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Chloro Complexes in Molten Salts. II.[1] Potentiometric and Spectrophotometric Study of Chloro Complexes Formed in KCl-AlCl3-TeCl4 at 300°

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The chloro complexes existing in the pCl^- range from 0.28 to 3.84 in $KAlCl_4$ at 300° were found both by potentiometric and spectrophotometric measurements to be $TeCl_6{}^{2-}$, $TeCl_5{}^-$, $TeCl_4$, and $TeCl_3{}^+$. The pK values based on molar concentrations for the reactions $TeCl_6{}^{2-} \rightleftharpoons TeCl_5{}^- + Cl^-$, $TeCl_5{}^- \rightleftharpoons TeCl_4 + Cl^-$, and $TeCl_4 \rightleftharpoons TeCl_3{}^+ + Cl^-$, were found to be in the regions 0.68–0.82, 2.13–2.32, and 3.66–3.92, respectively. The spectra of $TeCl_6{}^{2-}$, $TeCl_5{}^-$, $TeCl_4$, and $TeCl_3{}^+$ were calculated on the basis of the found equilibrium constants. Assuming that the composition of the precipitate at low pCl^- is K_2TeCl_6, the concentration of $TeCl_6{}^{2-}$ in a $KAlCl_4$ melt saturated with this precipitate at 300° was calculated to be in the range 0.159–0.177 M.

Introduction

Some predictions about the possible chloro complexes of tetravalent tellurium were given earlier.[2,3] Since then it has been shown that it is possible with the use of a chlorine–chloride electrode to treat quantitatively what are essentially acid-base equilibria in a chloroaluminate melt.[1] By means of this electrode and by means of spectrophotometric measurements it has been possible to identify and describe some of the chloro complexes formed.

Not much is known about tellurium complexes in melts, but by means of conductometric titrations[4] a 2:1 compound of KCl and $TeCl_4$ in molten $SbCl_3$ has been shown to exist. This is consistent with the formation of a $TeCl_6{}^{2-}$ ion. From phase diagrams of $MCl-TeCl_4$ (M = Li, Na, K, Rb, Cs), the solid compounds with overall composition M_2TeCl_6 (M = K, Rb, Cs) and $MTeCl_5$ (M = Rb, Cs) are known to exist.[5] The phase diagram of the $TeCl_4-AlCl_3$ system shows that a 1:1 compound is formed.[6] Raman spectra of both the liquid and the solid state indicate that the compound formed consists of $TeCl_3{}^+$ and $AlCl_4{}^-$.[7] Also, compounds like $(TeCl_3)$-AsF_6 are known to exist and the molecular weight of this compound in high dilution in nitrobenzene agrees with the above formula.[8] The structure of molten $TeCl_4$ is still unknown although several proposals have been put forward. However, solid $TeCl_4$ is known[9] to consist of Te_4Cl_{16} units. From this it was anticipated that both monomeric and polymeric tellurium complexes might be present in the chloroaluminate melt.

Experimental Section

Materials and Measurements. $AlCl_3$ was made from the pure metal (99.999%) and HCl gas (electronic grade from Matheson). KCl (analytical reagent from Riedel–de Haen) was purified by first passing HCl gas over the solid and then through the melt, flushing with pure N_2, and finally filtering the melt.[10,11] The $TeCl_4$ was made by reaction between tellurium (99.999%) and chlorine (Fluka, >99.9%).

The experimental techniques used in the present work are almost the same as those described previously.[1,12] The electrode cells were made of Pyrex with vitreous carbon rods from Carbone–Lorraine fused into the bottom. Chlorine (Fluka, >99.99%) was added under a known pressure to the cells, which were sealed vacuum-tight. A sintered disk from Radiometer separated the two cell compartments. This disk consisted primarily of α-Al_2O_3; it was considered to be satisfactorily mounted if the leak under a water pressure of 300 mm did not exceed 0.2 cm^3 of water over a 12-hr period. In order to secure the same pressure over the melt in both compartments they were connected by a small tube. The internal resistances of the operating cells were usually in the range 100–500 Ω. Furthermore, the electrodes had completely recovered within the experimental uncertainty of ±0.1 mV within about 30 sec after a removal of potential of 20 mV applied for 1 min. On the basis of this the electrodes were considered to be reversible.

The temperature of the main part of the potentiometric furnace was controlled by a Eurotherm regulator, Type LP96/CR/DHS/PID/FC, connected to a platinum resistance thermometer. The top and bottom heating elements were controlled by a simple regulator, Type LP96/MK2/PID/FC, operated by the small temperature difference measured by thermocouples placed on the middle and end part of the furnace. The temperature could be controlled within ±0.1° in the range 100–500°. The temperature variation over the middle 200 mm of the furnace was less than 0.3°. The temperature of the furnace was measured by a calibrated chromel–alumel thermocouple connected to a Type DM2022S digital voltmeter from Digital Measurements Ltd. with a built-in standard cell. The same instrument was also used for the potentiometric measurements.

The optical cells were of fused quartz (Ultrasil from Helma) and had a fixed path length in the range 10–1 mm. A path length around 0.1 mm could be obtained by placing a precision-ground fused-silica insert into a 5-mm cell. Absorption spectra were measured with a Cary 14R spectrophotometer equipped with a furnace regulated by an Eurotherm regulator, Type LP96/DHS/PID/P. The spectro-

(1) Part I: J. H. von Barner and N. J. Bjerrum, *Inorg. Chem.,* **12**, 1891 (1973).

(2) N. J. Bjerrum, *Inorg. Chem.,* **9**, 1965 (1970); **10**, 2578 (1971).

(3) N. J. Bjerrum, *Inorg. Chem.,* **11**, 2648 (1972).

(4) G. Jander and K.-H. Swart, *Z. Anorg. Allg. Chem.,* **301**, 54 (1959).

(5) V. V. Safonov, A. V. Konov, and B. G. Korshunov, *Zh. Neorg. Khim.,* **14**, 2880 (1969).

(6) H. Houtgraaf, H. J. Rang, and L. Vollbracht, *Recl. Trav. Chim. Pays-Bas,* **72**, 978 (1953).

(7) H. Gerding and H. Houtgraaf, *Recl. Trav. Chim. Pays-Bas,* **73**, 759 (1954).

(8) L. Kolditz and W. Schafer, *Z. Anorg. Allg. Chem.,* **315**, 35 (1962).

(9) B. Buus and B. Krebs, *Angew. Chem.,* **82**, 446 (1970).

(10) H. A. Laitinen, W. S. Ferguson, and R. A. Osteryoung, *J. Electrochem. Soc.,* **104**, 516 (1957).

(11) C. R. Boston and G. P. Smith, *J. Phys. Chem.,* **62**, 409 (1958).

(12) N. J. Bjerrum, C. R. Boston, and G. P. Smith, *Inorg. Chem.,* **6**, 1162 (1967).

Table I. Values of Cell Potential and Composition for Molten Electrolyte at 300°

0.10 F TeCl₄			0.20 F TeCl₄			0.30 F TeCl₄		
	Mole fraction			Mole fraction			Mole fraction	
$-\Delta E$, mV	KCl	AlCl₃	$-\Delta E$, mV	KCl	AlCl₃	$-\Delta E$, mV	KCl	AlCl₃
389.0	0.4950₅	0.4982₁	404.8	0.4899₈	0.4967₃	383.2	0.4856₈	0.4941₃
313.1	0.4965₂	0.4967₆	349.0	0.4919₁	0.4946₆	346.1	0.4879₄	0.4917₈
300.5	0.4965₉	0.4966₉	295.7	0.4936₉	0.4927₉	298.0	0.4905₂	0.4892₉
222.6	0.4982₈	0.4950₂	216.7	0.4971₇	0.4894₁	252.6	0.4930₅	0.4868₅
161.9	0.5002₆	0.4931₉	151.7	0.5001₃	0.4865₂	211.3	0.4958₀	0.4842₁
161.0	0.5000₄	0.4932₈	71.6	0.5065₇	0.4802₅	175.4	0.4983₆	0.4817₆
116.8	0.5020₆	0.4914₀	35.7	0.5118₃	0.4751₃	156.1	0.5002₁	0.4796₃
90.7	0.5036₄	0.4898₅	21.5	0.5145₇	0.4724₇	141.8	0.5008₅	0.4793₇
59.4	0.5065₇	0.4867₈	14.9	0.5176₀	0.4691₉	113.5	0.5036₉	0.4763₀
47.8	0.5084₅	0.4849₉	13.1	0.5172₇	0.4698₄	84.3	0.5067₈	0.4733₃
38.6	0.5092₄	0.4841₅	8.5	0.5193₀	0.4675₃	68.0	0.5085₂	0.4718₉
21.4	0.5127₈	0.4806₆	6.1	0.5189₃	0.4682₂	61.0	0.5100₀	0.4702₄
18.5	0.5136₄	0.4798₇	5.4	0.5202₀	0.4666₆	49.0ᵃ	0.5120₂	0.4682₆
10.2	0.5160₁	0.4775₂	3.0	0.5201₁	0.4670₇			

ᵃ Melt saturated with K₂TeCl₆.

photometer was equipped with a Datex digital system for punching out spectral data on paper tape.

Methods of Investigation

General Considerations. The initial molar amount of one of the added substances (in the present work KCl, AlCl₃, or TeCl₄) dissolved in 1 l. of the melt is defined as its formality. The formal absorptivity is defined by A/c' where A is the absorptivity (absorbance divided by the path length) corrected for the absorbance of cell and solvent, and c' is the formality (in the present work of TeCl₄). The densities of the KCl–AlCl₃–TeCl₄ solutions were calculated assuming ideal mixtures of TeCl₄ and KCl–KAlCl₄. This assumption will only give rise to a small error, as the amounts of TeCl₄ added were small compared to the amounts of KCl–KAlCl₄. The densities of TeCl₄ and of KCl–AlCl₃ were obtained from the work of Simons[13] and of Morrey and Carter,[14] respectively. In the present work, pCl⁻ is defined as the negative logarithm of the chloride concentration.

The potential of the cell used is generally given by[15]

$$\Delta E = \frac{1}{F} \int_{\mathrm{I}}^{\mathrm{II}} \sum_i t_i (-z_i^{-1} \, d\mu_i + z_{\mathrm{Cl}^-}^{-1} \, d\mu_{\mathrm{Cl}^-}) \tag{1}$$

(at constant T) since the chlorine pressure and hence the chlorine activity are the same in both cell compartments. t_i, z_i, and μ_i are the transference number, charge, and chemical potential for the ith ion, respectively.

In the spectral work the Bouguer–Beer law as well as the law of additive absorbance was assumed to be valid. The total absorbance at a given wave number could then be described by

$$A(\nu_1') = \sum_i \epsilon_i(\nu_1')lc_i \tag{2}$$

where $A(\nu_1')$ is the total absorbance at the wave number ν_1', $\epsilon_i(\nu_1')$ is the molar absorptivity for the ith complex at wave number (ν_1'), l is the path length, and c_i is the concentration of the ith complex.

In the present work the variation in the activity coefficients has been neglected. Due to lack of data it is impossible to make an exact calculation of this change. However, if we assume that we are dealing with a regular solution of two components, the activity coefficients can be calculated from the relation $RT \ln \gamma = kN_2^2$, where γ is the activity coeffi-

cient for one of the components, k is a constant, and N_2 is the mole fraction of the other component. The magnitude of k is usually less than ±3 kcal mol⁻¹.[16] At low pCl⁻ we are dealing essentially with a mixture of KAlCl₄ and K₂TeCl₆. If a value of ±3 kcal is used for k, it is found from the present measurements that the maximum variation of the activity coefficient is ±0.4% for KAlCl₄; this variation is negligible. By contrast, the maximum variation under the above assumption for K₂TeCl₆ is *ca.* ±20%. As we shall see later this variation is comparable to the variation calculated from the experimental data.

Cell Potentials. It can be shown[1] that under the present circumstances it is reasonable to give eq 1 the form

$$\Delta E = \frac{RT}{F} \ln \frac{[\mathrm{Cl}^-]_{\mathrm{II}}}{[\mathrm{Cl}^-]_{\mathrm{I}}} - \frac{RT}{F} t^0{}_{\mathrm{K}^+} \ln \frac{[\mathrm{K}^+]_{\mathrm{II}}}{[\mathrm{K}^+]_{\mathrm{I}}} +$$
$$\frac{RT}{F} t^0{}_{\mathrm{AlCl}_4^-} \ln \frac{[\mathrm{AlCl}_4^-]_{\mathrm{II}}}{[\mathrm{AlCl}_4^-]_{\mathrm{I}}} + \frac{RT}{F} k_{\mathrm{Cl}^-}([\mathrm{Cl}^-]_{\mathrm{II}} - [\mathrm{Cl}^-]_{\mathrm{I}}) \tag{3}$$

where $t^0{}_{\mathrm{K}^+}$ and $t^0{}_{\mathrm{AlCl}_4^-}$ are the transference numbers in pure KAlCl₄ and k_{Cl^-} is a constant such that $t_{\mathrm{Cl}} = k_{\mathrm{Cl}^-}[\mathrm{Cl}^-]$ at a low concentration of chloride ions. By assuming the mobilities of the ions considered to be inversely proportional to their ionic radii (an assumption which fits reasonably well for a number of molten salts, where the anions and cations are well defined[17]), it has also been shown that the last three terms in eq 3 for a 0.3 F solution of a metal salt have a maximum value of −0.8, +0.2, and +0.4 mV, respectively. These values are small compared to the maximum $|\Delta E|$ values encountered in these systems; furthermore the three terms cancel each other partially. On the basis of this they were neglected in the calculation of the chloride activity in the melt. The potential of the cell will then be given by

$$\Delta E = -\frac{RT}{F} \ln \frac{[\mathrm{Cl}^-]_{\mathrm{II}}}{[\mathrm{Cl}^-]_{\mathrm{I}}} \tag{4}$$

which at 300° becomes

$$\mathrm{pCl}^- = \frac{-\Delta E}{113.7} + 0.284 \tag{5}$$

since under the present circumstances the chloride activity

(13) J. H. Simons, *J. Amer. Chem. Soc.*, **52**, 3488 (1930).
(14) J. R. Morrey and D. G. Carter, *J. Chem. Eng. Data*, **13**, 94 (1968).
(15) E. A. Guggenheim, "Thermodynamics," North-Holland Publishing Co., Amsterdam, 1967, p 324.
(16) G. J. Janz, Ed., "Molten Salts Handbook," Academic Press, New York, N. Y., 1967, pp 206–211.
(17) See ref 16, pp 344–345.

is assumed equal to the chloride concentration. The last term is the pCl^- of $KAlCl_4$ saturated with KCl at 300° reported earlier.[1] The value 113.0 given previously[1] should have been 113.7. This error is, however, within the experimental uncertainty for the final data. It is worthwhile to mention here that eq 5 is only valid under the circumstances mentioned above and is probably not valid over much wider $KCl:AlCl_3$ proportions than used in the present work. From the obtained chloride activities the equilibrium constants for the different proposed equilibria in the melt can be calculated.

Spectra. It will now be illustrated how the measured spectra can give information about equilibrium constants, about spectra of individual species, and indirectly also about chloride concentrations. Equation 2 can be given the following form for each wave number measured

$$\sum_i c_i \epsilon_i(\nu_1') = A(\nu_1')/l \tag{6}$$

This can be written in the following way

$$[c_1 c_2 \ldots c_i]
\begin{bmatrix}
\epsilon_1(\nu_1') & \epsilon_1(\nu_2') \ldots \epsilon_1(\nu_n') \\
\epsilon_2(\nu_1') & \vdots & \vdots \\
\vdots & & \\
\epsilon_i(\nu_1') & & \epsilon_i(\nu_n')
\end{bmatrix} =
$$

$$\left[\frac{A(\nu_1')}{l}, \frac{A(\nu_2')}{l} \ldots \frac{A(\nu_n')}{l}\right] \tag{7}$$

If we now deal with m different compositions, a general equation involving three matrices can be put forward

$$[c_{im}][\epsilon_i(\nu_n')] = \left[\frac{A_m(\nu_n')}{l}\right] \tag{8}$$

where c_{im} is the concentration of the ith species for the mth composition and $A_m(\nu_n')$ is the total absorbance of the mth composition at the wave number ν_n'. This formulation is in principle identical with the formulation used by Lieto.[18] From the equilibria put forward to explain the behavior of the melt and on the basis of some arbitrarily chosen equilibrium constant, the concentration of each species c_i is calculated. This (together with the measured absorbances at different wave numbers and different compositions) is now put into eq 8 and the deviation (least squares) is calculated. By varying systematically the equilibrium constants the deviation is minimized to obtain the "best" equilibrium constants. This procedure can be applied to any equilibrium and the results used in a model discrimination. From the derived equilibrium constants the spectrum of each individual species can be calculated. It is, of course, also possible to calculate the chloride concentration on the basis of the composition and the equilibrium constants.

Results

Measurements and Calculations for Cell Potentials in the $KCl-AlCl_3-TeCl_4$ System. In Table I are shown the values of ΔE in terms of mole fractions of KCl and $AlCl_3$ for 0.10, 0.20, and 0.30 F $TeCl_4$. The measurements for 0.30 F $TeCl_4$ could not be performed at low pCl^- due to precipitation of a yellow compound believed to be K_2TeCl_6. A plot of the average coordination number ($\bar{n}$) as a function of pCl^-
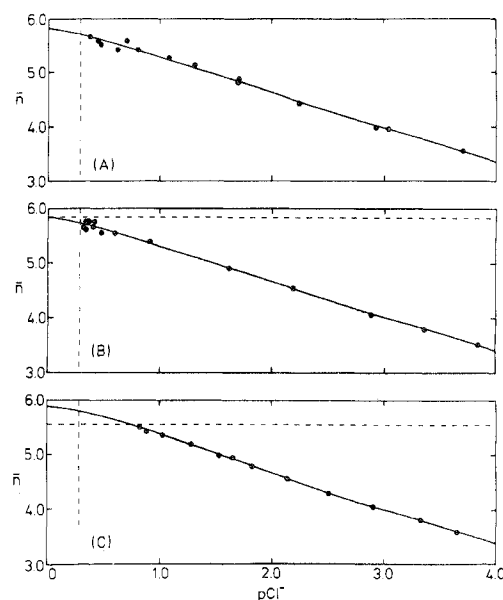

Figure 1. Average experimental coordination number for Te(IV) as a function of pCl^-: (A) 0.10 F Te(IV); (B) 0.20 F Te(IV); (C) 0.30 F Te(IV), compared with calculated values (full lines). The vertical dashed lines show the limiting pCl^-, due to saturation with KCl. The horizontal dashed lines show the limitation due to precipitation of a compound assumed to be K_2TeCl_6. The solvent was $KAlCl_4$ at 300°.

calculated from Table I is shown in Figure 1. In order to make such a plot accurately, the pK region for the self-dissociation reaction for the solvent, $2AlCl_4^- = Al_2Cl_7^- + Cl^-$, of 7.78–7.81 (earlier[1] erroneously given as 7.83 ± 0.02) at 300° was used. From this figure it can be seen that at the present temperature it is not possible to reach the average coordination number 6 even at the lowest possible pCl^- (indicated by a vertical dashed line) obtained by saturating the melt with KCl. The horizontal dashed line shows the limitation due to precipitation of the yellow compound. A closer inspection of the plot reveals that the curves are almost identical. This can only be explained if tellurium is present mainly as monomeric entities and little polymerization occurs. If only monomeric entities are present, the numerical treatment of the data is straightforward. As can be seen from Figure 1, the highest coordination number must be 6 and in the measured range the lowest 3. This leads to the equilibria

$$TeCl_6^{2-} \rightleftharpoons TeCl_5^- + Cl^- \tag{9}$$

$$TeCl_5^- \rightleftharpoons TeCl_4 + Cl^- \tag{10}$$

$$TeCl_4 \rightleftharpoons TeCl_3^+ + Cl^- \tag{11}$$

A computer program which could handle these three equilibria was set up. The iteration process to get the least-squares estimation of the nonlinear parameters was based on a program by Marquardt.[19] When the data from Table I were treated with this program, the pK regions shown in Table II were obtained. The regions are for nonlinear one-parameter confidence limits of 95%. As can be seen from this table the pK regions obtained at different concentrations agree very well with each other. For each concentration two columns are given, one obtained from data where pCl^- is >0.75 (high pCl^-) and another obtained where pCl^- is >0.28 (low pCl^-). This is done in order to compare pK values for the three different Te(IV) concentrations measured in the

(18) L. R. Lieto, Thesis, 1969; Report ORNL-TM-2714, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1969.

(19) D. W. Marquardt, IBM Share Library, Distribution No. 309401, Aug 1966.

Table II. Results for Te(IV) Equilibria in KAlCl₄ Based on Cell Potentials

Processes	pK regions in 0.10 F TeCl₄		pK regions in 0.20 F TeCl₄		pK regions in 0.30 F TeCl₄		pK regions for all data combined
	High pCl⁻	Low pCl⁻	High pCl⁻	Low pCl⁻	High pCl⁻	Low pCl⁻	
$TeCl_6{}^{2-} \rightleftharpoons TeCl_5{}^- + Cl^-$	0.66–0.92	0.56–0.85	0.59–0.94	0.60–0.85	0.82–0.92	...	0.68–0.82
$TeCl_5{}^- \rightleftharpoons TeCl_4 + Cl^-$	2.03–2.27	1.99–2.40	2.08–2.35	1.99–2.47	2.16–2.26	...	2.13–2.32
$TeCl_4 \rightleftharpoons TeCl_3{}^+ + Cl^-$	3.60–3.96	3.47–4.11	3.69–3.99	3.58–4.12	3.70–3.86	...	3.66–3.92

same pCl⁻ range. Due to precipitation of the yellow compound in 0.30 F TeCl₄ it is not possible to obtain pCl⁻ values lower than about 0.75. The last column in Table II shows the pK regions when all data are combined. This should be the best way to describe the behavior in the measured range. The good agreement between the obtained pK regions at different concentrations is, of course, a strong support for the above model.

The KCl–AlCl₃–TeCl₄ System Saturated with K₂TeCl₆. As mentioned above, in a 0.30 F solution of TeCl₄ in KAlCl₄ a yellow precipitate separated at low pCl⁻ values. With the present technique it was not possible to obtain this compound in a pure form. However, the phase diagram for KCl–TeCl₄[5] shows K₂TeCl₆ as the only intermediate compound and we therefore believe that the compound is K₂TeCl₆.

There are two experimental problems in obtaining the compound in a pure form. In order to press the melt through the filter in a reaction tube, different temperatures had to be developed alternately on top and bottom of the reaction tube. The other problem was to eliminate the solvent, which always adheres to the precipitate even after a filtration, but this can be overcome by centrifugation. In the present case a modified Christ centrifuge (Type UJ III) was used, so that the filtrate (placed in a small cell, which contained a filter) could be centrifuged at ca. 1500g at a temperature about 300°. This process removed the adhering solvent but the precipitate still contained KCl. This KCl is probably formed during the filtration, since the composition of the saturated melt is such that a small decrease in temperature will cause KCl to precipitate together with the yellow compound. In order to solve the problem a better temperature control of the filtration and centrifugation process as well as another method of applying suction in the filtration process will be required.

Since the potassium concentration in the melt is almost constant, the concentration of $TeCl_6{}^{2-}$ in the saturated melt may be taken as constant. A visual inspection showed that at a $TeCl_6{}^{2-}$ concentration of 0.159 M no precipitate was present, whereas at the concentration 0.177 M the yellow compound had precipitated. From this the concentration of $TeCl_6{}^{2-}$ in the saturated melt was estimated to be in the range 0.159–0.177 M. This range is in agreement with the values calculated from the cell potentials of a saturated melt with an initial Te(IV) concentration of 0.30 F, even if the variation in the calculated concentration is rather large. The results are shown in Table III. In this table the mean value of the pK for the reaction $TeCl_6{}^{2-} \rightleftharpoons TeCl_5{}^- + Cl^-$ obtained at low pCl⁻ and 0.20 F Te(IV) is used except for the first calculated concentration, where the mean value obtained at high pCl⁻ for 0.30 F Te(IV) is used.

Measurements of Spectra for the System KCl–AlCl₃–TeCl₄. In Figure 2 the spectra of a series of melts with a Te(IV) concentration of 0.10 F are shown. The variable is the chloride concentration. Te(IV) concentrations much higher than 0.10 F could not be examined due to the high value of the extinction coefficients for $TeCl_6{}^{2-}$ in the measured range. From the spectra it can be seen that at low pCl⁻ a well-

Table III. $TeCl_6{}^{2-}$ Concentrations in KAlCl₄ Saturated with K₂TeCl₆ at 300°

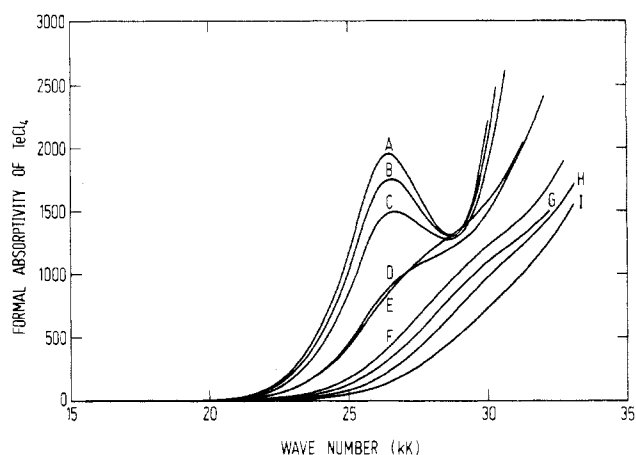|	Initial mole fraction		
$-\Delta E$, mV	KCl	AlCl₃	$[TeCl_6{}^{2-}], M$
49.0	0.5120₂	0.4682₆	0.182[a]
34.6	0.5146₀	0.4658₂	0.155
34.5	0.5141₄	0.4661₃	0.179
25.5	0.5163₆	0.4640₀	0.185
15.4	0.5194₁	0.4612₀	0.171
11.0	0.5204₀	0.4599₇	0.205

[a] Calculated from high pCl⁻ value of pK.

Figure 2. Series of spectra of 0.10 F TeCl₄ in KCl–AlCl₃ at 300°. Mole fraction of KCl and AlCl₃ respectively: A, 0.5091₈, 0.4842₃; B, 5071₄, 0.4862₅; C, 0.5039₁, 0.4894₄; D, 0.5001₈, 0.4931₂; E, 0.4996₉, 0.4936₅; F, 0.4974₀, 0.4958₄; G, 0.4966₂, 0.4966₃; H, 0.4956₁, 0.4976₈; I, 0.4944₈, 0.4987₉.

defined band is located at about 26.5 kK. The spectrum at the lowest possible pCl⁻ (melt saturated with KCl) has previously[2,3] been attributed to $TeCl_6{}^{2-}$. In the light of the present potentiometric measurements it is clear that we are dealing not with pure $TeCl_6{}^{2-}$ but with a mixture of $TeCl_6{}^{2-}$ and $TeCl_5{}^-$. The band at 26.5 kK, however, is due to the $TeCl_6{}^{2-}$ ion. From these spectra the equilibrium constants for the consecutive processes (9), (10), and (11) could be calculated by using all the shown spectra and the method outlined under "Methods of Investigation." The absorbance was measured for each wavelength in the range 332–420 nm. The calculated regions for the equilibrium constants are shown in Table IV. The regions are based on nonlinear confidence limits of 95%. As can be seen from this table the regions agree very well with the regions based on cell potentials. However, the regions are much larger in the latter experiments than in the former. Furthermore it should be noted that the regions are calculated from all the measured values of absorbance and wave number. This is appropriate as the uncertainty is mainly in the measured spectra and not in the composition of the melt. Finally, the spectra of each of the individual chloro complexes are shown in Figure 3. Here the equilibrium constants found by the potentiometric measurements for a 0.10 F Te(IV) solution have been used to calculate these spectra.

Table IV. Results for Te(IV) Equilibria in $KAlCl_4$ Based on Spectrophotometric Measurements

Processes	pK regions in 0.10 F $TeCl_4$ soln
$TeCl_6{}^{2-} \rightleftarrows TeCl_5{}^- + Cl^-$	0.17–1.06
$TeCl_5{}^- \rightleftarrows TeCl_4 + Cl^-$	1.10–3.25
$TeCl_4 \rightleftarrows TeCl_3{}^+ + Cl^-$	2.92–4.62

Discussion

As the measurements and calculations show, there seems to be a well-established case of stepwise chloro complex formation for Te(IV) in $KAlCl_4$. In the present work it was impossible to detect any special trend in the calculated pK regions as a function of concentration. However, if it is assumed that the difference between the pK regions calculated at 0.10 and 0.30 F Te(IV) for the reaction $TeCl_6{}^{2-} \rightleftarrows TeCl_5{}^- + Cl^-$ is due to a variation in the activity coefficient for K_2TeCl_6, a change of *ca*. 17% in the activity coefficient will bring the mean values to coincide. This change is, as mentioned above, comparable to the maximum variation expected for the activity coefficient.

As an extension of the present work it would be important to perform measurements at pCl^- values higher than those used here. If linear extrapolation is valid for the pK values for the formation of $TeCl_2{}^{2+}$, a value of about 4.3 is obtained. This value is still much smaller than the pK found for the self-dissociation of $KAlCl_4$ mentioned above. There are therefore reasons to expect that $TeCl_2{}^{2+}$ can be found in solutions. Contrary to this, Raman spectra of the $AlCl_3$–$TeCl_4$ system[20] do not indicate any formation of $TeCl_2{}^{2+}$, but it is of course possible that $TeCl_2{}^{2+}$ is only present in

(20) F. W. Poulsen, N. J. Bjerrum, and O. F. Nielsen, to be submitted for publication.
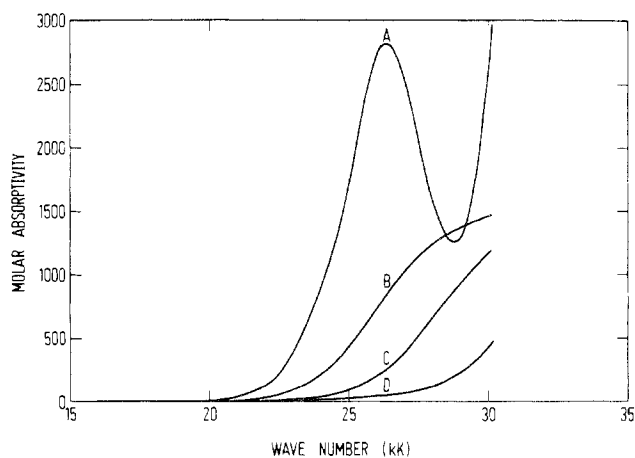
Figure 3. Calculated spectra: A, $TeCl_6{}^{2-}$; B, $TeCl_5{}^-$; C, $TeCl_4$; D, $TeCl_3{}^+$. The solvent was $KAlCl_4$ at 300°. Each spectrum was calculated on the basis of nine measured spectra by use of the pK values of 0.71, 2.19, and 3.76 for the reactions $TeCl_6{}^{2-} \rightleftharpoons TeCl_5{}^- + Cl^-$, $TeCl_5{}^- \rightleftharpoons TeCl_4 + Cl^-$, and $TeCl_4 \rightleftharpoons TeCl_3{}^+ + Cl^-$, respectively.

small concentrations. In another experiment we intend to measure the values of the pK's as a function of the reciprocal value of the absolute temperature. Here a linear dependence would only be expected, if the above models are correct.

Registry No. $TeCl_6{}^{2-}$, 20057-66-3; $TeCl_5{}^-$, 44246-02-8; $TeCl_4$, 10026-07-0; $TeCl_3{}^+$, 43644-19-5.

Kinetic Study of the Reaction Np(VII) + V(IV) → Np(VI) + V(V) in Aqueous Perchloric Acid Media[1]

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The title reaction has been investigated by the stopped-flow technique as a function of acidity, ionic strength, and temperature. At constant $[H^+]$ the empirical form of the rate law is $-d[Np(VII)]/dt = k''[Np(VII)][VO^{2+}]$ where k'' exhibits only a slight acid dependence most conveniently expressed as $\log k'' = \log k + n \log [H^+]$. At 25° and $\mu = 1.00$, with k'' expressed in units of F^{-1} sec^{-1}, $\log k = 3.159 \pm 0.005$ and $n = -0.112 \pm 0.076$. The temperature dependence of k over the range 2.7–25° results in a value of 7.3 ± 0.9 kcal/mol for the Arrhenius activation energy. Rate parameters for the title reaction, which is of one-to-one stoichiometry, are compared to the corresponding parameters governing the two-to-one oxidation of $Hg_2{}^{2+}$ by Np(VII), as well as to the corresponding parameters governing the one-to-one oxidation of VO^{2+} by the relatively weak oxidant Mn(III). While the relative rates of these reactions are reflected primarily in ΔH^*, the importance of considering S^* as well as ΔS^* values is pointed out. It is also qualitatively noted that of the reported oxidations of VO^{2+}, that by Np(VII) is the most rapid and Np(VII) is the most powerful oxidant.

Introduction

Our previous studies designed to characterize the chemistry and reaction dynamics of the extremely powerful 1-equiv

oxidant Np(VII) have utilized the multiequivalent reductants H_2O,[4a] Tl(I),[4b] and Hg(I).[4c] These reactions proceed at rates

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(2) Participant in the Argonne National Laboratory Summer Faculty Research Participation Program.

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(4) (a) J. C. Sullivan and A. J. Zielen, *Inorg. Nucl. Chem. Lett.*, 5, 927 (1969); (b) R. C. Thompson and J. C. Sullivan, *J. Amer. Chem. Soc.*, 92, 3028 (1970); (c) M. A. Thompson, J. C. Sullivan, and E. Deutsch, *ibid.*, 93, 5667 (1971).