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Lower Oxidation States of Tellurium. Tetratellurium(2+) in Molten Salt Solutions

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The solvated entity Te_4^{2+} was prepared by reduction of dilute solutions of TeCl_4 with elementary tellurium. Two different types of solvent were used, one consisting of eutectic 63 mol % AlCl_3 -37 mol % NaCl and the other consisting of KAlCl_4 , buffered with mixtures of KCl - ZnCl_2 or saturated with KCl . The reaction was found to be $7\text{Te} + \text{Te}^{4+} \rightleftharpoons 2\text{Te}_4^{2+}$. With molten 63 mol % AlCl_3 -37 mol % NaCl as a solvent spectrophotometric measurements showed that this equilibrium was shifted so far to the right that all tetravalent tellurium was consumed before a second reaction product was formed. It appears that apart from Te_4^{2+} at least two other tellurium species are formed in the eutectic melt at higher total tellurium concentrations. The charge of the first reaction product, *i.e.*, Te_4^{2+} , could be found from the absorbance spectra of equilibrated mixtures in which both solid tellurium and dissolved TeCl_4 participated. In this latter case KAlCl_4 buffered with KCl - ZnCl_2 and also KAlCl_4 saturated with KCl were used as solvents.

Introduction

In a previous publication¹ it was pointed out that the entity Te_{2n}^{n+} is the first product of the reaction between elementary tellurium and dilute solutions of TeCl_4 in the liquid AlCl_3 - NaCl eutectic. The most likely value of n was indicated to be 2.

In the present paper further details supporting this claim are given. As in the papers^{2,3} concerning the lower oxidation states of bismuth, both Te_4^{2+} and Te^{4+} are intended only to specify the oxidation states and numbers of tellurium atoms per molecular unit of the reaction products.

With the one obvious exception of Te(II) there have been few studies on the oxidation states of tellurium between zero and +4. TeCl_2 exists but is not very stable and decomposes to tellurium and TeCl_4 if attempts are made at dissolution in common solvents.^{4,5} On the other hand, tellurium dissolves easily in molten TeCl_4 forming intensely colored melts. Damiens⁴ tried, without success, by phase diagram and vapor pressure studies to obtain more information about the species formed in such mixtures. In the present investigation dilute solutions of TeCl_4 have been used but the results obtained will probably be indicative of the composition of more concentrated solutions.

Shortly after the publication of our letter¹ about

Te_4^{2+} Gillespie and coworkers⁶ published a letter in which they reported the existence of Te_4^{2+} in fluorosulfuric acid. The spectrum reported was very similar to the spectrum of ref 1. More recently the same group has documented evidence for the Te_n^{n+} species.⁷ Their results agree best with a value of n equal to 8, but other values of n cannot be ruled out.

Definitions and Assumptions

The initial molar amounts of tellurium and TeCl_4 dissolved in 1 l. of the melt will be referred to as the formality of tellurium and TeCl_4 , respectively. In the same way, the formality ratio (or formal ratio) between the amounts of Te and TeCl_4 refers to the initial molar amounts which were dissolved in the melt.

The absorbance values given always refer to the absorbance of the tellurium in solution; *i.e.*, the absorbance of cell and solvent have always been subtracted. The absorbance of the reaction products will be given by

$$A(\text{product}) = A(\text{mixture}) - A(\text{TeCl}_4 \text{ mixture}) \quad (1)$$

where $A(\text{mixture})$ is the absorbance of the reaction mixture and $A(\text{TeCl}_4 \text{ mixture})$ the absorbance of the TeCl_4 in solution. As a first approximation the concentration of TeCl_4 in solution was put equal to the formality of TeCl_4 . Later, when more was known about the reactions, the amount of TeCl_4 which had been reduced could be calculated.

(6) J. Barr, R. J. Gillespie, R. Kapoor, and G. P. Pez, *J. Amer. Chem. Soc.*, **90**, 6855 (1968).

(7) J. Barr, R. J. Gillespie, G. P. Pez, P. K. Ummat, and O. C. Vaidya, *ibid.*, **92**, 1081 (1970).

(1) N. J. Bjerrum and G. P. Smith, *J. Amer. Chem. Soc.*, **90**, 4472 (1968).
(2) N. J. Bjerrum, C. R. Boston, and G. P. Smith, *Inorg. Chem.*, **6**, 1162 (1967).
(3) N. J. Bjerrum and G. P. Smith, *ibid.*, **6**, 1968 (1967).
(4) A. Damiens, *Ann. Chim. (Paris)*, **19**, 44 (1923).
(5) E. E. Aynsley, *J. Chem. Soc.*, 3016 (1953).

The absorptivity refers to the absorbance in a 1-cm layer of the melt. Similarly, the formal absorptivity refers to $A/C_F l$ where l is the path length in centimeters and C_F is the formality. The formal absorptivity can be calculated either from the formality of tellurium or from the formality of TeCl_4 .

By the formal charge of a species is meant the charge on the tellurium atoms involved, when all ligands are removed. Similarly, by the oxidation state is meant the formal charge divided by the number of tellurium atoms.

As in the papers on bismuth,^{2,3} several assumptions, generally valid for dilute solutions, are used in the interpretation of the results. The first of these is the law of additive absorbances, the second is the Bouguer-Beer law, and the third is Henry's law with respect to the activities of tellurium species. Among the justifications for supposing these laws to hold are the facts that the total tellurium concentration never exceeded 2.5 mol % and that the ionic strengths of the solvents used were very high and not expected to change much by addition of small amounts of solute ions. A fourth assumption is that it is possible to buffer the chloride activity to keep it essentially constant in each experiment. The AlCl_3 - NaCl eutectic melt itself is a buffer due to the reaction $\text{Al}_2\text{Cl}_7^- + \text{Cl}^- = 2\text{AlCl}_4^-$. This has been treated in more detail in the work of Trémillon and Letisse.⁸ Molten KAlCl_4 has no buffer capacity of its own, but buffering can be accomplished by adding ZnCl_2 - KCl mixtures or by saturating the melt with KCl . The buffering effect of KCl - ZnCl_2 is due to the ambivalent character of ZnCl_2 with respect to chloride ions. Important figures are the formality ratio between KCl and ZnCl_2 and the formality of ZnCl_2 . The buffering due to the saturation of the melt with KCl can be explained as follows. For KAlCl_4 the potassium ion concentration is high and the solubility of KCl is comparatively small (3.4 mol % at 300°). The presence of a solid phase of KCl will keep the ionic product of KCl in the melt constant, and since the reactions studied will cause only negligible changes in the potassium ion activity, the melt will be buffered with respect to chloride ions.

Experimental Section

The materials and experimental techniques used in the present work are the same as those used in previous work.^{2,3} Sodium chloride and potassium chloride were reagent grade material purified by treatment in the molten state by HCl gas followed by filtration. The AlCl_3 was made from aluminum metal (99.999%) and HCl . The ZnCl_2 was similarly made from zinc metal (99.999%) and HCl . The TeCl_4 was made by reaction between tellurium (99.9995%) and an excess of chlorine and purified by distillation in an atmosphere consisting of nitrogen and chlorine.

The reaction between elementary tellurium and solutions containing TeCl_4 was followed spectrophotometrically with a Cary 14R spectrophotometer equipped with a furnace. A few of the measurements were made on a Cary 14H spectrophotometer. Both spectrophotometers were equipped with digital systems for punching out spectral data on paper tape. The data obtained were transferred to magnetic tape and fed to an IBM-

7094 computer for numerical analysis. The results were plotted on a Calcomp plotter.

The furnace constructed so as to be accommodated by the cell compartment for the Cary 14R spectrophotometer consisted of an inner cylindrical core of aluminum (diameter 55 mm and length 165 mm). In this core, provision was made for a square cross section cell holder (12.7 × 12.7 mm) and holes were drilled for the optical pathway. The furnace was heated by a Thermo-coax element (2-mm outside diameter) wound in a groove around the aluminum block. The aluminum block was suspended inside a water-cooled cylindrical housing (diameter 140 mm and length 222.5 mm) by means of thin-walled stainless steel tubes, one horizontal tube permitting the light beam to traverse the furnace and one vertical tube providing access to the cell holder. Two circular windows of fused quartz (2 mm × 30 mm) were used to seal the horizontal tube. In order to prevent heat losses at the end of the block and from the windows, special heating coils were placed around the stainless steel tubes. The insulating material between the block and the housing consisted of porous aluminum oxide. A separately heated cylindrical furnace (of outer diameter 42 mm and length 260 mm) was placed as a lid on the top of the main furnace to exclude any stray light.

The temperature of the main furnace was controlled by an on-off regulator equipped with a compensation coil for the time lag between the start of the heating and the change in the temperature indicator, which in this case was a platinum resistance thermometer. The whole furnace was mounted on a plate of the same dimensions as a normal Cary 14R lid, so that the lower part of the furnace could be placed in the optical pathways of the Cary 14R. With this setup, the temperature in the melt could be kept constant within $\pm 0.3^\circ$ in the range 100-500°.

The optical cells were made from fused quartz ("Ultrasil") and had 1-cm² cross section. The path length of a cell could be reduced by placing a precision quartz insert inside the cell.² Completely sealed-off cells were used in order to avoid the contamination by the atmosphere and the loss of evaporated AlCl_3 .

The initial amounts of tellurium and TeCl_4 and the remaining amounts of unreacted tellurium were weighed using a microbalance in a nitrogen-filled glove box. Additions to the sealed cells were accomplished with the technique described previously.² The reaction between tellurium and the TeCl_4 solution was rather slow. It was therefore necessary to place the charged cell in a special furnace which was gently rocked over an extended period of time. Even after additions of TeCl_4 to a homogeneous melt in which one would expect the reaction to go to completion quickly, the equilibrium was reached only after several hours. Therefore all spectrophotometric measurements were repeated until they remained constant for at least 1 day.

The two different AlCl_3 -containing mixtures mentioned above were used as solvents. The densities of these solvents were obtained from the work of Boston⁹ and from the work of Morrey and Carter.¹⁰ The density of the buffered KAlCl_4 was calculated assuming ideality in the mixture of KCl - ZnCl_2 and KAlCl_4 ; this assumption must hold fairly accurately, because the amounts of ZnCl_2 - KCl added were small compared to the amount of KAlCl_4 .

The solvents were completely transparent in the near-infrared and visible regions and in parts of the ultraviolet region of the spectrum. Dilute solutions of TeCl_4 in AlCl_3 - NaCl eutectic only absorbed far out in the ultraviolet region and only the absorption edge of a band could be observed. On the other hand a solution of TeCl_4 in the buffered KAlCl_4 solvent absorbed in the visible range. In this mixture a band was found around 26.7 kK with a molar absorptivity of 1.28×10^3 l./mol cm, when the formality ratio KCl/ZnCl_2 was 2.89. This band is probably due to TeCl_6^{2-} .

Results and Discussion

Species Formed in the AlCl_3 - NaCl Eutectic.—When

(8) B. Trémillon and G. Letisse, *J. Electroanal. Chem. Interfacial Electrochem.*, **17**, 371 (1968); **17**, 387 (1968).

(9) C. R. Boston, *J. Chem. Eng. Data*, **11**, 262 (1966).

(10) J. R. Morrey and D. G. Carter, *ibid.*, **13**, 94 (1968).

the $\text{AlCl}_3\text{-NaCl}$ was used as solvent, the spectra of the reaction product approximated the Bouguer-Beer law with respect to the formality of tellurium quite well as long as the formality ratio Te/TeCl_4 was kept below 7. This means that a spectrum calculated with respect to the formality of tellurium should not change in this range. Such a spectrum in the Bouguer-Beer law range is given in Figure 1. A band maximum was found at 18.0 kK and a shoulder was found at a somewhat higher wave number. A numerical Gaussian analysis made by digital computer indicated that two bands were present in the shoulder, one located at 22.0 kK and the other at 25.4 kK. These Gaussian curves are shown by dotted lines on Figure 1. Changes in the

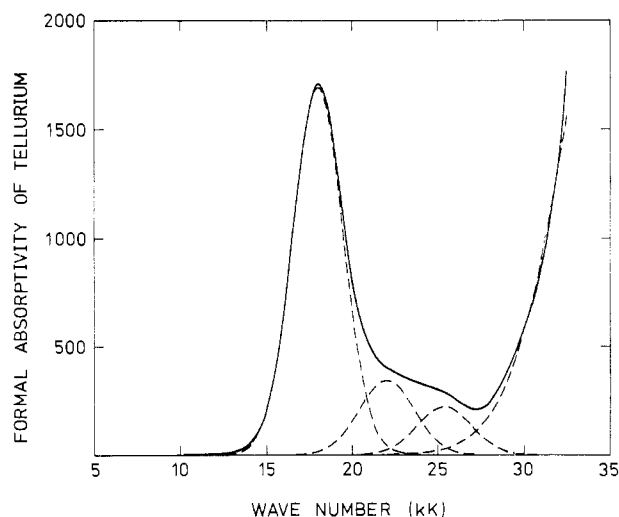


Figure 1.—Spectrum of reaction product in the range where the Bouguer-Beer law is obeyed. The dashed lines show the resolution of this spectrum into Gaussian curves. The spectrum was obtained from 0.0293 *F* Te and 0.00562 *F* TeCl_4 in an $\text{AlCl}_3\text{-NaCl}$ eutectic solvent at 250°.

temperature over the range 130–310° produced only minor changes in the spectrum in Figure 1. The bands sharpened somewhat by lowering the temperature, but the band areas did not change significantly.

The Bouguer-Beer law behavior in the formality ratio range below 7 indicates that either a single reaction product is formed, or else, if there are two or more products, their concentrations are in constant proportions. The insensitivity toward temperature suggests that only one single reaction product is present. If there had been more than one reaction product, changes in temperature would most likely have produced shifts in the equilibrium and this would have caused more pronounced changes in the observed spectrum. For convenience this reaction product will be labeled I.

If the formality ratio Te/TeCl_4 is increased to values higher than 7, the main peak at 18.0 kK begins to decrease on an absorptivity scale calculated with respect to the formality of tellurium. This is shown in Figure 2. In this figure, spectrum A is in the formality ratio range below 7, whereas the others are in the range above 7. As seen from this figure, the curves A to C form three isosbestic points located at 15.2, 22.0, and 32.5

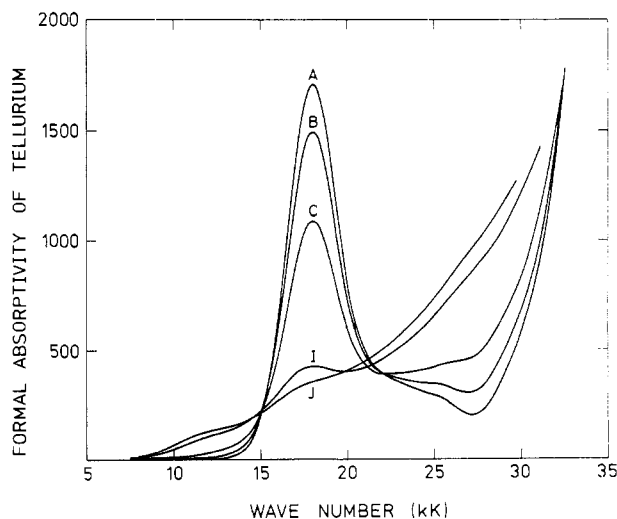


Figure 2.—Series of spectra of reaction products measured in an $\text{AlCl}_3\text{-NaCl}$ eutectic at 250°. For clarity the spectra between C and I are not shown on the figure. The formality of added TeCl_4 was 0.00562 *F*. Formality ratio Te/TeCl_4 : A, 5.22; B, 7.49; C, 8.46; I, 12.02; J, 13.59.

kK. A closer analysis of the spectra shows that these are internally linear dependent. This suggests that two absorbing reaction products are present and for convenience the additional species will be labeled II. The significance of isosbestic points and linear relationships between spectra has been treated in the paper by Brynstad and Smith.¹¹

At even higher ratios of Te/TeCl_4 , the two-species model proves insufficient. It is obvious that curves I and J on Figure 2 have a different point of intersection than A, B, and C. This is an indication that at least one new reaction product is formed.

As seen on J in Figure 2 there are two shoulders present in this spectrum, one located at 11.5 kK and the other located at 17.3 kK. That at 17.3 kK could be due to species II, but the band located at 11.5 kK must be due to a new species. For convenience the new species is denoted III.

The functional dependence of the formal absorptivity of TeCl_4 for these spectra on the formality ratio Te/TeCl_4 is shown in Figure 3. It is evident from this figure that the Bouguer-Beer law is approximated quite well at Te/TeCl_4 values below 7. Close to the value 7 is a very sharp break in the curve. Between 7 and 8.5 there is still a linear relationship between the absorptivity and the ratio Te/TeCl_4 , but the absorptivity is now decreasing with increasing Te/TeCl_4 . This was the range in which two reaction products were found. At higher ratios (*i.e.*, higher than 8.5) the linear dependence breaks down, a phenomenon corresponding to the disappearance of the isosbestic points in Figure 2.

Determination of Oxidation States in the $\text{AlCl}_3\text{-NaCl}$ Eutectic.—From the above discussion it is clear that only two species, Te(IV) and I, are present, as long as the formality ratio Te/TeCl_4 is less than 7. As the formality ratio Te/TeCl_4 is increasing in this range the

(11) J. Brynstad and G. P. Smith, *J. Phys. Chem.*, **72**, 296 (1968).

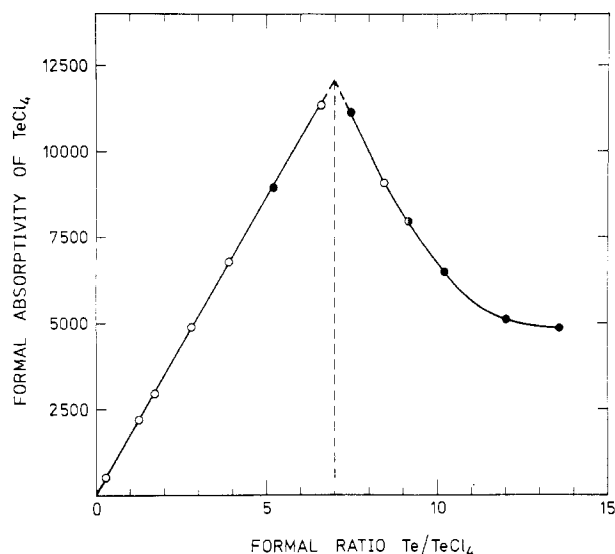
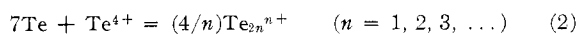


Figure 3.—The relation between the formal absorptivity of TeCl_4 and the formality ratio Te/TeCl_4 . Formalities of TeCl_4 were 0.00726 F (open circles) and 0.00562 F (filled circles). The half-filled circle represents a coincidence of an open and a filled circle.

concentration ratio $\text{Te(IV)}/\text{I}$ must be decreasing until Te(IV) disappears at a formality ratio for Te/TeCl_4 of 7. It can therefore be concluded that the reaction



continues until all Te(IV) is consumed, and then the tellurium starts to reduce Te_{2n}^{n+} forming II.

The oxidation state of I will then have to be $+1/2$. A least-squares determination of the intersection of the straight lines on Figure 3 gave the value of 7.03 for the formality ratio at the point of intersection. Reasonable formulas (*i.e.*, formulas with a possibility for a formal charge below 8) can only be obtained when the ratio at the intersection point is an integer. This makes 7 a very reasonable value.

At this stage in the investigation little can be said about the oxidation state of species II and III. This is so primarily because there is no sharp break in the curve on Figure 3 for the formation of these species and also because the exact shape of the spectra of these species is unknown. However, the value of their oxidation state most likely will lie between $+1/2$ and $+1/4$, since an extrapolation of the curve on Figure 3 seems to give a completely flat curve at the formality ratio 15. A completely flat curve must mean that the melt is saturated with respect to tellurium. A formality ratio between Te and TeCl_4 of 15 corresponds to the oxidation state $+1/4$.

Species Formed in the KAlCl_4 Melt.—As mentioned above, molten KAlCl_4 has very little buffer capacity of its own. It was not possible to weigh out KCl and AlCl_3 (from which KAlCl_4 is made) so accurately that the same chloride ion activity could be obtained each time. However the chloride ion activity could be stabilized by the addition of small amount of ZnCl_2 . Furthermore, additions of AlCl_3 or KCl to this melt changed the chloride ion activity in small and reproducible steps.

In such a buffered melt the spectra of the products from the reaction between tellurium and TeCl_4 changed with changing chloride ion activity. These spectra formed at 300° a set of curves which intersected at about 26.3 kK with a formal absorptivity of around 250. A closer analysis of the spectra revealed their linear dependence. As before this indicates the presence of two reaction products. The spectrum found at low chloride ion activity is almost identical in shape and absorptivity with the spectrum of I in the AlCl_3 - NaCl eutectic. It is therefore reasonable to assume that it is due to I. The spectrum found at high chloride ion activity has no pronounced bands in the visible range. In this respect it is similar to the spectra of II and III but the formal absorptivity is much lower at comparable wavelengths. Because of the low absorptivity in general and as there are no bands around 11.5 kK where III has a band, it must be due to a new species which will be labeled IV.

At this stage in the investigation little can be said about the oxidation state of tellurium in IV, other than that recent measurements indicate that the oxidation state lies between that of I and that of Te(IV) .

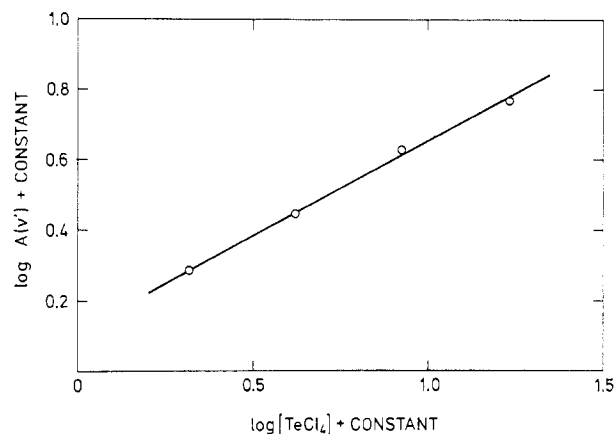
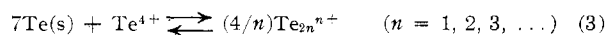


Figure 4.—Plot used to deduce the charge on one of the reaction products. $\nu' = 14.3$ kK. The concentration of TeCl_4 varied between 0.0204 and 0.167 M . (The concentration of the TeCl_4 cannot be calculated exactly without knowing the oxidation state of tellurium(IV). In this figure the oxidation state of tellurium(IV) has been put equal to +1, but other values of the oxidation state in the range 0.5–4 will not change the slope appreciably.)

Formal Charge of the Species Formed in the KAlCl_4 Melt.—One way of determining the formal charge of an elemental species is to study an equilibrium involving the pure element in solid or liquid form and another species of the same element with a known formal charge. Such an equilibrium could be



In a molten AlCl_3 - NaCl eutectic, the equilibrium is displaced so strongly to the right that it is impossible to measure or calculate the amount of Te(IV) present. This calculation is possible for the equilibrium in KAlCl_4 as solvent. In order to obtain a high chloride ion activity, the melt was saturated with KCl . As indicated previously this should stabilize species IV. A com-

parison between the spectrum found in KAlCl_4 buffered with KCl-ZnCl_2 and the spectrum found in KAlCl_4 saturated with KCl reveals that the two spectra were almost identical up to about 18 kK where the absorptivity of the latter increased much more rapidly than that of the former. It is reasonable to assume that the absorbance at wave numbers above 18 kK is the result of a superposition of an unknown species. The absorbance at wave numbers below 18 kK did not rise in proportion to the concentration of Te(IV) . A log-log plot (Figure 4) gave a straight line with a slope of 0.53, corresponding to the charge +2.12. A charge of +2.12 is of course not physically possible, but it is not much different from +2, which is considered to be the correct value for the charge on IV. At wave numbers higher than 18 kK a steeper rise of absorbance with added TeCl_4 is observed. This indicates that the unknown species had a charge higher than +2.

It is not possible to establish a similar equilibrium between I and Te(IV) , only between I and IV. Fortunately this permits the determination of the charge on I because the charge on IV is now known. The experiments showed that the ratio between I and IV did not change when the formality of tellurium was changed as long as elementary tellurium was present in excess in the melt and the chloride ion activity was constant. This phenomenon is illustrated in Figure 5. Here the absorbance (from a series of spectra of mixtures containing both I and IV in varying total concentrations) at 22.2 kK is plotted against the absorbance at 18.0 kK. The values 18.0 and 22.2 kK are used since at 18.0 kK I is responsible for the main part of the absorbance (see Figure 1), whereas at 22.2 kK IV is responsible for the main part of the absorbance.

The linear dependence borne out by Figure 5 shows that the concentration ratio of I/IV is invariant against their total concentration. By similar argument as above, this is compatible only with the assumption that

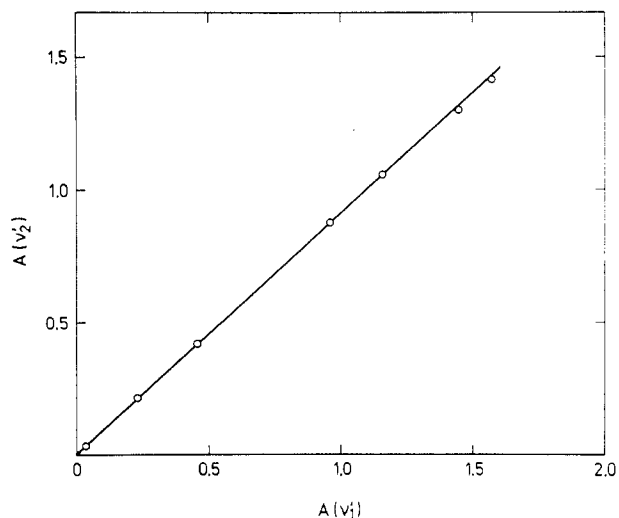


Figure 5.—The relation between the absorbance at two different wave numbers of a solution saturated with tellurium at 260° and at different total concentrations of I and III. $\nu_1' = 18.0$ kK; $\nu_2' = 22.2$ kK. The solvent was KAlCl_4 , buffered with KCl-ZnCl_2 of formality ratio 0.86. The formality of ZnCl_2 was 0.605 F . The exact values of the formalities of tellurium and TeCl_4 are not known.

I and IV have the same formal charge and hence the formula for I must be Te_4^{2+} . With this information the formal absorptivity scale in Figure 1 may be converted to the molar absorptivity scale of Te_4^{2+} by multiplying by $7/2$.

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