

CONTRIBUTION FROM THE TECHNICAL UNIVERSITY OF DENMARK,  
CHEMISTRY DEPARTMENT A, DK-2800 LYNGBY, DENMARK**Lower Oxidation States of Tellurium. Tellurium(II) in Chloroaluminate Melts**

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The solvated entity  $\text{Te}^{2+}$  has been identified in reaction mixtures of dilute solutions of  $\text{TeCl}_4$  and elementary tellurium. The solvent was  $\text{KAlCl}_4$  buffered with  $\text{KCl-ZnCl}_2$ . Spectrophotometric measurements showed that  $\text{Te}^{2+}$  is formed in the equilibrium  $\text{Te}^0 + \text{Te}^{\text{IV}} \rightleftharpoons 2\text{Te}^{\text{II}}$  at high chloride activity. The observed absorption bands of divalent tellurium (possibly as planar  $\text{TeCl}_4^{2-}$ ) are interpreted as p-p transitions within the  $5p^2$  configuration.

**Introduction**

Evidence has been obtained from recent investigations<sup>1-6</sup> in  $\text{H}_2\text{SO}_4$ ,  $\text{H}_2\text{S}_2\text{O}_7$ ,  $\text{HSO}_3\text{F}$ , and molten salt for the ability of tellurium to form species in low positive oxidation states, such as  $\text{Te}_4^{2+}$ ,  $\text{Te}_n^{n+}$ , and  $\text{Te}_{6n}^{2n+}$ .

As mentioned in a preceding paper<sup>5</sup> in salt melts made from  $\text{KCl}$ ,  $\text{AlCl}_3$ , and  $\text{ZnCl}_2$  four different tellurium species have been observed spectrophotometrically by varying systematically the composition of the chloroaluminate melt and the concentrations of the dissolved substances  $\text{TeCl}_4$  and elementary tellurium. Of these only one (I) has been identified with certainty,  $\text{Te}_4^{2+}$ . Two other species (II and III) have low oxidation states and could be  $\text{Te}_6^{2+}$  and  $\text{Te}_8^{2+}$ , but this is by no means certain. Species IV has been shown to have the charge  $2+$  and is probably  $\text{Te}_2^{2+}$ . In the present paper evidence is given for the first time for the formation of a new solvated entity,  $\text{Te}^{2+}$ . This species (labeled V) is formed when dilute solutions of  $\text{TeCl}_4$  are reduced with elementary tellurium in molten chloroaluminate solutions of high chloride activity.

Several tellurium complexes in the oxidation state  $2+$  are known, notably the square-planar complexes with thiourea,<sup>7</sup> but only a few simple compounds. The existence of  $\text{TeCl}_2$  in the gas phase has been proved beyond doubt,<sup>8</sup> and until recently this compound was also believed to exist as a solid.<sup>9</sup> However, this as well as solid  $\text{Te}(\text{AlCl}_4)_2$  has been questioned in the light of the results from recent experiments by Corbett and co-workers.<sup>6</sup>

**Experimental Section**

**Materials and Measurements.**—The materials and the experimental technique were almost the same as described previously.<sup>5</sup>  $\text{KCl}$  and  $\text{ZnCl}_2$  were reagent grade material purified by treatment in the molten state by  $\text{HCl}$  gas followed by filtration. The  $\text{AlCl}_3$  was made from aluminum metal (99.999%) and  $\text{HCl}$ . The  $\text{TeCl}_4$  was made by reaction between tellurium (99.9995%) and  $\text{Cl}_2$  and purified by distillation. The reaction between elementary tellurium and solutions containing  $\text{TeCl}_4$  was followed spectrophotometrically with a Cary 14R spectrophotometer equipped with a furnace, the temperature of which could be kept constant within  $\pm 0.1^\circ$  in the range  $100$ – $500^\circ$ .

The optical cells were made of fused quartz and had fixed path length in the range 5–1 mm. The cells used at high temperature were constructed in such a way that the volume not occupied by the melt was kept as small as possible in order to keep all tellurium compounds dissolved in the melt. The density of the buffered  $\text{KAlCl}_4$  solutions was calculated assuming ideal mixtures of  $\text{KCl}$ ,  $\text{ZnCl}_2$ , and  $\text{KAlCl}_4$ . This assumption is reasonable as the amounts of  $\text{ZnCl}_2$  and  $\text{KCl}$  added were small compared to the amounts of  $\text{KAlCl}_4$ . The density of  $\text{KAlCl}_4$  was obtained from the work of Morrey and Carter.<sup>10</sup>

**Definitions and Assumptions.**—The definitions in the present work are the same as those used in previous work.<sup>5</sup> They can be summarized as follows. *The initial molar amounts of elementary tellurium and  $\text{TeCl}_4$  dissolved in 1 l. of the melt will be referred to as the formality of these substances, respectively. The absorptivity refers to the absorbance in a 1-cm layer of the melt. Similarly the formal absorptivity refers to the absorptivity of a solution of formality 1.*

The absorbance of the reaction products refers only to those of low oxidation states in the equilibrated solution; *i.e.*, the absorbance of cell and solvents have been subtracted. If the absorbance of  $\text{Te}^{\text{IV}}$  is known, it is also subtracted; otherwise the absorbance is only given in the range where  $\text{Te}^{\text{IV}}$  does not absorb.

Three assumptions are made concerning the dilute solutions—that the absorbances are additive, that the Bouguer–Beer law is valid, and that the activity coefficients of the tellurium species are constant. Among the justifications for these assumptions are the facts that the total tellurium concentration never exceeded 1 mol %, that the ionic strengths of the solvents were almost constant, and that the melts were buffered with respect to the chloride activity.

**Results**

**Oxidation State of Species V.**—At low formality of dissolved tellurium the spectra of the reaction products in  $\text{KAlCl}_4$ , buffered to a high chloride activity, seemed to follow the Bouguer–Beer law with respect to the formality of elementary tellurium at all wavelengths where  $\text{Te}^{\text{IV}}$  did not absorb. Since the range of the Bouguer–Beer law depends on temperature and the formality of  $\text{TeCl}_4$ , no general limits of validity can be given, but with a temperature of  $500^\circ$  and a formality of  $\text{TeCl}_4$  of 0.00544 *F*, the range of validity was approximately 0–0.003 *F* for tellurium. In this range, a spectrum calculated with respect to elementary tellurium should stay constant. Such a spectrum is given in Figure 1. Since the main features of this spectrum did not change in the range  $300$ – $500^\circ$ , except for an increase of the formal absorptivity, it is reasonable and in agreement with previous work to assume that only one single reaction product is present. This will, as already mentioned, be labeled V. If the formality of tellurium in the present example is increased to values higher than 0.003 *F*, the calculated spectra will no longer be independent of the formality of tellurium, due to the absorbance of species IV, which, in contrast to II and

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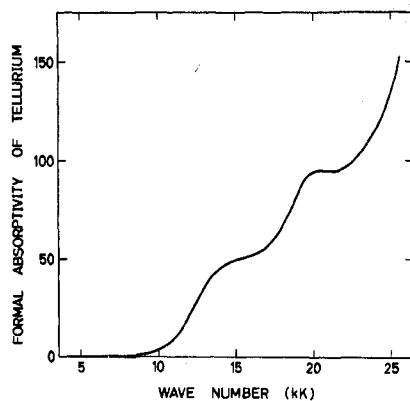


Figure 1.—Spectrum of reaction product V in the range where the Bouguer–Beer law is obeyed. The spectrum was obtained from 0.00228 *F* Te and 0.00544 *F* TeCl<sub>4</sub> in an KAlCl<sub>4</sub> solvent, buffered with 0.447 *F* KCl and 0.293 *F* ZnCl<sub>2</sub> at 500° (the high-energy part of this spectrum was calculated assuming an oxidation state of 2+ for the reaction product, a value which will be confirmed later in the article).

III, is stable at high chloride activity. Previously,<sup>5</sup> only IV was detected at high chloride activity as V has a very formal absorptivity and is present only in very small concentrations at low temperature. The behavior described is illustrated graphically in Figure 2.

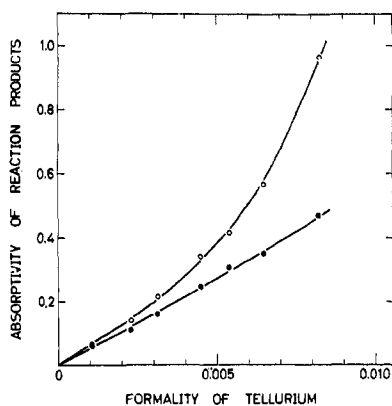


Figure 2.—Relations between the formality of elementary tellurium in the buffered KAlCl<sub>4</sub> melt at 500° and the absorptivity of the reaction products at 15.0 kK (filled circles) and 18.2 kK (open circles). The formality of TeCl<sub>4</sub> was 0.00544 *F*, of KCl 0.447 *F*, and of ZnCl<sub>2</sub> 0.293 *F*.

Here the absorptivities measured at 15.0 and 18.2 kK are plotted against the formality of tellurium. V has a band at 15.0 kK, but IV has no bands in the visible range. At the chosen wave number 18.2 the absorptivity of IV is reasonably high, and the absorptivity due to Te<sup>IV</sup> is still negligible.

At wave numbers higher than 18.2 kK, Te<sup>IV</sup> (in the form of chloro complexes) begins to absorb. At very high chloride activity a band is found at 26.7 kK,<sup>5</sup> probably due to TeCl<sub>6</sub><sup>2-</sup>. In the present studies where the chloride activity is lower, no band at 26.7 kK was observed, but the absorbance is still high. In Figure 3, the formal absorptivity of Te<sup>IV</sup> measured at 28.6 kK is plotted against the Te:TeCl<sub>4</sub> formality ratio. At 500° (filled circles) and low formality of tellurium the absorptivity is high due to the absorbance of Te<sup>IV</sup>. A linear decrease in formal absorptivity is observed with increasing formality ratio due to the disappearance of

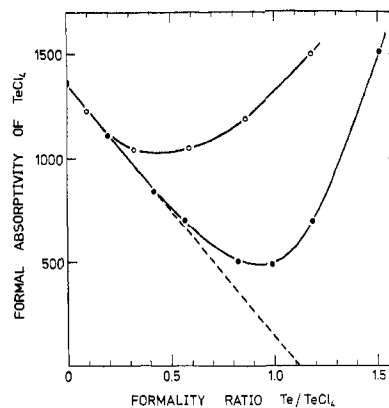


Figure 3.—Relations between the formal absorptivity of TeCl<sub>4</sub> and the Te:TeCl<sub>4</sub> formality ratio at 500° (filled circles) and 300° (open circles). Formalities of TeCl<sub>4</sub> were 0.00544 *F* (filled circles) and 0.00532 *F* (open circles). The solvent was KAlCl<sub>4</sub> buffered with KCl (0.447 *F* at 500°) and ZnCl<sub>2</sub> (0.293 *F* at 500°).

Te<sup>IV</sup>. This range corresponds to the Bouguer–Beer range found in Figure 2. When the Te:TeCl<sub>4</sub> formality ratio reaches values between 0.5 and 1.0, a decreasing slope is observed until the value 1.0 where the absorptivity starts to increase.

Unfortunately, this phenomenon is very much dependent on the temperature. At 300° (open circles) the increase occurs around a Te:TeCl<sub>4</sub> formality ratio of 0.5. However, it is still possible to deduce something definite about the oxidation state of species V. The linear decrease must correspond to the formation of V by reduction of Te<sup>IV</sup>. If V does not absorb at 28.6 kK, we are actually watching the disappearance of Te<sup>IV</sup>. An extrapolation of this linear decrease at 500° (dashed line) shows that if IV was not formed then at the Te:TeCl<sub>4</sub> formality ratio 1.1, all Te<sup>IV</sup> was reduced to species V. Similarly, at 300° and a formality ratio of 1.1, all Te<sup>IV</sup> was reduced to V. Any absorption of V at 28.6 kK will only result in a steeper descent of the line showing the actual disappearance of Te<sup>IV</sup>. This means that the formality ratio at which all Te<sup>IV</sup> is reduced to V will be smaller than 1.1. A formality ratio equal to 1.1 corresponds to an oxidation state of 1.90+, while a lower value will only result in a higher oxidation state.

**Formal Charge of Species V.**—If the formality of tellurium is increased to still higher values than shown in Figure 2, a saturation point will be reached, and further addition of elementary tellurium will not change the composition of the melt. One way of determining the formal charge of a species is to study an equilibrium involving some other species of known formal charge in the saturated melt. Since the formal charge of IV has previously<sup>5</sup> been found to be 2+, there should be a possibility of obtaining the formal charge of V. Unfortunately, even under the best circumstances (high temperature, reasonably high chloride activity), the concentration of V is so small compared with the concentration of IV in the saturated melt that it is impossible to observe clearly the bands due to V. If, however, the activity of the tellurium phase is lowered by alloying it with gold, which is inert under the present circumstances, the bands of V can be observed. Gold and tellurium form an alloy which can be saturated with solid gold at 500°. The composition of the molten al-

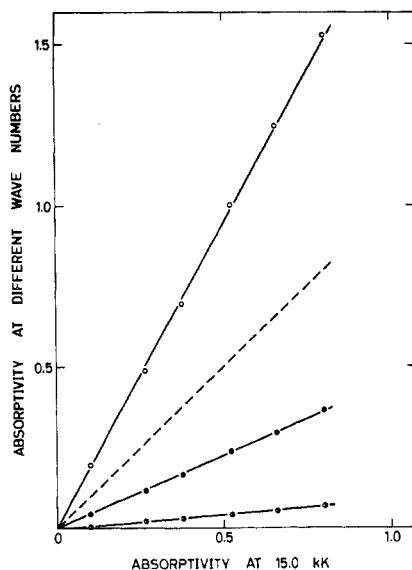


Figure 4.—Relations between the absorptivity at 15.0 kK and the absorptivity at 10.0 kK (half-filled circles), 12.5 kK (filled circles), and 18.2 kK (open circles) of a solution saturated with a liquid gold-tellurium alloy (in equilibrium with solid gold) at 500° and at different formalities of  $\text{TeCl}_4$ . The solvent was  $\text{KAlCl}_4$ , buffered with  $\text{KCl}$  and  $\text{ZnCl}_2$ . The formality of  $\text{KCl}$  was 1.85  $F$  and of  $\text{ZnCl}_2$  1.48  $F$ . The exact values of the formalities of tellurium and  $\text{TeCl}_4$  were not known. The highest formality of  $\text{TeCl}_4$  was ca. 0.104  $F$ .

loy at 500° is close to 50 mol % Au–50 mol % Te.<sup>11</sup> The activity in such a saturated alloy should stay constant, even if some of the tellurium participates in a reaction. The experiments showed that the ratio between IV and V remained constant when the formality of elementary tellurium was changed, as long as the gold-tellurium alloy was present, and the chloride activity was constant. This is illustrated in Figure 4 and is compatible only with the assumption that IV and V have the same formal charge 2+.

#### Discussion

Since the oxidation state of species V must be equal to or greater than 1.90+ and the formal charge has to

(11) M. Hansen, "Constitution of Binary Alloys," McGraw-Hill, New York, N. Y., 1958, p 234.

be 2+, the only possibility of the formula of species V is  $\text{Te}^{2+}$ . This agrees well with the experimental data for the observed species. A high temperature would favor the formation of a mononuclear unit. As seen from Figure 3, the formation of  $\text{Te}^{2+}$  is in fact favored by a high temperature.  $\text{Te}^{2+}$  with the configuration  $5p^2$  should have a ligand field spectrum of low intensity in the visible range. This is in fact observed, as seen in Figure 1. In order to obtain the molar absorptivity of  $\text{Te}^{2+}$  the formal absorptivity shown should here be multiplied by  $1/2$  according to the reaction  $\text{Te}^0 + \text{Te}^{IV} = 2\text{Te}^{II}$ .

$\text{Te}^{2+}$  has the same outer electron configuration as  $\text{Bi}^+$ , but no direct comparison can be made between the two spectra, as the spin-orbit forces are much stronger in  $\text{Bi}^+$  than in  $\text{Te}^{2+}$ . In the case of  $\text{Bi}^+$  there is only a little difference between the band positions of the gaseous state and the band positions in the  $\text{AlCl}_3$ - $\text{NaCl}$  eutectic,<sup>12,13</sup> because of an almost cubic environment in solution. If one, however, compares the energy levels of  $\text{Te}^{2+}$  in the gaseous phase<sup>14</sup> with the spectra of  $\text{Te}^{2+}$  obtained in  $\text{KAlCl}_4$ , it is obvious that there is no direct correlation. This could be caused by a noncubic complex of  $\text{Te}^{2+}$  in solution, such as  $\text{TeCl}_4^{2-}$ , which would be expected to be square planar (see Gillespie<sup>15</sup>). In contrast to  $\text{Te}^{2+}$ ,  $\text{Bi}^+$  is stable only at very low chloride activities where there is little possibility of formation of chloro complexes. This explains why no square-planar complex of  $\text{Bi}^+$  is formed. Ligand field calculations are now being made to see whether the spectra of solvated  $\text{Te}^{2+}$  might possibly be explained by a planar configuration.

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