+}$ .

The yellow residue, insoluble in sulfur dioxide, that was obtained in the reaction of antimony pentafluoride with tellurium was heated at  $100^\circ$  for 6 hr and a white solid sublimate of antimony trifluoride was obtained. The remaining yellow material was involatile and appeared to be quite stable up to  $120^\circ$ . Analysis of this yellow material gave results consistent with the formulation  $\text{TeSbF}_6$ . This supports our conclusion that the yellow species contains tellurium in the +1 oxidation state. Magnetic measurements showed the solid compound to be diamagnetic and the infrared spectrum showed that it contains the  $\text{SbF}_6^-$  ion. The absorption spectrum of a solution of the compound in  $\text{HSO}_3\text{F}-\text{SbF}_5$  was identical with B in Figure 1. We conclude that the compound contains the same  $\text{Te}_n^{n+}$  cation as in the  $\text{HSO}_3\text{F}$  solutions. It did not appear to be possible to oxidize tellurium to this yellow cation by using arsenic pentafluoride as the oxidizing agent.

It seems very probable that the yellow  $\text{Te}(\text{I})$  species is  $\text{Te}_4^{4+}$  but we cannot rule out the possibility that it might be  $\text{Te}_6^{6+}$  or  $\text{Te}_8^{8+}$ . It would appear that a final answer to this problem will only be obtained by an X-ray crystallographic investigation.  $\text{Te}_4^{4+}$  would be expected to have a tetrahedral structure like  $\text{P}_4$  (I);  $\text{Te}_6^{6+}$  could have a trigonal prism (II) or a benzene-like structure (III) while  $\text{Te}_8^{8+}$  would be likely to have a cubic structure (IV).



**The  $+1/3$  Oxidation State.**—In the work described in the preceding sections no evidence was obtained for a  $\text{Te}_3^{2+}$  species which might have been expected by analogy with  $\text{S}_3^{2+}$  and  $\text{Se}_3^{2+}$ . We therefore further investigated the oxidation of tellurium with the rather mild oxidizing agent  $\text{AsF}_5$  in sulfur dioxide solution and with the use of excess tellurium in an attempt to identify this lower oxidation state. However even in experiments using amounts of tellurium and arsenic pentafluoride appropriate for the formation of  $\text{Te}_3^{2+}$ , *i.e.*, 8 g-atoms of Te to 3 mol of  $\text{AsF}_5$ , unreacted tellurium remained even after very long reaction times. Therefore further experiments were carried out using somewhat larger amounts of arsenic pentafluoride, *e.g.*, Te:  $\text{AsF}_5$  ratios of approximately 2. In such experiments the sulfur dioxide solution acquired a deep red color after stirring at room temperature for approximately 3 hr, but this color diminished considerably on stirring for a further 24 hr and a voluminous gray solid remained which proved to be insoluble in sulfur dioxide. This solid did not contain elemental tellurium and the analysis was in good agreement with the composition  $\text{Te}_3\text{AsF}_6$ . The compound decomposes to give black tellurium when added to water. The infrared spectrum of the solid and the  $^{19}\text{F}$  nmr spectrum of an acetone solution (in which the cation is decomposed) showed the presence of the  $\text{AsF}_6^-$  ion. No suitable solvent for absorption spectra measurements has been found as the compound is insoluble in liquid sulfur dioxide, reacts with  $\text{BCl}_3$  and  $\text{AsF}_3$ , and is rapidly oxidized to  $\text{Te}_4^{2+}$  in 100%  $\text{H}_2\text{SO}_4$  and in  $\text{HSO}_3\text{F}$ . A reflectance spectrum gave a broad peak at  $485\text{ cm}^{-1}$ . The solid has a very small paramagnetism which is independent of temperature. The paramagnetism is however much too small for an odd-electron species. We conclude that the compound  $\text{Te}_3\text{AsF}_6$  contains a polyatomic cation of tellurium  $\text{Te}_{3n}^{n+}$  in which tellurium is in the  $+1/3$  oxidation state. Since the magnetic results indicate that the species contains an even number of electrons, the most probable formulas are  $\text{Te}_6^{2+}$  or  $\text{Te}_{12}^{4+}$ . Assuming that the cation is  $\text{Te}_6^{2+}$ , its formation from tellurium and  $\text{AsF}_5$  is described by the equation



This  $+1/3$  oxidation state is presumably the lower oxidation state species reported by Divers and Shimose<sup>10</sup> and by Bjerrum and Smith<sup>11</sup> although there is some discrepancy in color between our material and that reported by Divers and Shimose.

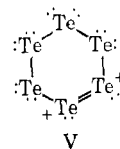
A similar gray product can be obtained from the reaction between tellurium and antimony pentafluoride in a 2:1 mole ratio, but mainly because of the difficulty of

separating the product from the simultaneously produced  $\text{SbF}_3$ , it was not obtained in a pure state.

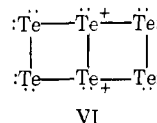
No evidence has yet been obtained for the  $+1/4$  oxidation state of tellurium.

In our investigations of the polyatomic cations of sulfur and selenium we have as yet found no cation analogous to the  $\text{Te}_{3n}^{n+}$  species. It may be significant that tellurium initially reacts with  $\text{AsF}_5$  or  $\text{SbF}_5$  to give the red  $\text{Te}_4^{2+}$  cation which subsequently reacts further with elemental tellurium to give  $\text{Te}_{3n}^{n+}$ . This behavior which is in contrast to the stepwise oxidation of sulfur or selenium suggests that the oxidation of  $\text{Te}_6^{2+}$  to  $\text{Te}_4^{2+}$  is more rapid than either the oxidation of Te to  $\text{Te}_6^{2+}$  or the reduction of  $\text{Te}_4^{2+}$  by elemental tellurium.

The structure of the  $\text{Te}_{3n}^{n+}$  ion is clearly of great interest and an X-ray crystallographic study is planned. A plausible structure for  $\text{Te}_6^{2+}$  would be V and related resonance structures which are similar to that proposed for the "isoelectronic"  $\text{S}_4\text{N}_2$  molecule.<sup>20</sup> This might also



be called an "aromatic" 10- $\pi$ -electron system and is clearly closely related to the hexagonal ring structure (6- $\pi$ -electron system) proposed as a possible structure for  $\text{Te}_6^{6+}$ . Another possible structure would be VI in which the two rings would presumably be at an angle of  $<180^\circ$  to each other as in Dewar benzene.



## Experimental Section

**Electrical Conductivity and Cryoscopic Measurements.**—The apparatus and technique for these measurements have been described previously.<sup>21,22</sup>

**Magnetic Susceptibility Measurements.**—Magnetic susceptibilities were determined by the standard Gouy method using a permanent magnet and a sample tube was calibrated with standardized nickel(II) chloride solutions. The usual corrections for the susceptibilities of the sample tube and the air displaced by the sample were applied.

**Spectrophotometric Measurements.**—Measurements on solutions were made in 1-cm rectangular silica cells with inserts to give path lengths from 0.1 to 1 mm. Optical densities were measured against a reference cell containing solvent on a Cary Model 14 recording instrument. Measurements on solids were made using a reflectance attachment. Solutions in  $\text{HSO}_3\text{F}$  with various Te: $\text{S}_2\text{O}_6\text{F}_2$  ratios were prepared by stirring the two reactants together in the solvent at room temperature until all the tellurium had dissolved, and the spectrum was then recorded. The dissolution of the tellurium was rapid when  $\text{S}_2\text{O}_6\text{F}_2$ :Te > 0.5 and was complete in a few minutes, but when  $\text{S}_2\text{O}_6\text{F}_2$ :Te < 0.5, it took as long as several hours to obtain the solutions.

**Vibrational Spectroscopy.**—Raman spectra were obtained

(20) H. G. Heal, "Inorganic Sulphur Chemistry," G. Nickless, Ed., Elsevier, Amsterdam, 1968, p 469.

(21) J. Barr, R. J. Gillespie, and R. C. Thompson, *Inorg. Chem.*, **3**, 1149 (1964).

(22) R. J. Gillespie, J. B. Milne, and R. C. Thompson, *ibid.*, **5**, 468 (1966).

using a Spex double monochromator and Spectra Physics helium-neon and argon ion lasers.

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

**The Reaction of Tellurium with Antimony Pentafluoride.**—In a typical experiment antimony pentafluoride (0.139 mol) was added to powdered tellurium (0.047 g-atom) in liquid sulfur dioxide at  $-63^\circ$  and the mixture was stirred for several days at  $-23^\circ$ . The red solution was filtered leaving a yellow residue which was repeatedly washed with sulfur dioxide until the washings were colorless 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 sulfur dioxide. *Anal.* Calcd for  $\text{Te}_2\text{Sb}_2\text{F}_{11}$ : Te, 35.97; Sb, 34.45; F, 29.60. Found: Te, 35.88; Sb, 34.23; F, 32.21. The yellow residue was heated at  $100^\circ$  under vacuum for 6 hr and a white sublimate was obtained. This was identified as antimony trifluoride by comparison of its Raman spectrum with that of an authentic sample. A yellow solid remained which appeared to be stable and nonvolatile up to at least  $120^\circ$ . *Anal.* Calcd for  $\text{TeSbF}_6$ : Te, 35.11; Sb, 33.50; F, 31.17. Found: Te, 35.42; Sb, 33.45; F, 31.13. The infrared spectrum of the solid had the characteristic strong broad band of  $\text{SbF}_6^-$  at  $699\text{ cm}^{-1}$ .

**The Reaction of Tellurium with  $\text{S}_2\text{O}_8\text{F}_2$** —In a typical experiment 2.00 g (0.0101 mol) of  $\text{S}_2\text{O}_8\text{F}_2$  was condensed onto powdered red tellurium (0.03 g-atom) in sulfur dioxide at  $-196^\circ$  and the mixture was allowed to warm up very slowly to  $-63^\circ$  over a period of a few days. The mixture was stirred for 1 day at  $-63^\circ$  and for 1 further day at  $-23^\circ$ . At this time the dark red solution contained a dark red solid, and  $\text{SO}_2$  and excess  $\text{S}_2\text{O}_8\text{F}_2$  were then pumped off leaving 5.31 g of a red amorphous solid. This corresponds to an essentially quantitative yield of 0.0075 mol of  $\text{Te}_4(\text{SO}_3\text{F})_2$ . *Anal.* Calcd for  $\text{Te}_4(\text{SO}_3\text{F})_2$ : Te, 36.03. Found: Te, 35.85.

With excess  $\text{S}_2\text{O}_8\text{F}_2$  a yellow solid was obtained but this appeared to be unstable at any temperature above  $\sim -20^\circ$  rapidly becoming dark. However solutions of tellurium(I) fluorosulfate could be obtained in fluorosulfuric acid which were stable if kept at all times below  $-23^\circ$ . These were prepared as described in the following section.

**Preparation of  $\text{TeSO}_3\text{F}$  Solutions in  $\text{HSO}_3\text{F}$ .**—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  $\text{S}_2\text{O}_8\text{F}_2$  in 35 g of  $\text{HSO}_3\text{F}$  at  $-75^\circ$ . The red solution obtained was allowed to warm up to  $-23^\circ$  with constant stirring. After a few hours the solution had become dark yellow. Small further additions of tellurium were then made, the whole quantity being added in a period of about 30 hr. The solution was then kept for a further 18 hr to ensure complete reaction. On addition of excess sulfur dioxide to this solution, a bright yellow compound was precipitated, and after this had been allowed to stand overnight to settle, a red solution was decanted off. The yellow solid was then extracted several times with sulfur dioxide until the sulfur dioxide remained colorless. The solid was kept under vacuum for 48 hr at  $-63^\circ$  to remove all the sulfur dioxide. The product was a

fine bright yellow powder. This solid decomposed if allowed to warm up to  $-23^\circ$ . Cold fluorosulfuric acid was then added to the cold solid drop by drop until all the yellow solid had dissolved. This deep yellow solution was kept under vacuum at  $-23^\circ$  for 24 hr to ensure removal of any remaining sulfur dioxide. Samples of the solution were analyzed as follows. The solution was hydrolyzed by adding ice that had previously been cooled in liquid nitrogen. It was then oxidized 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 and elemental tellurium was filtered off and weighed.

**The Reaction of Tellurium with Arsenic Pentafluoride.**—In a typical experiment arsenic pentafluoride (0.015 mol) was condensed onto powdered tellurium (0.02 g-atom) in liquid  $\text{SO}_2$  at  $-196^\circ$  and the mixture was allowed to warm up to room temperature. A red solution was obtained after stirring for 24 hr. The solid was filtered off and  $\text{SO}_2$ ,  $\text{AsF}_3$ , and excess  $\text{AsF}_5$  were removed under vacuum. *Anal.* Calcd for  $\text{Te}_4(\text{AsF}_6)_2$ : Te, 57.46. Found: Te, 57.64. The infrared spectrum had a strong band at  $700\text{ cm}^{-1}$ . ( $\text{CsAsF}_6$  has an absorption band at  $699\text{ cm}^{-1}$ .<sup>23</sup>) The  $^{19}\text{F}$  nmr spectrum of a solution in acetone gave a 1:1:1:1 quartet of  $\text{AsF}_6^-$  ( $\delta(\text{CCl}_3\text{F})$  62 ppm;  $J_{\text{As-F}} = 920\text{ Hz}$ ; cf. an aqueous solution of  $\text{AsF}_6^-$  with  $\delta(\text{CCl}_3\text{F})$  60.5 ppm and  $J_{\text{As-F}} = 930\text{ Hz}$ .<sup>24</sup>)

In a typical experiment using the same general procedure but with a Te:AsF<sub>5</sub> mole ratio of approximately 2 the deep red color of the sulfur dioxide solution began to diminish after approximately 3 hr and after 24 hr a voluminous gray solid remained which proved to be insoluble in sulfur dioxide. The product was extracted several times with liquid sulfur dioxide to remove the soluble  $\text{Te}_4^{2+}$  and the volatiles were then removed under vacuum leaving a gray powder. The X-ray powder pattern showed no lines that could be attributed to elemental tellurium. *Anal.* Calcd for  $\text{Te}_2\text{AsF}_6$ : Te, 66.96; As, 13.10; F, 19.94. Found: Te, 67.41; As, 13.40; F, 19.20. The  $\text{AsF}_6^-$  ion was identified by means of its infrared and  $^{19}\text{F}$  nmr spectra as described above for  $\text{Te}_4(\text{AsF}_6)_2$ .

**Analyses. Tellurium.**—Weighed samples were decomposed with water, concentrated nitric acid was added, and the solution was warmed to dissolve any precipitate. Tellurium was then precipitated as the element by adding an excess of hydrazine and warming the solution for 1 hr. The tellurium was filtered, dried, and weighed.

**Sulfate.**—Weighed samples were decomposed with water in a sealed tube. The tube was opened, the tellurium was filtered off, and the sulfate in the solution was determined gravimetrically as barium sulfate.

Other analyses were performed by Alfred Bernhardt Mikroanalytisches Laboratorium, 5251 Elbach über Engelskirchen, West Germany.

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