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A spectrophotometric study of the equilibrium formation of the gaseous species bismuth (I) Tetrachloroaluminate and Tellurium (II) Chloride

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A SPECTROPHOTOMETRIC STUDY OF THE EQUILIBRIUM FORMATION OF THE GASEOUS SPECIES BISMUTH(I) TETRACHLOROALUMINATE AND TELLURIUM(II) CHLORIDE

by

Richard Arthur Lynde

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INTRODUCTION

The present work is a continuation of previous studies (1, 2) of the vapor species present at equilibrium in high temperature, metal-metal salt systems. The two systems reported on in this study, $Bi-BiCl_3-AlCl_3$ and $Te-TeCl_4$, are of particular interest in view of the extensive work performed in this lab on similar condensed systems.

The $Bi-BiCl_3$ system has been the object of numerous investigations, over the last 15 years, designed to elucidate the mechanism by which bismuth dissolves in bismuth trichloride and to isolate and define the incongruently melting "BiCl". The large solubility of metal in the salt, 45% Bi at 320°[1] decreasing to 28% Bi at 550° and increasing to a consolute point at 51% Bi and 780°, was indicated in the phase diagram reported for the $Bi-BiCl_3$ system (3). EMF (4), spectral (5) and vapor pressure (6) data established that Bi^+ was the sole solute product in dilute solutions ($\leq$ 0.6 mole % metal) and that it polymerized to Bi_4^{4+} (or Bi_3^+) at higher concentrations (< 6.0 mole % metal, although the vapor pressure data indicated that an ideal solution of Bi_4^{4+} gave a satisfactory description of the solvent pressure of solutions containing up to 25 mole % metal). At the present time there appears to be no satisfactory inter-

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[1] All temperatures are °C except where °K is specified.

pretation of the solution mechanism at high metal concentrations (> 6.0 mole %). A crystal structure determination of "BiCl" (7) revealed that the stoichiometry was actually $BiCl_{1.167}$ ($Bi_{12}Cl_{14}$), and that it contained the homopolyatomic cation Bi_9^{5+} and the complex anions $[BiCl_5]^{2-}$ and $[Bi_2Cl_8]^{2-}$.

The simple monochloride, BiCl, does exist in the vapor state. Saper (8) was the first to observe and correctly identify the 459 mμ band system with BiCl(g). The work was repeated by Morgan (9) in order to resolve the disagreement between Saper and Ghosh (10), who assigned the same band system to BiO, and to make a more extensive analysis of the band system. Within the last ten years a series of vibrational and rotational analyses (11, 12, 13) of the 459 mμ band system have yielded molecular constants for BiCl(g). Cubicciotti (14, 15) investigated the reaction

$$2/3\ Bi(l) + 1/3\ BiCl_3(g) = BiCl(g)$$

by transpiration and obtained values for the enthalpy and entropy of the reaction and the dissociation energy of BiCl(g).

Recent studies have shown that additional polybismuth cations exist in condensed Bi-$BiCl_3$-$AlCl_3$ systems. The cations Bi_5^{3+} and Bi_8^{2+} were identified by both Bjerrum _et al._ (16, 17) and Corbett (18). The former were investigating the solution of bismuth in dilute solutions of bismuth trichloride in a molten eutectic mixture of aluminum trichloride and sodium chloride and the latter was studying the species present in the Bi-($BiCl_3 \cdot 3AlCl_3$) pseudobinary. Bjerrum et al. (16) also identified Bi^+ in the eutectic melts and Davis et al. (19) interpreted the visible-near infra-red spectrum as $6p^2 \leftrightarrow 6p^2$ intraconfigurational transitions in Bi^+.

Aluminum trichloride has been shown to form remarkably volatile vapor complexes with alkaline earth chlorides (20), 3d transition metal dichlorides (20), and representative 4f (neodymium) (21) and 5f (uranium) (22) chlorides. A driving force for these reactions is the strong affinity of the aluminum trichloride for the chloride ions in these rather ionic compounds, $\sim -78 \pm 7$ Kcal/mole (23). No investigations of the vapor phase above metal-metal chloride-aluminum trichloride systems have been reported in the literature.

The immediate impetus for the study of the bismuth system was supplied by G. P. Smith[1] in the form of a suggestion that the Bi^+ $p^2 \leftrightarrow p^2$ intraconfigurational transitions observed in the $AlCl_3$-NaCl eutectic melt might be observable

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[1] Dr. G. P. Smith, Oak Ridge National Laboratory of the United States Atomic Energy Commission, Oak Ridge, Tennessee. Private communication. 1966.

in the visible-near infra-red spectrum of BiCl(g). Such spectra, obtained in a system of known geometry, would provide a valuable check on the ligand field theory developed to account for the splittings of the p^2 configurations and the intensities of the $p^2 \leftrightarrow p^2$ transitions in Bi^+. Initial results indicated that the visible-near infrared region of the BiCl(g) spectrum was devoid of spectral features and the investigation was extended to include the Bi-$BiCl_3$-$AlCl_3$ system. The study was designed to determine the nature of the vapor species which were in equilibrium with the condensed phase and to evaluate the equilibrium constants for the interactions observed.

Consideration of the factors which appear to have lent stability to the polybismuth cations indicated that tellurium might reasonably be expected to form homopolyatomic cations. The study of polytellurium cations, in which tellurium would be expected to exhibit intermediate oxidation states, was preceded by a study of the possible existence of Te(II) chloride. The standard procedure for preparing tellurium dichloride has been to react stoichiometric amounts of tellurium and chlorine or of tellurium and tellurium tetrachloride (24, 25, 26). The phase diagram of Damiens (27), however, shows no clear evidence of $TeCl_2$(s) in the condensed Te-$TeCl_4$ system. Aynsley (28) reported that good yields of tellurium dichloride may be obtained from the reaction of tellurium with difluorodichloromethane.

In an effort to clarify the situation regarding the existence of $TeCl_2(s)$, Prince and Zaluski[1] performed a new phase study of the Te-$TeCl_4$ system. They found no evidence of tellurium dichloride in their diagram, and x-ray powder diffraction patterns of the samples exhibited no lines other than those attributable to the components, tellurium and tellurium tetrachloride. The latter observation was reconfirmed by the present author using several Te-$TeCl_4$ samples containing 50 mole % metal. The samples were heated until they were liquid and then quenched and annealed for several days just below the reported melting point of tellurium dichloride (208° (28)). These results indicate that unless the dichloride condenses as a poorly diffracting, amorphous solid, it comprises less than ten percent of the mixture in contradiction to the earlier studies which indicated that excellent yields might be expected.

The observation that tellurium metal was transported in ampoules containing Te-$TeCl_4$ mixtures at temperatures as low as 150° was recorded by Prince. This suggests the presence of $TeCl_2(g)$ which may act as the transporting gas. The existence of gaseous tellurium dichloride, the vapor of which has been described as red to dark brown (23, 24, 25)

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[1] D. J. Prince. Ames Laboratory of the United States Atomic Energy Commission, Iowa State University, Ames, Iowa. Study of the Te-$TeCl_4$ system. Private communication. 1969.

is well established. The vibrational fine structure of the band system which appears in the visible region has been analyzed several times with varying conclusions (29, 30, 31). The analysis of Spinnler (31), which accounts for the vibrational structure and isotope shifts expected for the C_{2v} molecule ($< \mathrm{Cl{-}Te{-}Cl} = 76°$) in a consistent manner, is generally accepted as correct (32). A study of the vapor phase above the Te-$TeCl_4$ system was undertaken to determine the nature of the species present and to describe the thermodynamics of the reactions involved. Particular attention was given to determining the mechanism of the tellurium transport.

Recent studies have shown that the polytellurium cations Te_4^{2+} and Te_n^{n+} are formed when tellurium dissolves in sulfuric and fluorosulfuric acid (33, 34). The Te_4^{2+} cation is also found, as $Te_4(AlCl_4)_2$, in the Te-($TeCl_4 \cdot 4AlCl_3$) pseudo-binary system (35) as is a polytellurium cation with an empirical composition of Te_3AlCl_4 (36). Crystals of the latter compound were grown by means of a vapor transport process. In an effort to obtain further information about this process, the species involved and the thermodynamic parameters of the reactions involved, the spectrum of the vapor phase above the Te-$TeCl_4$-$AlCl_3$ systems was also investigated.

Electronic absorption spectroscopy is a very useful tool for investigating multicomponent systems. It permits qualitative identification and quantitative measurements of individual components of the multicomponent systems particularly at concentrations below those possible with more classical analytical means. It also permits accurate determinations with the sample at selected temperatures where sample temperature would be a function of the arc or discharge characteristics in emission or discharge spectroscopy. Knowledge of the sample temperature is of the utmost importance since data obtained at a constant temperature with variable composition are necessary to determine the nature of the species present, while data obtained over a range of known temperatures are necessary to evaluate the thermodynamic parameters.

EXPERIMENTAL

Materials

Reactor grade bismuth metal (99.999%) was obtained from the supply of Physical and Inorganic Chemistry Group IX, Ames Laboratory, Ames, Iowa. The metal was vacuum fused to allow physical removal or decomposition of oxide or carbon impurities and iron chips. After purification the bismuth, as well as the other reactants, was broken into small pieces for convenience in handling and weighing.

Bismuth trichloride was prepared from the elements. The vapor from condensed chlorine at -33° was allowed to react in a sealed quartz apparatus with the metal at 750°. The resulting trichloride was distilled several times under active vacuum ($< 10^{-5}$ torr) at 350° to give a white product. Since $BiCl_3$ is readily contaminated by carbonaceous impurities, all apparatus used in the preparation and distillation of the salt was carefully cleaned, rinsed and baked-out under active vacuum.

The aluminum trichloride was supplied by Dr. R. A. Potts. Its preparation from high purity aluminum and "transistor grade" HCl has been described earlier (37). This material was sublimed twice under active vacuum at 180° before being used.

The tellurium used in this study was obtained from the

United Mineral and Chemical Corp. and was reported to be 99.999%. Impurities were decomposed or removed by vacuum fusion of the metal.

The tellurium tetrachloride was prepared by Dr. D. J. Prince.[1] A chlorine-argon mixture was passed over tellurium and the latter was heated gently to initiate the reaction. The product $TeCl_4$ was carried from the reaction cell by the gas stream and deposited further along the apparatus. This material was sublimed under active vacuum several times at 250° to give a faintly yellow, fairly soft product.

Apparatus

A Cary 14 recording spectrophotometer was modified to permit measurements of high temperature samples. The normal order of components in a spectrophotometric system is source-sample-monochromator-detector. When measurements are made above 500°, however, thermal radiation from the furnace increases the long wavelength noise level and causes a significant decrease in the signal-to-noise ratio (38). This decrease may be minimized by exchanging the positions of the sample and monochromator. This is termed "reversing the optics", and allows the monochromator to deflect a major portion of the furnace thermal radiation. The reversal was

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[1] D. J. Prince, Ames Laboratory of the United States Atomic Energy Commission, Iowa State University, Ames, Iowa. Preparation of $TeCl_4$. Private communication. 1969.

accomplished by moving the photomultiplier compartment to the position on the back of the instrument normally occupied by the visible lamp housing and mounting a specially supplied UV-VIS-IR lamp housing in its place on the sample compartment.

In order to accommodate the high temperature sample compartment, the optical path length was extended about 44-cm over the normal design. The focal point was maintained near its original position at the enterance slit of the monochromator by mounting two fused-silica condensing lenses (Perkin-Elmer, 35-mm diameter, 55-mm focal length; Oriel, 25-mm diameter, 27-mm focal length) in adjustable holders in each beam. The additional lenses also restrict the quickly diverging beam from the source compartment to a well defined, slowly diverging path which preserves most of its original intensity at the monochromator enterance slit. When the instrument is properly aligned the slit widths are similar to those of an unmodified instrument.

The normal sample-reference compartment has been replaced with a specially constructed furnace and light-tight enclosure which has been previously described quite completely (1). The enclosure has been modified to permit its use with the double beam Cary 14 by drilling holes to permit the passage of the reference beam. One end is bolted directly to the chopper compartment of the Cary while the special UV-VIS-IR lamp housing is mounted adjustably (vertical, horizontal, inclination) to the other. Inside the enclosure the furnace may be positioned in the sample beam without interfering with the reference beam.

The furnace is a 42-cm long, hinged, tubular muffle furnace. The feet of the furnace have been tapped and the furnace rests on four bolts which may be used to adjust its inclination and height. Once it has been aligned, lateral movement of the furnace is prevented by passing two threaded rods through the lower front and back frame members of the enclosure and the lower, lengthwise frame member of the furnace to allow "locking" it in place with nuts. The 10-cm long, 7.5-cm diameter, semicylindrical heating elements are wired to enable separate control of the two 10-cm end sections and the 20-cm center section containing the cell holder.

The cell holder was constructed from 2.5-cm thick Marinite. Two 7.5-cm diameter discs were held parallel and 7-cm apart by Alundum rods placed around their periphery, and a 2.2-cm diameter hole was drilled, slightly off center, through the discs to accommodate the cells. All but about 0.3-cm of each center hole was redrilled with a 2.5-cm bit so that, in the finished product, the cells were supported on two 0.3-cm wide, 2.2-cm diameter rings 7-cm apart. Some shrinkage occurred when the Marinite was first heated, but it maintained dimensional stability throughout subsequent heatings.

Heat loss at the ends of the furnace was minimized by the use of end plugs. These were similar in design to the cell holder except that 1.2-cm Transite was used in place of Marinite. A 0.015-cm quartz plate was mounted at each end of the furnace over the hole drilled for the light beam, and two similar quartz plates were mounted in the reference beam in order to maintain the similarity of the sample and reference paths.

The cylindrical, fused-silica cells were obtained from Pyrocell Manufacturing Co. (S18-260 UV Silica), and were of 2.2-cm diameter and 10.0 or 15.0-cm path length, with the windows fused in place. Specifications supplied by Pyrocell list the cell lengths as accurate to ± 0.01-mm, although measurements with a cathetometer indicated that errors of up to 0.2-mm were present in these custom fabricated cells. The extreme length of the cells tended to minimize the error due to variations in cell length ($\leq$ 0.2%) and calculations were performed using the nominal cell lengths. An 0.8-cm O.D. sidearm was sealed on near the midpoint to permit the loading and evacuation of the cells.

Two Honeywell transistorized on-off controllers were used to control the furnace temperature in the Bi-$BiCl_3$-$AlCl_3$ study. A Celetray on-off controller and a transistorized

Honeywell controller modified for low temperature operation were used for the Te-$TeCl_4$ study. Temperatures were read on a direct-reading Leeds and Northrup temperature potentiometer. The chromel-alumel thermo-couples used to measure the temperature were placed in a protective silica tube which was held snugly against the cell by the cell holder. One junction was positioned at the midpoint of the cell while another, in a separate circuit, was placed near one end of the cell.

The limit of error of the temperature potentiometer is given by Leeds and Northrup as 0.2% of the temperature range span, or ±1.2°. There will also be gradients across the thermal barriers provided by the cell wall and the thermocouple protection tube, although these can be minimized by extending the sample equilibration time. In the temperature range covered by these studies the on-off operation of the controllers generally caused fluctuations of ±1 to 2° with cycle times of 2-3 minutes. The combined uncertainty in the actual cell temperature is estimated to be ±3 to 5°. Temperature reproducibility from run to run, which is dependent upon the reproducibility of the controller settings, is ± 2°.

Procedure

Because of the sensitivity of the salts used to oxygen and moisture, all manipulations, except where the metals alone were involved, were performed in an argon atmosphere or under vacuum. After purification all salts were stored under vacuum in sealed glass ampoules.

The cells, with ball joints attached to the sidearms, were prepared by washing with a warm chromic acid solution and then a warm, dilute nitric acid solution after which they were thoroughly rinsed with deionized and then doubly distilled water. They were then evacuated and flamed out twice with a hand torch under an active vacuum. The evacuated cells were taken into the drybox along with preweighed metal samples, the sealed salt ampoules,and weighing bottles constructed from 0.8-cm tantalum tubing with tantalum caps welded to one end and snugly fitting plastic caps on the other. Pieces of salt were placed in sample bottles which were capped while the dry-box had a slightly positive pressure of argon. The bottles were then brought out of the drybox, weighed on a Mettler single pan balance and returned to the drybox. The bottles were held closed by C-clamps while pumping down in the drybox lock. The weighed metal and salt samples were transferred to the cells, the cells reclosed by means of a stopcock with appropriate socket and ball points and the weighing bottles capped.

The weighing bottles were reweighed and the sample weights determined (to ± 0.2 mg) by difference. The cells were evacuated and the sidearms sealed off under active vacuum about 0.8-cm from the cell wall. At the conclusion of a run the cells were reopened by cutting the tips off the sealed sidearms with a Carborundum cutting wheel. After dissolving the salt and metal from the cells, the volumes were determined (to ±0.2-ml or <0.5%) by filling the cells from a buret. Under the conditions at which quantitative measurements were made on the bismuth and tellurium systems there was always a condensed metal phase present while the salts were always completely vaporized. The initial pressures of the gaseous reactants were determined from the weights used and the cell volume.

Before placing a cell in the cell holder the windows were carefully cleaned on the outside and then flamed with a hand torch to remove any metal or salt which might have lodged on the inside of the windows. The large pieces of metal and salt were shaken into the sidearm so they would not interfere with the beam. Baselines were set at room temperature with cells in the sample beam and the reference beam empty. A series of blank runs using unloaded, evacuated cells demonstrated that there was no cell contribution to the absorption in the region of interest (300-1800 mμ, 200-1000°).

Somewhat arbitrary but constant absorbance contributions ($\leq \pm$ .02 A) resulted from transmission losses or furnace radiation as described in (38). All spectral scans were made from longer to shorter wavelengths since the wavelength mechanism of the instrument is driven positively in this direction, while it is dependent on spring return forces in the other direction. The uncompensated reference beam was maintained at or slightly above room temperature.

Spectral measurements were made over a range of increasing temperatures during each run. On several occasions the temperature was cycled two or three times over a 50-100° range, and the results were found to be quite reproducible in both systems. During runs the end furnace units were generally maintained 30-40° warmer than the center section in order to make up for heat losses and to prevent condensation on the cell windows. As a result of this procedure, the windows were 5-7° warmer than the center of the cell. The recorded temperatures were always mid-cell temperatures and were generally read at a spectrally significant (e.g. λ_{max}) point in the scan. Spectral measurements were made only after allowing the cell and sample to equilibrate for 20-40 minutes after the attainment of each new temperature. Plots of the absorbance at a given wavelength vs. time indicate that in both systems equilibrium conditions are attained very quickly as the temperature changes.

The $BiAlCl_4$ transition of interest at 723 mμ (Figure 4) is superimposed on the smoothly decreasing, low energy tail of an intense BiCl band. The band head of the latter is located near 460 mμ and at the temperatures and concentrations used for quantitative measurements on $BiAlCl_4$ an absorbance of 2 is reached at 500-540 mμ. The total background intensity under the $BiAlCl_4$ peak ($A_{BiCl} + A_{CELL}$) was determined by fitting a flexible draftsman's spline to the smooth background on either side of the peak. The region spanned extended for 180 mμ or 15-cm on the chart and was subject to relatively little uncertainty since the curve was rather shallow at this point.

The $TeCl_2$ spectrum (Figure 9) is situated on the sharply decreasing, low energy tail of an intense $TeCl_4$ band at 290 mμ. In the absence of Te, the $TeCl_4$ band extends well across the region of the $TeCl_2$ spectrum, but when metal is added to the system, the $TeCl_4$ absorption is reduced so it is significant only under the high energy side of the $TeCl_2$ spectrum. The absorbance data for the Te-$TeCl_4$ study was obtained from the low energy side of the $TeCl_2$ spectrum. It was read directly from the chart paper with only the small A_{CELL} correction being applied. The fine structure in the spectrum of $TeCl_2$ is associated with the higher energy of the two $TeCl_2$ bands but it extends well across the low energy band. However, the outline of the low energy band appears clearly between the fine structure peaks so the band has been drawn in by connecting the "valleys" with a smooth curve. In most cases the "valleys" are wide enough to show the proper curvature for the low energy band. The wavelengths at which absorption readings were made were chosen to give the best spread over the entire peak so some of the readings were made off the actual pen trace and some were made off the smoothed-in line.

THE Bi-$BiCl_3$-$AlCl_3$ SYSTEM - RESULTS

Qualitative spectral studies were performed on all of the possible one, two, and three component systems except the Bi-$AlCl_3$ system. Spectra were obtained over the 2500 to 200 mμ region at temperatures ranging from 250 to 1050°. As a result of the information obtained in these preliminary studies both the spectral scan width (1050 to 500 mμ) and temperature span (400 to 650° or 600 to 950°) were significantly decreased in a majority of the quantitative studies of the Bi-$BiCl_3$-$AlCl_3$ system. Spectra were obtained at 50° intervals within each temperature range. It became obvious early in the study that the systems behaved differently at high and low temperatures and that the change occurred between 600 and 650°. In view of this differentiation, the results are discussed in terms of high temperature behavior (600 to 950°) and low temperature behavior (400 to 650°). A large excess of bismuth was used in each run so a condensed phase was always present in the equilibrium systems. The salts ($BiCl_3$ b.p. 447°, $AlCl_3$ s. 180°) were assumed to be completely vaporized under the experimental conditions in the high temperature range. At low temperatures there was evidence that some of the salt dissolved in the Bi(l) raising the possibility of additional condensed phases in the Bi-$BiCl_3$-$AlCl_3$ ternary system.

Spectra

The spectrum of the vapor phase above Bi(l) was featureless in the 2500 to 325 mμ, 500 to 900° range investigated. The presence of $Bi_2(g)$, a major component of the vapor phase above condensed Bi (39), was indicated by a slight increase in the absorbance ($A \simeq .4$ at 325 mμ) at short wavelengths ($\lambda < 360$ mμ) at temperatures above 800°. This was presumably the low energy edge of the Bi_2 band located at 274 mμ (40). The reported 563 mμ Bi_2 band was not observed.

The spectrum of $BiCl_3(g)$ was measured above the condensed salt from 250 to 447° and as an all gas system from 400 to 750° between 2500 and 190 mμ. It consisted of a very high intensity, high energy band ($\lambda_{max} < 240$ mμ; A=2 at 240 mμ over $BiCl_3(l)$ at 250°) of which only the low energy edge was visible, and a less intense band at 296 mμ situated on the edge of the high energy band. Under the conditions at which the preliminary runs were performed, the absorbance due to $BiCl_3$ attained a value of 2 between 360 mμ (450°) and 380 mμ (750°). Due to the absence of a readable absorbance maximum and the steep slope of the band edge, it was impossible to make quantitative determinations of the amount of $BiCl_3$ present in equilibrium systems from the $BiCl_3$ spectrum.

A high intensity, high energy ($\lambda_{max} < 190$ mμ) band edge was the only distinguishing feature of the $AlCl_3$ spectrum in the 2500 to 190 mμ, 300 to 800° investigation range. Maximum absorbance (A=2) was attained between 196 mμ (300°) and 240 mμ (800°).

Significant cell attack, which resulted in severe scattering of the light beam, was noted in $AlCl_3$-containing runs at temperatures above 650°. This attack was similar to the attack above 627° described by Øye and Gruen (21) from the reaction

$$2Al_2Cl_6(g) + 3SiO_2(s) = 2\ \alpha\text{-}Al_2O_3(s) + 3SiCl_4(g)\ .$$

They calculated $\Delta F^\circ_{500} = -2.98$ Kcal and $\Delta F^\circ_{1000} = -3.295$ Kcal for this reaction and noted that, despite the favorable thermodynamics, the reaction did not occur to any significant extent below 627°. The thin, white film formed on the inside of the cell was uneffected by any cleaning technique used, as would be expected of α-Al_2O_3, and the cumulative effect of the attack was to render a cell useless after one to three high pressure ($P_{AlCl_3} \simeq 2$ atm. at 900°) runs. Cell life could be extended to four to six high temperature (900°) runs by maintaining the equilibrium pressure of $AlCl_3$ below 1 atm. at 900°.

No experiments were performed on the Bi-$AlCl_3$ binary system since it was considered highly unlikely that any reactions would occur. The $BiCl_3$-$AlCl_3$ system was investigated for evidence of $BiCl_3$-$AlCl_3$ adduct formation. The spectra were measured from 2500 to 325 mμ at temperatures from 400 to 800° and no new features were observed.

The Bi-$BiCl_3$ binary system was extensively studied over the 2500 to 190 mμ region from 250 to 1050°. The system has previously been the subject of rather intensive spectroscopic studies (9, 11, 12, 13, 41), mainly vibrational and rotational analyses of the fine structure associated with the 450 mμ band system of BiCl.

The 392 mμ band system of BiCl is shown in Figure 1. The line splitting, which was particularly evident in the lowest energy peak, resulted from the different vibrational frequencies associated with $Bi^{209}Cl^{35}$ and $Bi^{209}Cl^{37}$. At higher temperatures and pressures this spectrum exhibited a far more complex fine structure. The BiCl spectrum appeared at 300-350° in the Bi-$BiCl_3$ systems. It was also observed, with very low intensities ($A < .025$), in several Bi runs at higher temperatures ($T > 500°$), apparently the result of the reaction of Bi with residual amounts of chloride in the cells. The 459 mμ system, Figure 2, exhibited a very complex fine structure and generally appeared near 400° in these systems. The sum of the $BiCl_3$ and BiCl absorbances usually exceeded 2 at $\lambda < 500$ mμ in the high temperature range of this study. Quantitative measurements of the Bi-$BiCl_3$-$AlCl_3$ spectra were generally not carried out below 600 mμ so only the low energy edge of the $BiCl_3$-BiCl

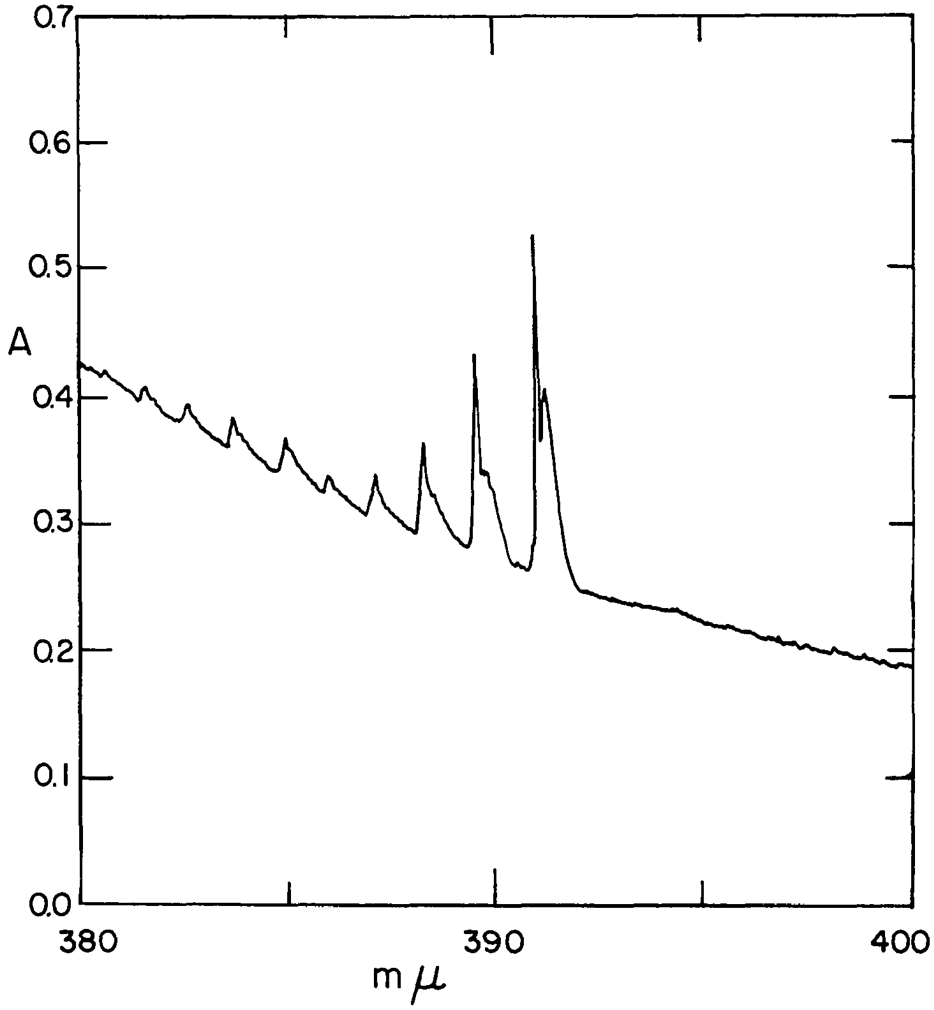

Figure 1. The spectrum of BiCl. The 392 mμ band system (P_{BiCl}=2.55 x 10^{-4} atm, path length 10.0-cm, temperature 446°)

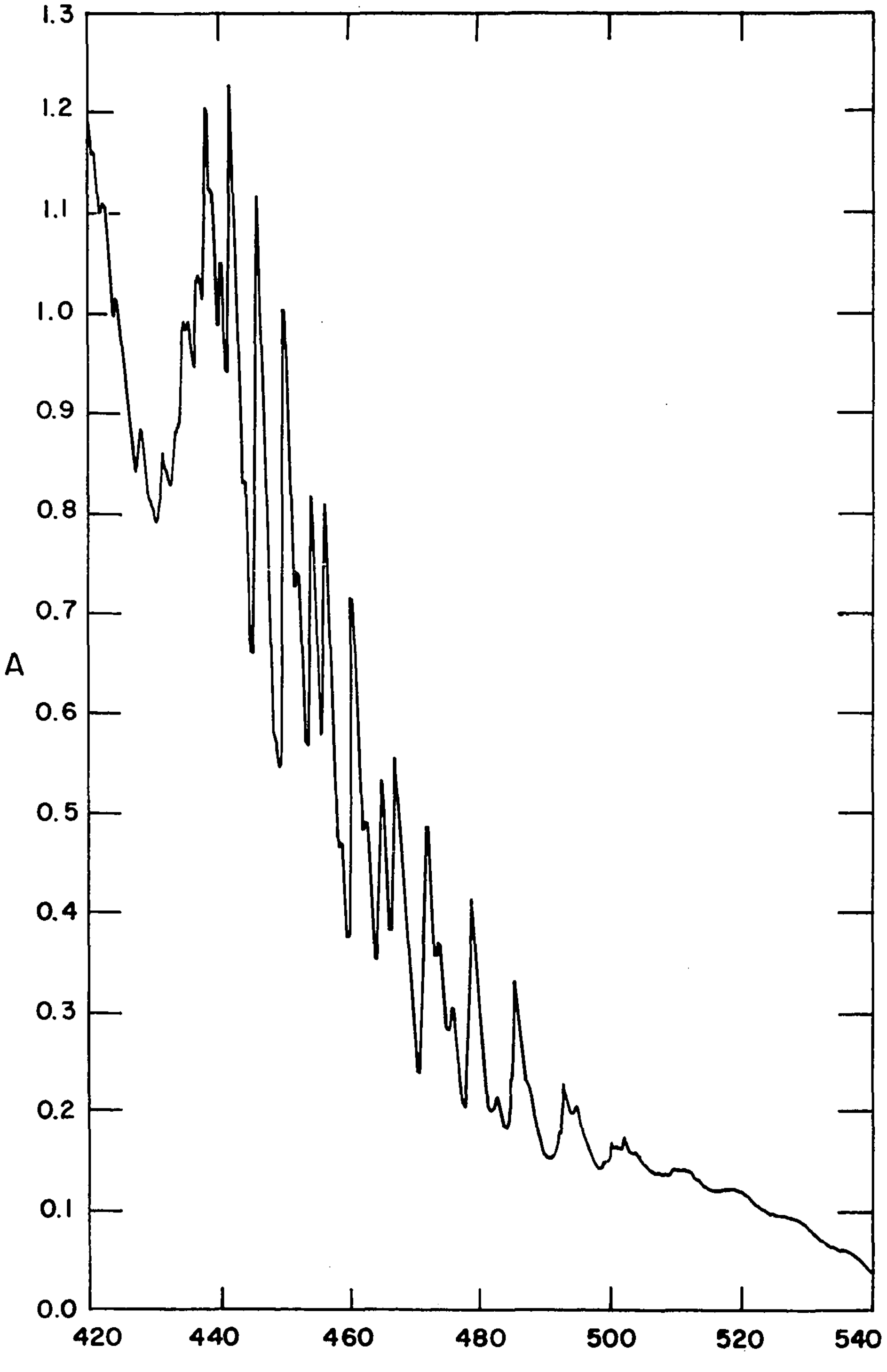

Figure 2. The spectrum of BiCl. The 450 mμ band system (P_{BiCl}=1.26 x 10^{-2} atm, path length 10.0-cm, temperature 600°)

absorption was normally observed. A comparison of BiCl peak positions chosen at random with those reported by Morgan (9) shows agreement between the two data sets to ± 0.2 mμ or less.

A totally unexpected set of peaks (Figure 3) was observed in Bi-$BiCl_3$ containing systems at temperatures above 650°. The system consisted of five distinct bands (∿ 1620, 1555, 1490, 1420, and 1350 mμ) each of which exhibited fine structure (peak separation in the 1555 mμ band is ∿ 20 cm^{-1}, in the 1490 mμ band ∿ 15 cm^{-1}). The band at 1390 mμ is an overtone of the 2730 mμ band characteristic of -OH groups in silica. The intensity of these bands increased with increasing P_{BiCl_3} and also with increasing temperature.

The spectrum of the Bi-$BiCl_3$-$AlCl_3$ (ternary) system was investigated between 2500 and 190 mμ from 250 to 950°. All of the spectral features which appear in the Bi-$BiCl_3$ system were observed in the ternary system. In addition, a broad, symmetric band with λ_{max} = 723 mμ appeared at temperatures above 400 to 450°.

Changes in the character of this band with either concentration or temperature suggest that it results from a single transition. The half-width (δ) equals 594 cm^{-1} and remains reasonably constant (± 5%) on varying the amounts of reactants used at a given temperature or the temperature.

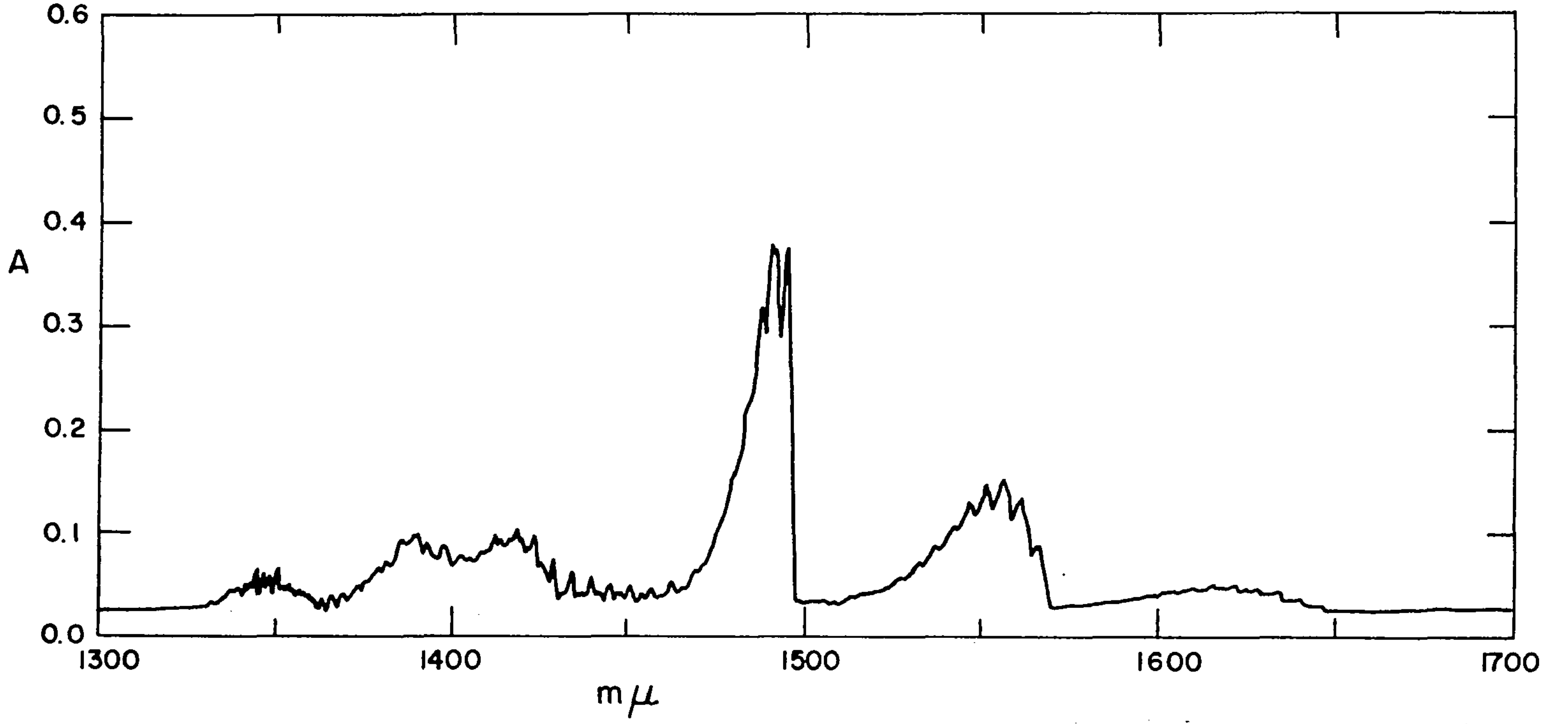

Figure 3. The Bi-$BiCl_3$ system. The near I.R. spectrum (P_{BiCl}=1.05 atm, path length 15.0-cm, temperature 1051°)

Table 1. Representative positions and half-widths of the 723 mμ peak

run	$[BiCl_3]$ mM	$[AlCl_3]$ mM	T °C	λ_{max} mμ	δ cm^{-1}
VIII-11	3.98	5.25	500.0	720.0	614
VIII-12	2.43	5.45	501.0	722.5	622
VIII-13	17.7	5.74	501.0	725.0	562
VIII-33	5.49	2.77	500.0	723.0	591
	5.42	6.90	650.0	723.5	573
	5.21	8.60	749.5	723.0	609
	4.71	9.32	849.5	723.5	589
VIII-34	5.97	2.42	499.5	723.5	586
	5.89	5.80	650.0	724.0	577
	5.68	6.72	749.0	723.0	612
	5.16	7.53	850.0	723.0	591
VIII-35	9.37	2.61	500.0	723.0	595
	9.27	6.35	650.5	723.0	577
	9.01	7.84	752.5	724.0	602
	8.39	8.42	851.5	723.5	603

Values of the calculated absorbance, A_{calc},

$$A_{calc} = A_{max}\, e^{-(\nu-\nu_{max})^2/\theta^2}$$

A_{max} = .289 (T = 650°, P_{BiCl_3} = 1.02 atm, P_{AlCl_3} = 8.18×10^{-1} atm, b = 10.0-cm)

$$\nu_{max} = 13.83 \text{ kK}$$

$$\Theta = \delta/\sqrt{\ln 2} = 694 \text{ cm}^{-1}$$

are in excellent agreement with the observed absorbances indicating a Gaussian distribution of energy for the 723 mμ peak. A typical spectrum (Figure 4) shows the peak superimposed on the edge of the BiCl and $BiCl_3$ bands.

In a given run the intensity of this peak increases rapidly between 400-650°. Above 750° very little change in intensity is observed with a slight, reversible, decrease observed in the absorbances of the highest temperatures (850-950°). Increased pressure of $BiCl_3$ and/or $AlCl_3$ results in increased absorbance for the band.

Numerical Data

The experimental data are tabulated in the Appendix. They have been broken down as follows: Table 4 - high temperature data (650-900°), Table 5 - low temperature data (400-700°), Table 6 - near I.R. data.

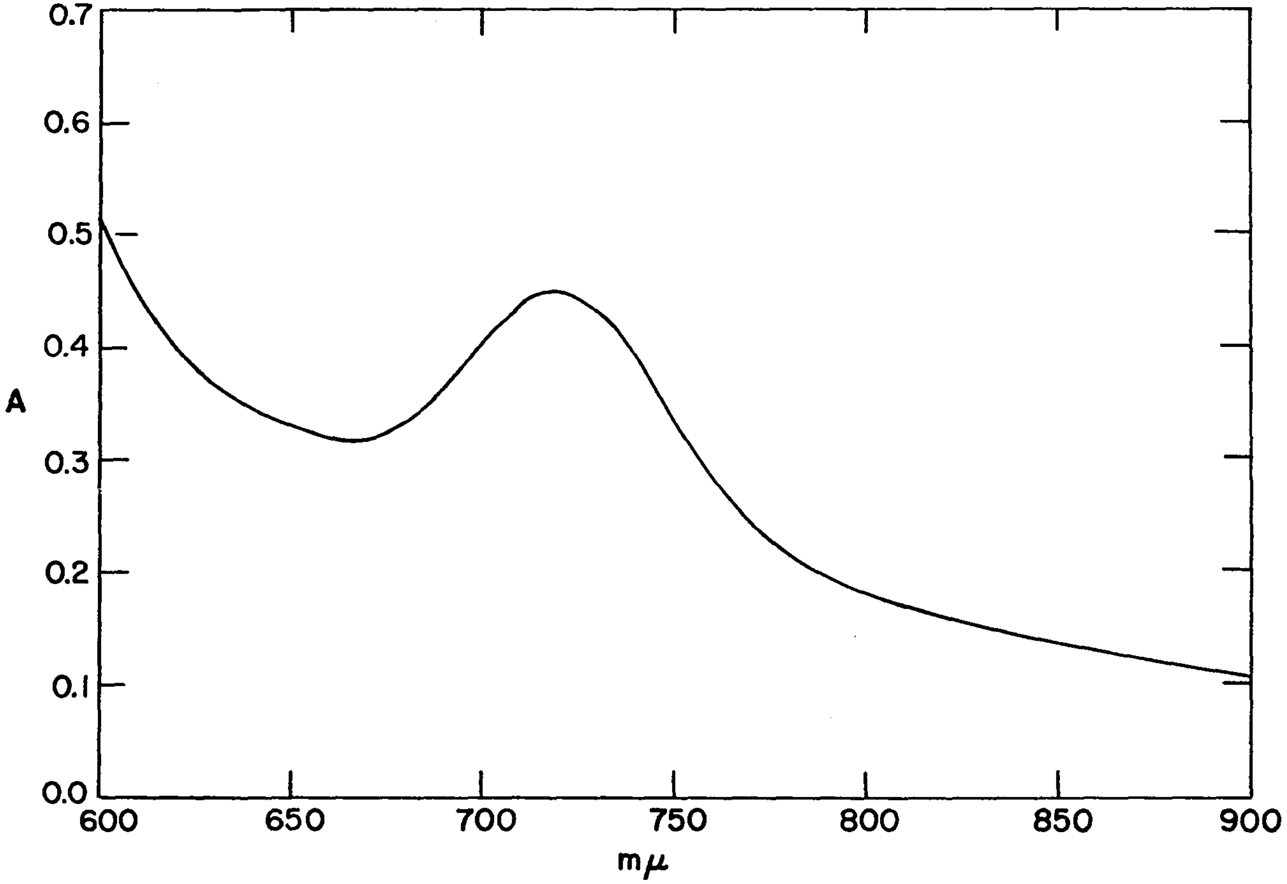

Figure 4. The Bi-$BiCl_3$-$AlCl_3$ system. The 723 mμ peak (P_{BiCl_3} = 5.54 x 10^{-1} atm, P_{AlCl_3}= 6.53 x 10^{-1} atm, path length 10.0-cm, temperature 654.5°)

THE $Bi-BiCl_3-AlCl_3$ SYSTEM - DISCUSSION

Calculations were performed assuming that A_{723} at constant path length was proportional to concentration (i.e., ε_{723} was constant) and that K_p for the reaction was so small that the equilibrium pressures of the reactants did not differ substantially from the initial pressures. Initial calculations indicated that these assumptions were valid for the ternary system at temperatures of 650° and above. The following discussion is concerned mainly with the high temperature behavior of the ternary system although the low temperature behavior will be discussed subsequently.

Product Identification

A comparison of the transitions occurring in the ternary systems with those in the spectra of the pure components and binary systems reveals the presence of $BiCl_3(g)$ and $BiCl(g)$ and a peak at 723 mμ which is unique to the ternary systems. The latter observation requires that the 723 mμ peak be characteristic of the product of a reaction between bismuth, bismuth trichloride and aluminum trichloride.

$$n_1Bi(l) + n_2BiCl_3(g) + n_3Al_2Cl_6(g) \qquad \mathrm{I}$$

$$= Bi_{n_1+n_2}Al_{2n_3}Cl_{3n_2+6n_3}(g)$$

The most likely possibilities are compounds containing either the well documented Bi^+, or Bi^{++}, of which no examples are known. Polybismuth species are expected to be less likely for reasons of entropy, although the presence of the condensed bismuth phase would not permit a differentiation between species of the same charge and different numbers of bismuth atoms. At the temperatures at which these experiments are performed the equilibrium is expected to be very dependent on ΔS and the entropy change is prohibitively negative for all but the most simple product molecules. Polybismuth species are dropped from further consideration.

There are five possible combinations of the nominal anions $AlCl_4^-$ and $Al_2Cl_7^-$ with the cations Bi^+ and Bi^{++} which may form neutral species. These correspond to coefficients of $n_1 = \frac{2}{3}$, $n_2 = \frac{1}{3}$, $n_3 = \frac{1}{2}$ or 1 (for Bi^+) or $n_1 = \frac{1}{3}$, $n_2 = \frac{2}{3}$, $n_3 = 1$, $\frac{3}{2}$, or 2 (for Bi^{++}) in Equation I A generalized equilibrium expression may be written

$$K_c = [\text{Product}]/[BiCl_3]^{x/3}[AlCl_3]^y[Al_2Cl_6]^z$$

$$x = 1,2;\ y,z = 0,\ 1,\ 2;\ y+z = x.$$

A Beer's Law test of A_{723} (T°) vs. different forms of $[BiCl_3]^{x/3}[AlCl_3]^y[Al_2Cl_6]^z$ (= $[\text{Product}]/K_c$) was drawn for each possible product. The result for all combinations of x, y, z other than x=1, y=1 and z=0 was distinctly nonlinear.

Figure 5 is a plot of A_{723} (650°) vs. $[BiCl_3]^{1/3}[AlCl_3]$ for twelve independent measurements. The linearity of the data over a 40-fold variation in the concentration product is taken as verification that the 723 mμ peak is characteristic of $BiAlCl_4$, and the equilibrium may be written

$$\frac{2}{3}\,Bi(l) + \frac{1}{3}\,BiCl_3(g) + AlCl_3(g) = BiAlCl_4(g)\ . \qquad \text{II}$$

If other reaction products are present, they have such small concentrations or the molar absorptivities of their transitions are so small that they are undetectable. Although it is possible that the presence of an additional species is masked by the intense $BiCl_3$-BiCl bands, there is no evidence to suggest that such a species is present in significant concentration.

Thermodynamic Calculations

All calculations were based on the equilibrium

$$BiCl(g) + AlCl_3(g) = BiAlCl_4(g) \qquad \text{III}$$

which yields the more general form, II, upon addition of the equilibrium

$$\frac{2}{3}\,Bi(l) + \frac{1}{3}\,BiCl_3(g) = BiCl(g) \qquad \text{IV}$$

The latter equilibrium has been studied by Cubicciotti (14,

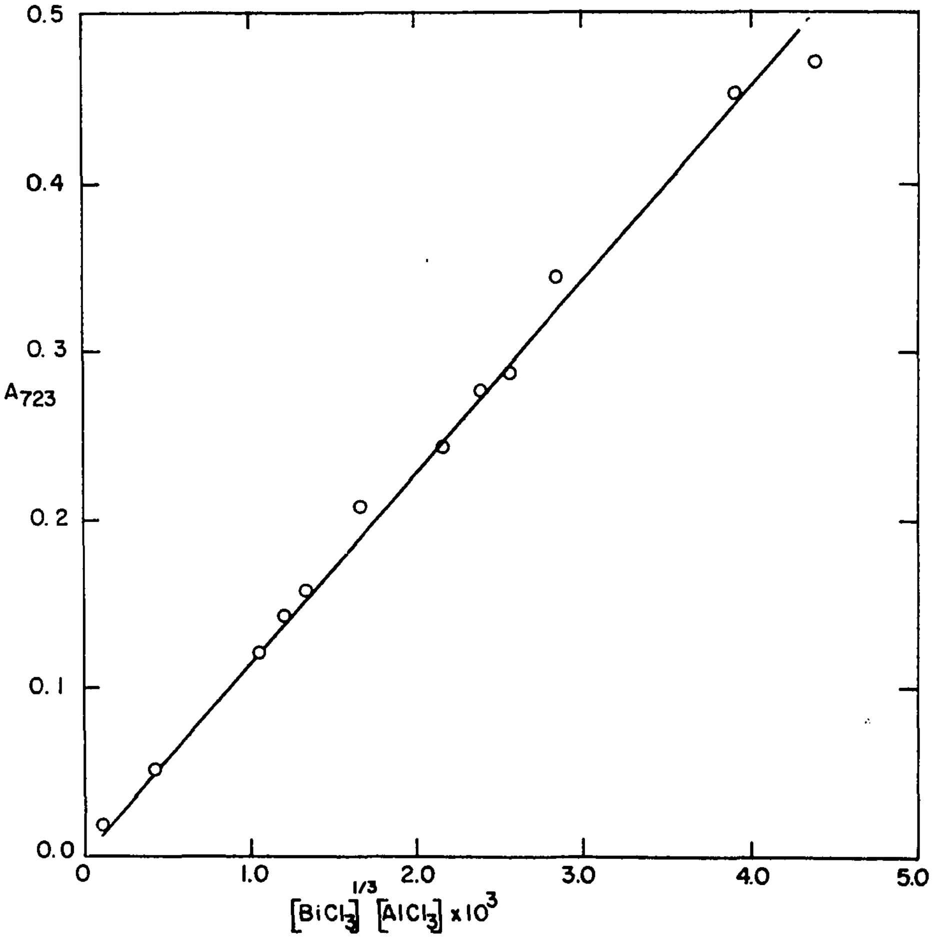

Figure 5. Absorbance at 723 mμ vs. $[BiCl_3]^{1/3}[AlCl_3]$ (temperature 650°, concentration in moles/liter)$^{4/3}$)

15) using transpiration techniques in the range 600-700°. His data have been extrapolated to higher and lower temperatures to cover the range of the present study. Under the experimental conditions of this study 1-33% of the $BiCl_3$ was found to be reacted in the high temperature regions so there would be no significant decrease in the number of calculations required if equilibrium II were used instead of equilibrium III. In either case it was necessary to calculate the position of equilibrium IV in order to obtain the initial pressure of the bismuth chloride reactant.

An additional equilibrium must be considered in order to calculate the initial pressure of aluminum trichloride,

$$\frac{1}{2}\, Al_2Cl_6(g) = AlCl_3(g) \; . \qquad \text{(V)}$$

The equilibrium constant for this dissociation calculated from values tabulated in the JANAF Tables (42) by Øye and Gruen (21) is

$$\log K_{pV} = 3.325 - 2.842\ (10^3/T) - .804\ (10^5/T^2)$$

For this equilibrium, $K_{pV} = 1$ at 609° and the monomer is the major component of the aluminum chloride vapor in all but a few cases in the high temperature region, with partial pressures of $AlCl_3(g)$ of 0.5 to 2.0 atm.

A modified second law method has been used to calculate the enthalpy of equilibrium III. An apparent equilibrium constant, K_a, for Equilibrium III is given by

$$K_a = \frac{A_{723}\ RT/b}{P_{BiCl}\ P_{AlCl_3}}$$

where b is the path length. All of the bismuth trichloride and aluminum trichloride initially added was assumed to be vaporized for the calculations of P_{BiCl} and P_{AlCl_3}. The heat of reaction is determined from a plot of ln $K_{a_{III}}$ vs. 1/T ($°K^{-1}$), Figure 6. This plot will have a slope equal to that obtained from a plot of ln $K_{p_{III}}$ vs. 1/T and an intercept offset from the intercept of the latter by ln ε. The data are adequately described in this manner over a 250° range (650-900°) with no indication of any systematic irregularity outside of experimental error. The linear least-squares description of the data in Figure 6 yields a ΔH°_{1050} value of -28.1 ± 0.5 Kcal for reaction III.

In order to evaluate ΔF°_{1050}, $K_{p_{II}\ 1050}$ and ε_{723} it is necessary to estimate ΔS°_{1050} for this reaction. The information necessary to make a statistical estimate is tabulated in Table 7 of the Appendix. The estimate of the moment of inertia of $BiAlCl_4$ was based on a structure in which the Bi atom was located above a face of a tetrahedral $AlCl_4$ entity. The bond distances so used were those observed in $BiCl_3(g)$ and $NaAlCl_4(s)$ (the Al-Cl distance in the latter

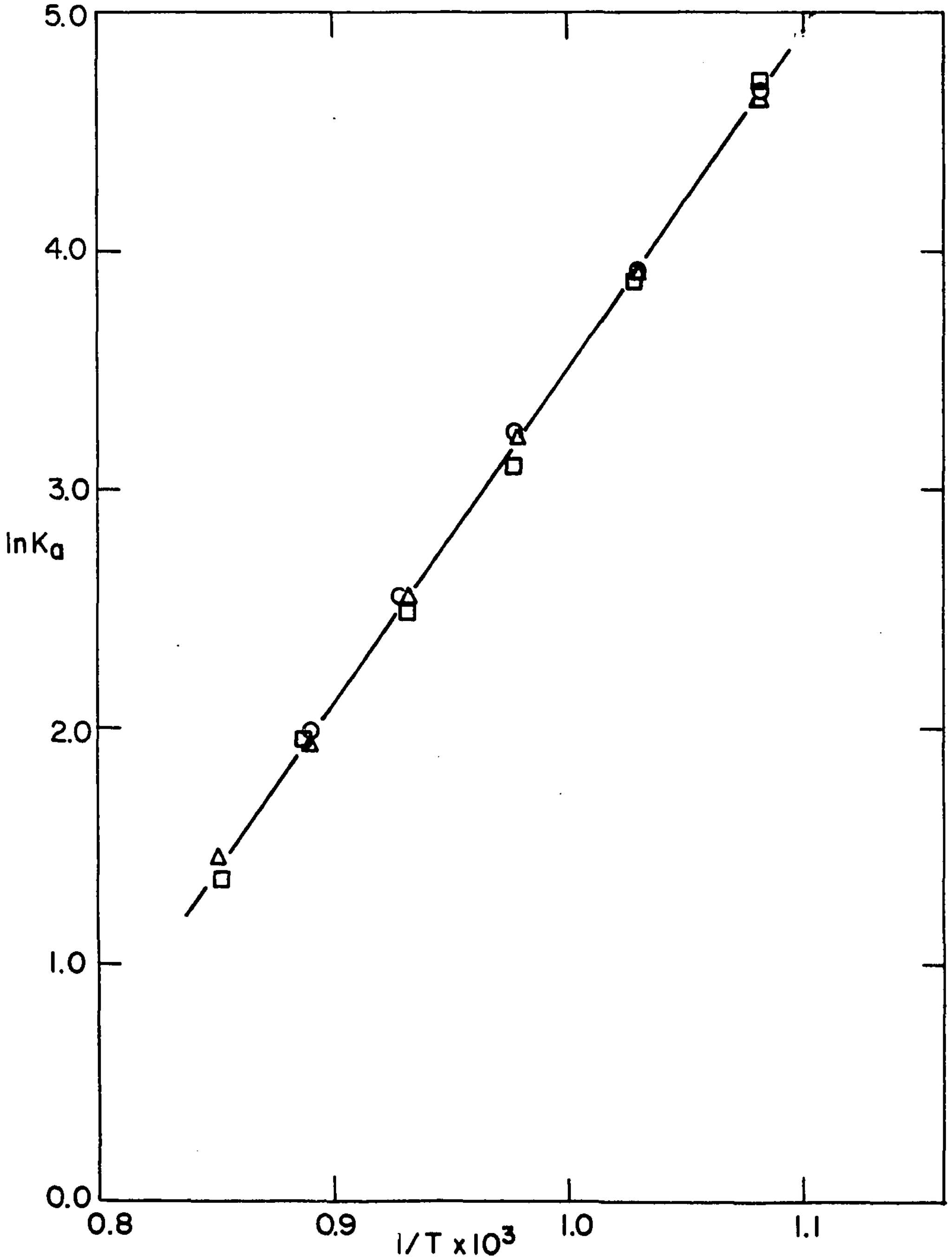

Figure 6. Temperature variation of ln K_a for equilibrium (III) - high temperature region. (O, run 33; Δ, run 34; □, run 35)

(2.13 Å) falls mid-way between the Al-terminal Cl (2.06 Å) and Al-bridge Cl (2.21 Å) distances in Al_2Cl_6(g)) (43). Stull and Prophet have shown (44) that the entropy contribution of the moment of inertia is a slowly varying function of log $I_AI_BI_C$ and that for any molecule a 10% error in all bond lengths would lend to maximum uncertainty of ± 0.6 eu in S_{rot}. The only other reasonable structure for the species, the Bi atom positioned on one of the apices of the tetrahedron, would be expected to have a slightly larger moment of inertia. This estimate will contribute the largest part of the ± 1.0 eu uncertainty in ΔS_{rot}.

An estimate of the vibrational frequencies of $BiAlCl_4$ must be made in order to calculate the vibrational entropy of the molecule. If the range over which these frequencies are spread is not too large a reasonable approximation may be made by using an average frequency (44). Using the frequencies of BiCl(g), $AlCl_3$(g) and $BiCl_3$(g) as guides (see Appendix, Table 7), it is estimated that the twelve vibrational frequencies of $BiAlCl_4$(g) lie between 100 and 600 cm^{-1}, and that the "average" frequency is 250 cm^{-1}. This "average" is adjusted to account for the fact that low energy vibrations contribute considerably more to the entropy of a molecule than high energy vibrations (e.g. at 1000°K a vibration for which the frequency = 100 cm^{-1} contributes ∿ 6 eu to the entropy while one for which the frequency

$= 600\ \mathrm{cm}^{-1}$ contributes ∿ 2.5 eu). The error in ΔS_{vib} for reaction III is estimated to be ± 3.0 eu.

On the basis of an analysis of the rotational structure of the 459 mμ band system, Khanna (11) has assigned BiCl a ground state of $^3\Sigma^-$ which results in an electronic contribution to the entropy of 1.4 eu. All of the electrons are paired and there are no low-lying excited states in $AlCl_3$ so there is no electronic contribution to its entropy. The nature of the ground state and the position of excited states are unknown for $BiAlCl_4$ and its electronic entropy contribution is assumed to be zero.

The estimated entropy, ΔS°_{1050}, for reaction III is -42.8 ± 4.0 eu (S°_{1050} ($BiAlCl_4$) = 130.7 ± 4.0 eu) with which one calculates $\Delta F^\circ_{1050} = 16.8$ Kcal/mole and an equilibrium constant of $K_{p_{1050}} = 3.13 \times 10^{-4}\ \mathrm{atm}^{-1}$. Under the experimental conditions this equilibrium constant corresponds to a product pressure $<$ 0.1% of the smaller of the two reactant pressures. This is consistent with the initial assumption that a relatively small fraction of BiCl is converted to $BiAlCl_4$. Considering the magnitude of the overall experimental error, correction for these small pressure changes would be meaningless.

These results may be combined with a statistically calculated $\Delta(H^\circ_{1050} - H^\circ_{298})$ of 2.4 Kcal/mole to yield $\Delta H^\circ_{298} = -30.5$ Kcal/mole for equilibrium III.

The molar absorptivity, ε_{723} (= $K_{a_{III}}/K_{p_{III}}$) = 5.4 x 10^4 ℓ./mol cm^2, and the oscillator strength, f (= 3.0 x 10^{-1}), indicate that the 723 mμ peak results from an allowed transition. Although the exact nature of this transition is unknown, it certainly has little in common with the Bi^+ $6p^2 \leftrightarrow 6p^2$ intraconfigurational transitions observed by Davis et al. (19) in an NaCl-$AlCl_3$ eutectic melt. These nominally unallowed transitions exhibited oscillator strengths of $\leq 3.7 \times 10^{-3}$. The molar absorptivities of these transitions would have placed them well within detection limits under the experimental conditions of this study, but nothing similar was observed.

Low Temperature Deviations

When similar calculations are performed on data obtained in the low temperature region (400-650°) the results exhibit varying deviations with respect to an extrapolation of the high temperature data. As Figure 7 shows, the calculated values of ln $K_{a_{III}}$ are smaller than the extrapolated values. Possible sources of error in the calculation of K_a are those in A and the reactant pressures. The consistent half-width of the 723 mμ band over the entire range of experimental conditions is evidence that the absorbance readings are reliable.

At 500° the run numbers may be arranged in order of

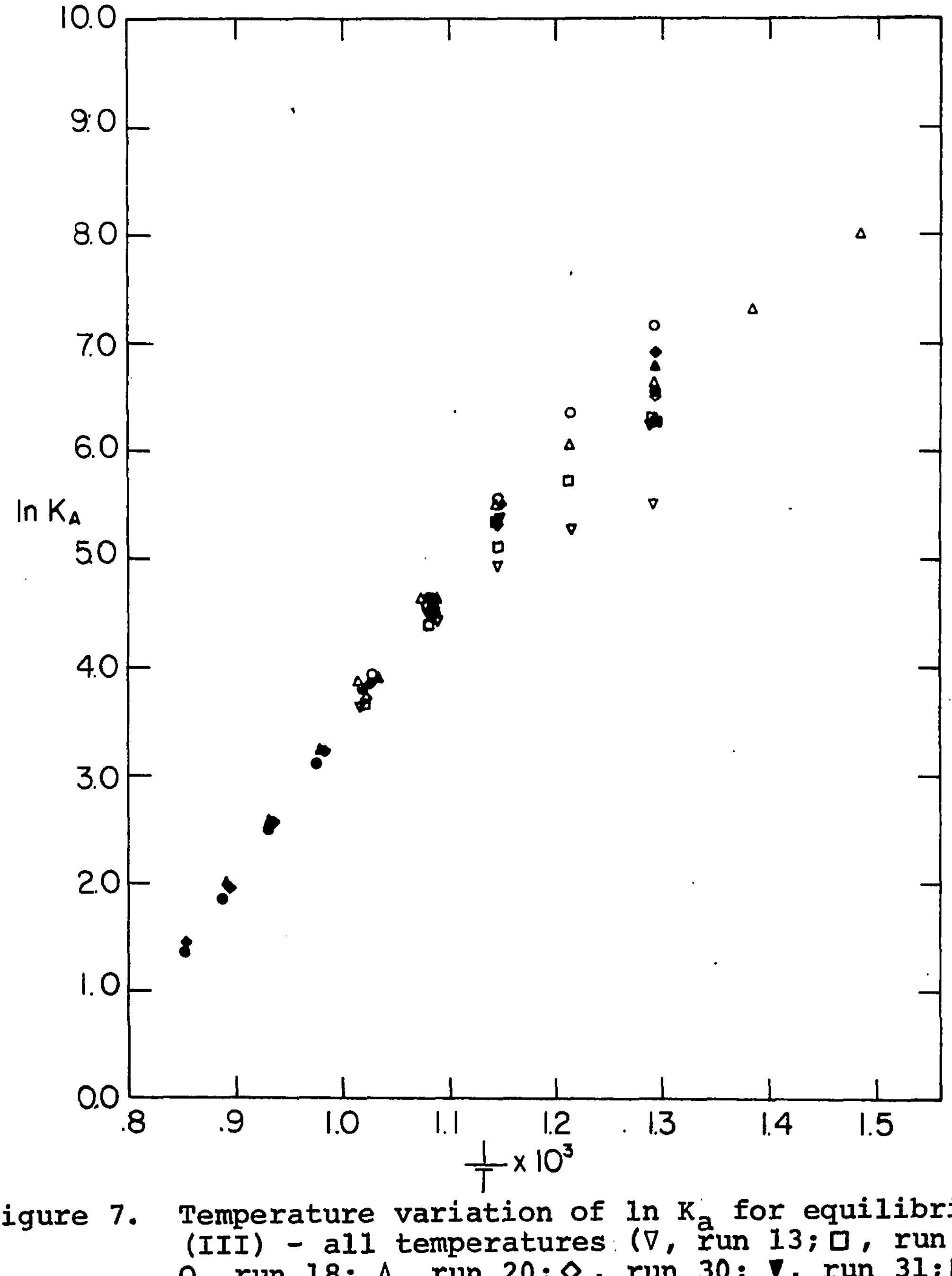

Figure 7. Temperature variation of ln K_a for equilibrium (III) - all temperatures (▽, run 13; □, run 14; O, run 18; Δ, run 20; ◇, run 30; ▼, run 31; ■, run 32; ▲, run 33; ◆, run 34; ●, run 35)

increasing deviation as follows:

$$18 < 34 < 33 < 20 < 35 < 30 < 14 \simeq 32 \simeq 31 < 13$$

There is no correlation between the observed deviations and the amount of bismuth metal (approximately constant throughout all runs) or the amounts of $BiCl_3$ or $AlCl_3$ added to the systems. However the total amount of salt in the system (moles $BiCl_3$ + moles Al_2Cl_6) correlates quite well with the observed deviations, the form being

$$18 < 34 < 33 < 35 < 20 < 30 = 32 < 31 < 14 < 13 \cdot$$

This suggests that both P_{BiCl} and P_{AlCl_3} are in error.

Results from studies of similar condensed systems (Bi-$BiCl_3$, $BiCl_3$-$AlCl_3$, Bi-$BiCl_3$-$AlCl_3$) provide extensive evidence of mutual solubilities and compound formation. $BiCl_{1.167}$, which melts incongruently at 323°, has been shown to exist in condensed Bi-$BiCl_3$ systems (3, 45, 46), and these same systems exhibit considerable solution of both metal in salt and salt in metal at high temperatures (a consolute point is reached at 780°, and 51 mol % Bi). In the $BiCl_3$-$AlCl_3$ system Korshunov et al. (47) have recently reported the existence of a 1:1 compound, $BiCl_3$-$AlCl_3$ which melts congruently at 184°. Recent studies of Bi-$BiCl_3$-$AlCl_3$ containing systems have confirmed the existence of $Bi_5(AlCl_4)_3$ (melts congruently at 326°) and Bi_4AlCl_4

(decomposes irreversibly at 398°) in the metal rich portion of the Bi-$BiCl_3 \cdot 3AlCl_3$ pseudo-binary system (18), and Bi^+, Bi_5^{3+} and Bi_8^{2+} have been identified as the products of the reaction between varying amounts of bismuth metal and dilute solutions of bismuth trichloride in molten eutectic mixtures of aluminum trichloride and sodium chloride (16, 17). In light of this evidence, it is reasonable to expect that both $BiCl_3$ and $AlCl_3$ will condense with the bismuth to give a ternary condensed phase and reduce pressures of both above the condensed phase.

Near I. R. Spectrum

At temperatures above 650°, bands appeared in the near I.R. region (Figure 3) in the Bi-$BiCl_3$ and Bi-$BiCl_3$-$AlCl_3$ systems. Their presence in these systems and absence in all others, and their well defined structure, suggest that they are characteristic of a simple species containing bismuth in a lower oxidation state. For a general equilibrium

$$\frac{3-n}{3} \text{ Bi(l)} + \frac{n}{3} \text{ BiCl}_3\text{(g)} = \text{BiCl}_n\text{(g)} \qquad \text{VI}$$

$$[\text{BiCl}_3]^{n/3} = A_{1495} \frac{1}{\varepsilon b K_{c\ VI}} \quad .$$

The value of n may be determined from the slope of a plot of ln A (1495 mμ) vs. ln $[BiCl_3]$ as shown in Figure 8 where

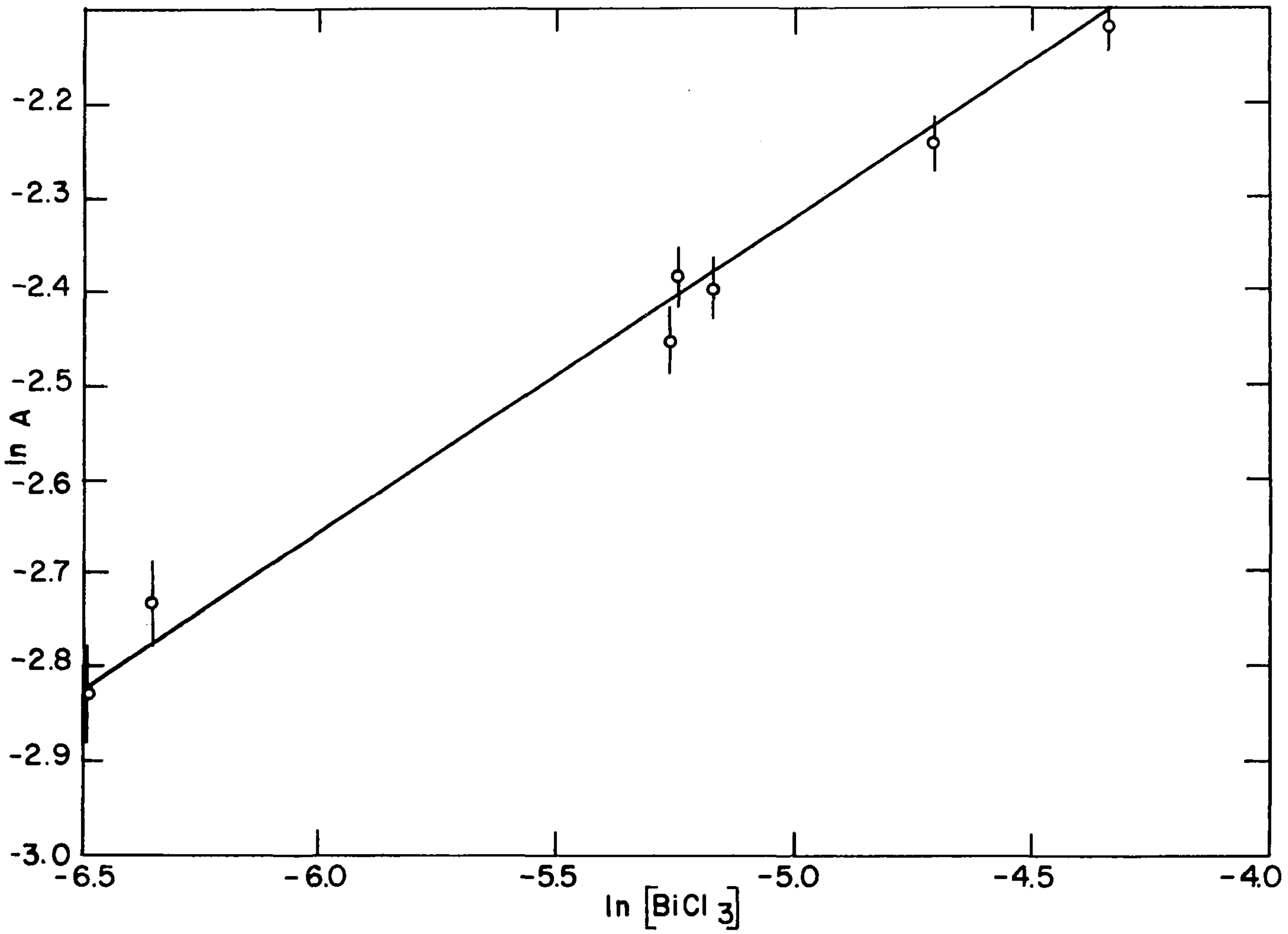

Figure 8. In A_{1495} vs. ln[$BiCl_3$] (1495 mμ peak, temperature 775°)

the trace is drawn with a slope of 1/3. The agreement between the experimental points and the trace indicate that n=1 and that the absorbing species is BiCl. For the 1495 mμ (6.6 kK) peak $\varepsilon_{max} \simeq 10$ ℓ/mol cm.

The position and intensity of these bands suggest a comparison with the $6p^2 - 6p^2$ intraconfigurational transitions of Bi^+ observed by Davis et al. (19) in $AlCl_3$-NaCl eutectic melts where a peak observed at 11.1 kK (e ≃ 15 ℓ/mol cm) arose from ligand field components of the free-ion $^3P_o \rightarrow {}^3P_1$ transition. In view of this assignment it is not unreasonable to assign the near IR spectrum to the band system of a $^3P_o \leftrightarrow {}^3P_1$ transition. A closer inspection of the "vibrational" and "rotational" structure reveals, however, that this is probably not a correct assignment. Although the band separation (ω_e, ≃ 300 cm^{-1}) is not unreasonable for vibrational levels, the size of the progression ($\omega_e x_e \simeq 30$ cm^{-1}) would indicate an unexpectedly large anharmonicity when compared with the vibrational constants for the ground and excited states of BiCl given in Herzberg (40).

Table 2. Vibrational constants of BiCl

State	Level kK	ω_e cm^{-1}	$\omega_e x_e$ cm^{-1}
B	25.49	403.5	3.77
A	21.80	220.3	2.50
X	0	308.0	0.96

In addition the "rotational" level separation ($\simeq$ 20 cm^{-1}) is larger by a factor of 10^2 than the value expected for BiCl (13). These discrepancies indicate that the near I.R. spectrum of BiCl may not be explained as easily as first thought and that a more detailed study would probably yield spectroscopically interesting results.

THE Te-$TeCl_4$ SYSTEM - RESULTS

Qualitative spectral studies were performed on Te, $TeCl_4$ and Te-$TeCl_4$ systems between 190 and 2500 mμ. All spectral measurements on Te-$TeCl_4$ systems were obtained below 450°, the melting point of tellurium, to eliminate the solution of tellurium tetrachloride in excess tellurium. The spectra of tellurium and tellurium tetrachloride were investigated to higher temperatures (500 and 600° respectively). Low temperature spectra were of particular interest since the impetus for this study was the apparent transport of tellurium at low temperatures (∿ 150°) observed by Prince in Te-$TeCl_4$ systems.[1] The minimum temperature employed in these studies was generally 100°. All spectra, except where specifically noted, were obtained using 10.0-cm path lengths.

Spectra

The characteristic spectrum of $Te_2(g)$ (40) appears at 400° in the Te(s) system and increases in intensity rapidly as the temperature is raised. The main features of the spectrum are a broad band with A_{max} at 410 mμ and a series of sharp, strong bands between 190 and 220 mμ. A

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[1] D. J. Prince, Ames Laboratory of the United States Atomic Energy Commission, Iowa State University, Ames, Iowa. Study of the Te-$TeCl_4$ system. Private communication. 1969.

series of sharp, low intensity peaks is superimposed on the 410 mμ band at wavelengths longer than 385 mμ. The abrupt disappearance of the peaks at 385 mμ is the result of predissociation of the $Te_2(g)$ molecule (40).

The spectrum of the $TeCl_4(s)$ system exhibits an intense, high energy band edge ($\lambda_{max} < 190$ mμ) at temperatures above 150° and a broad band ($\lambda_{max} = 292.5$ mμ) at temperatures near 200°. The only feature visible above the $TeCl_4(l)$ system at 250° is the long wavelength edge of the high energy bands for which maximum absorbance (A=2) is attained at 370 mμ. At 400° broad, low intensity bands appear at 510 and 670 mμ. These are the same bands that have been subsequently assigned to $TeCl_2(g)$ and presumably arise from the high temperature dissociation which has been invoked to account for the vapor density of $TeCl_4(g)$ above 500° (48). In the analogous selenium system this disproportionation is essentially complete, $SeCl_4(s)$ yielding $SeCl_2(g)$ and $Cl_2(g)$ upon vaporization at 196° (49, 50). Hussain and Samuel (51) report absorption bands of $TeCl_4(g)$ at 324 and 247 mμ however they provide no information about the preparations and handling of their materials.

A qualitative study of the spectrum of the Te-$TeCl_4$ system reveals that a narrow band with a small amount of fine structure centered at 207 mμ appears at 150°. At temperatures of 250° and above the tellurium tetrachloride absorption is so intense that only the low energy edge of the band (A=2 at λ = 370 mμ) is visible as in the tellurium tetrachloride system. As a result of the extremely small amount of tellurium tetrachloride used in run XII-20 (4.77 mg), spectra were obtained in the 370-280 mμ region up to 325° and a new peak ($\lambda_{max} \simeq 325$ mμ) was observed in the 250 to 325° range. Lack of additional data prevented the determination of the source of this peak. Under the conditions at which quantitative studies were performed on the Te-$TeCl_4$ systems both the 207 and the 325 mμ peaks were buried in the intense high energy absorption.

A series of narrow, low intensity bands occurs between 500 and 650 mμ in the visible region superimposed on two broad bands centered at 510 and 670 mμ (Figure 9). The narrow bands have been observed several times (29, 30, 31) and are ascribed to vibrational fine structure associated with an electronic transition in tellurium dichloride. The agreement between peak positions ($\pm$ 0.2 mμ) and intensities obtained in this study and those of Spinnler (31) is very good. The fine structure and the broad bands are first observed at 200° in all of the systems examined.

The behavior of the broad bands of tellurium dichloride was investigated at constant temperature and varying tellurium tetrachloride pressure to determine whether they were characteristic of the same species. The following

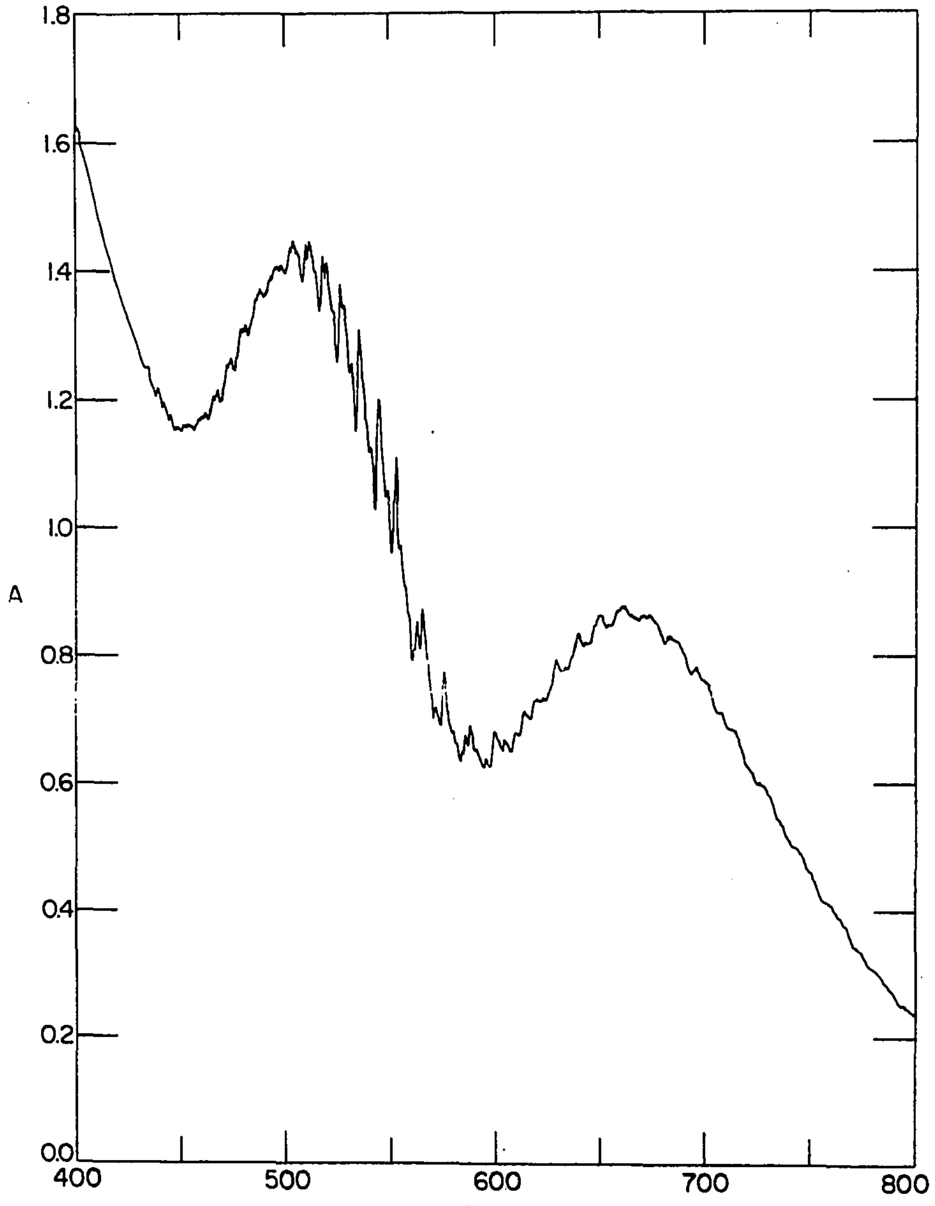

Figure 9. The Te-$TeCl_4$ system. Visible spectrum (P_{TeCl_4}=9.41 x 10^{-3} atm, path length 10.0-cm, temperature 350.0°)

absorbance ratios were obtained from experiments performed at 325° (runs 9, 11, 14, 15, 19, 22; data in Table 8 of Appendix).

$$A_{720}/A_{660} = 0.732 \pm 0.015$$

$$A_{640}/A_{660} = 0.941 \pm 0.005$$

$$A_{720}/A_{560} = 0.824 \pm 0.020 \quad .$$

The consistency of the ratios indicates that the 510 and 670 mμ bands are characteristic of a single species or of two species related by a pressure independent equilibrium, which is unlikely for chemically realistic products. The absorbance of tellurium tetrachloride is negligible above 560 mμ in these systems.

The presence of an additional, high temperature equilibrium in the Te(s)-$TeCl_4$(g) system is indicated by the high temperature behavior of the 510 and 670 mμ bands. The absorbance of these features increases quickly to maximum values in the 350 to 400° region and decreases significantly at higher temperatures. The decrease in A_{660} ranges from 20 to 30 % between 400 and 425° and from 40 to 50% between 400 and 440°.

Data

The experimental data are tabulated in Table 8 of the Appendix. Spectral investigations of the Te-$TeCl_4$ systems were generally limited to the 1200-400 mμ region.

Temperatures were varied from 275 to 440°, with spectra recorded at 25° intervals in the 275 to 425° range. The invariance of absorbance with the amount of tellurium tetrachloride added to the systems for most runs at 250° and below indicated that the systems were saturated in tellurium tetrachloride. The systems used for quantitative measurements were all unsaturated with respect to tellurium tetrachloride at 275° and contained a large excess of Te(s) at experimental temperatures.

THE Te-$TeCl_4$ SYSTEM - DISCUSSION

Data Treatment

The appearance of the fine structure and the 510 and 670 mμ bands in the Te-$TeCl_4$ system requires the formation of a chloride in an intermediate oxidation state. Possible products contain Te(I), Te(II), Te(III) or polytellurium cations. Although the existence of polytellurium cations has been demonstrated in various condensed systems (33, 34, 35, 52) it is unlikely that they exist in the vapor state. The entropy of formation for these is much less favorable than for species containing a single tellurium and polytellurium species have been dropped from further consideration. The remaining possibilities are Te(I) and Te(III) of which no other examples are known, and Te(II) for which both gaseous (30, 31) and condensed (24, 26, 28) compounds have been reported.

The general approach to the problem involves performing a complete set of calculations for each model, $x = 1.33$, 2, and 4, in

$$(x-1)\ Te(s) + TeCl_4(g) = x\ TeCl_{4/x}(g)\ , \qquad \text{VI}$$

and determining which yields the most reasonable results. It was assumed that the intensities obey Beer's Law and that only a single equilibrium is involved.

A graphical procedure was employed in the initial calcultions. The equilibrium constant for reaction VI

$$K_c = \frac{[TeCl_{4/x}]^x}{[TeCl_4]_0 - \frac{1}{x}[TeCl_{4/x}]} \qquad \text{VII}$$

$[TeCl_4]_0$ = initial concentration of $TeCl_4(g)$

yields

$$K_c^{-1} = [TeCl_4]_0 (\frac{b}{A})^x \; \varepsilon_i^{\,x} - \frac{1}{x}(\frac{b}{A})^{x-1} \; \varepsilon_i^{\,x-1} \qquad \text{VIII}$$

A = absorbance of $TeCl_{4/x}$ at λ_i

ε_i = molar absorptivity of $TeCl_{4/x}$ at λ_i

b = path length

when combined with the Beers Law expression. When x is assigned a value corresponding to one of the acceptable models (x = 1.33, 2, or 4) this reduces to an equation in two unknowns, so that data from two or more runs may be solved simultaneously at any λ_i to yield values for K_c^{-1} and ε_i. The graphical solution involves substituting various values of ε_i into equation VIII and constructing a plot of K_c^{-1} vs. ε_i. Ideally the plots of separate runs should all intersect at one point the coordinates of which are the correct values of K_c^{-1} and ε_i, but in practice the intersections representing all pair solutions are widely scattered. The scatter in intersections, attributed to lack of precision in the data, was severe enough to preclude significant results from graphical methods.

The problem of poor precision was circumvented by making more extensive use of the available spectral data and culling the results statistically. In the graphical method, the use of data from six runs yielded fifteen values of K_c and ε_i for each model at each temperature. By using absorbance values from six wavelengths between 560 and 720 mμ fifteen values of ε_i were obtained at each wavelength for each model and temperature, but ninety values of the equilibrium constant were obtained since it is invariant in wavelength.

Each data pair yielded a molar absorptivity

$$\varepsilon_i = \left.\frac{A'\,{}^{x}A'' - A''\,{}^{x}A'}{A'\,{}^{x}P_o'' - A''\,{}^{x}P_o'}\;\frac{RT}{b}\;\frac{1}{x}\right|_{T,\,x,\,\lambda_i}$$

A' = absorbance run I, wavelength = λ_i

A'' = absorbance run II, wavelength = λ_i

P_o' = initial pressure $TeCl_4(g)$ run I

P_o'' = initial pressure $TeCl_4(g)$ run II

These molar absorptivities were substituted into

$$K_p = \frac{(A'RT/b\varepsilon_i)^x}{P_o'-A'RT/xb\varepsilon_i}$$

to evaluate the equilibrium constant. The statistical refinement of the K_p values involved three cycles of data culling. Individual values of K_p were discarded if their deviations from $K_{p_{ave}}$ were greater than twice the standard deviation in the first two cycles and three times the standard deviation in the last cycle. Preliminary calculations demonstrated that a set of equilibrium constants very often contained one or two values which were considerably different than the majority of the others. The first cycle would throw these values out but would generally not refine the data further. The last two cycles were used to refine the main body of the data. More than three cycles gave no significant change in $K_{p_{ave}}$.

Calculated Results

Results from the graphical solution and early analytical calculations indicated that the formation of $TeCl_3(g)$ in the Te-$TeCl_4$ system was unlikely. In addition, it would be very unusual for a tetraatomic molecule to exhibit the extensive fine structure observed so $TeCl_3(g)$ was dropped from further consideration. The choice between $TeCl_2(g)$ and $TeCl(g)$ was based on the precision of the calculated equilibrium constants as reflected by $\sigma/K_{p_{ave}}$ where σ is the standard deviation in K_p. The amount of $TeCl_4(s)$ added to the cells was limited to approximately 0.5 to 2.0 mg. Lower weights could not be measured with sufficient accuracy and higher weights would saturate systems with tellurium tetrachloride at temperatures of 273° and above. The small amounts of tellurium tetrachloride used led to large errors in the values of the molar absorptivity and the equilibrium constant, the calculations of which involve the subtractions of very similar numbers. Trial calculations with selected data indicated that fractional errors of 0.25 to 1.0 could be expected in the values obtained for the equilibrium constant. The large standard deviations reflect the uncertainty in these calculations.

The results of the calculations, given in Table 3, indicate that x=2 (in equilibrium VI) generally leads to more precise results, thus the predominant reaction is

$$Te(s) + TeCl_4(g) = 2TeCl_2(g) \quad . \qquad \text{IX}$$

The enthalpy of reaction IX was obtained from a plot of $\ln K_p$ vs. 1/T (Figure 10). A least squares fit of the low temperature data (275 to 350°, with midpoint temperature of 585°K) yielded $\Delta H^\circ_{585}=23.5\pm2$ Kcal. The entropy, ΔS°,

Table 3. Te(s)-$TeCl_4$(g) systems. Calculated $K_{p_{ave}}$, σ

Product	Temperature °C	$K_{p_{ave}}$	σ	$\sigma/K_{p_{ave}}$
$TeCl_2$	275	0.096 atm	0.126 atm	1.30
	300	0.453	0.449	1.00
	325	0.821	0.536	0.64
	350	1.368	1.724	1.26
	375	1.039	1.825	1.76
TeCl	275	0.119 atm^3	0.127 atm^3	1.06
	300	0.616	0.827	1.34
	325	1.172	1.096	0.94
	350	1.624	3.827	2.36
	375	1.835	2.511	1.37

was calculated using K_p and this ΔH° and is 38.7 ± 4 eu.

The entropy provides a check on the validity of the model since it may be estimated reasonably well from data which are available in the literature (42, 53, 54, 55) and which are tabulated in Table 9 of the Appendix. For reaction IX such an estimated entropy, 44.7 eu, agrees quite well with the calculated value, 38.7 ± 4 eu. The estimated entropy for

$$3Te(s) + TeCl_4(g) = 4TeCl(g) \qquad X$$

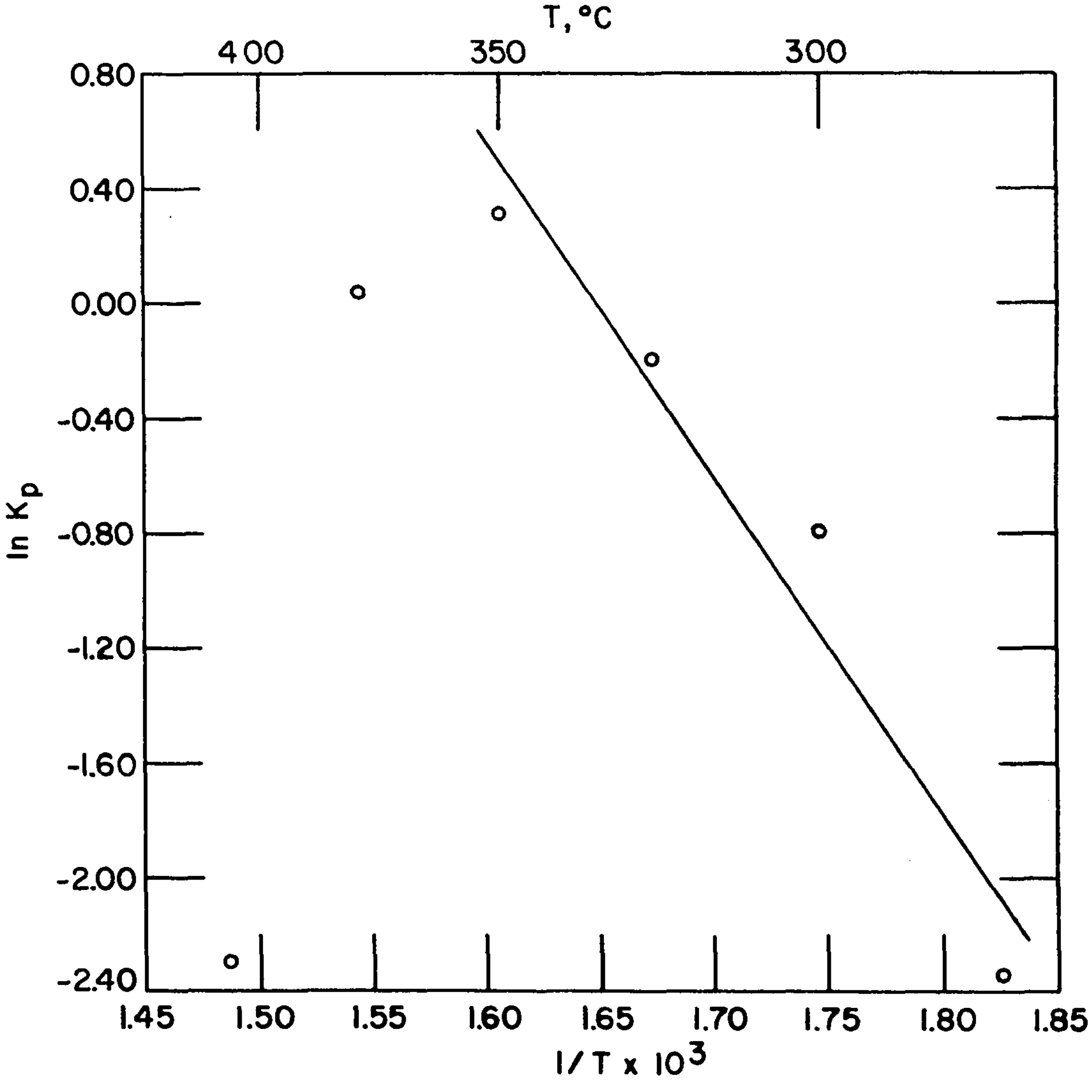

Figure 10. Temperature variation of ln K for equilibrium IX

is 107.9 eu, considerably different than the value of approximately 40 eu obtained from the enthalpy estimated for this model (x=4). The entropy for the formation of polytellurium species would be very small, if not negative.

The tellurium dichloride model fits the data reasonably well in the 275 to 350° range but at higher temperatures the equilibrium constants calculated from the data are considerably smaller than those expected from an extrapolation of the low temperature data. The existence of an additional equilibrium above 350° is indicated by the behavior of the spectra. The $TeCl_2$ absorbance reaches maximum values in the 350 to 400° range and decreases, reversibly with temperature, above 400°. The magnitude of the decrease indicates that the assumption of a single equilibrium in the system is invalid at high temperatures. In the 350 to 450° range Te-$TeCl_4$ systems are characterized by at least two major equilibria, one of which is IX. It follows from the entropies of equilibria IX and X that TeCl(g) will become relatively more important with respect to $TeCl_2$(g) as the temperature of the Te(s)-$TeCl_4$(g) system is increased, and that the second equilibrium might well be X. Calculations designed to elucidate the nature of the second equilibrium yielded uninterpretable results because of the lack of precision of the tellurium dichloride calculations. No new spectral features of the added component were observed.

Equilibrium IX meets all the criteria stipulated by Schäfer (56) for the transport of tellurium from higher to lower temperatures including a positive ΔH°, a ΔS° of the same sign as ΔH°, and a non-extreme equilibrium. The presence of this equilibrium in Te-$TeCl_4$ systems accounts for the transport of tellurium observed by Prince at low temperatures (T ∿ 150°).

The formation of reduced polyatomic cations with empirical compositions $TeAlCl_{3.5}$, Te_2AlCl_4,and Te_3AlCl_4 has been observed in a study of the Te-($TeCl_4$ + $4AlCl_3$) pseudo-binary system (36). Crystals of the most reduced phase, Te_3AlCl_4, were grown via vapor transport reaction and it appeared that a study of the vapor species in a Te-$TeCl_4$-$AlCl_3$ equilibrium system might yield interesting results.

The spectrum of the $TeCl_4$-$AlCl_3$ system is characterized by an intense high energy band of which only the low energy edge is visible (A=2 at 320 mμ, temperature 300°). The composition of the Te-$TeCl_4$-$AlCl_3$ system investigated (Table 7 in Appendix) places it approximately mid-way between $TeAlCl_{3.5}$ and $TeAlCl_4$ (5.2 Te per ($TeCl_4 \cdot 4AlCl_3$)) with some excess aluminum trichloride. There are no spectral features down to 190 mμ in the visible/ultra-violet region below 300° in this system. Between 300 and 400° the absorbance increases rapidly below 250 mμ in a manner similar to the behavior of aluminum trichloride systems. At 400° a new peak is observed at 207 mμ on the steep band edge but increasing the temperature to 450° increases the absorbance to values greater than two below 220 mμ. At 450° and above the spectrum of $Te_2(g)$ is visible and a new band appears at 325 mμ. The position of the latter is the same as for a peak observed qualitatively at low temperatures (< 325°) in run XII-20. The characteristic fine structure and broad band spectrum of $TeCl_2(g)$ appeared weakly at 550°.

Visual observations of the cell and its contents indicated that the condensed phase remained substantially undiminished as the temperature was raised from room temperature to 550°. The probable cause of the lack of spectral features in this system below 300° appears to be the greatly reduced activities of the components caused by compound formation in the melt. Extensive formation of vapor phase aluminum trichloride complexes is ruled out by the qualitative observations just described. If any are formed they are either formed in such small quantities that they remain below the detection limit (.005 A) or they exhibit no spectral features in the range of the instrument. Until a more complete description of the Te-$TeCl_4$-$AlCl_3$ ternary system is obtained, quantitative studies of the vapor phase above such systems are impossible. At present the nature of the mechanism by which Te_3AlCl_4 transports is still unknown.

FUTURE WORK

A perusal of the literature indicates that there are relatively few elements that have not been investigated spectroscopically, and that a large majority of the data available date back to the period between 1925 and 1940. In addition, most of these studies were attempts to detect new spectroscopic entities under non-equilibrium conditions (in flames, arcs, or discharge tubes), with only minimal concern expressed about sample preparation. Many of the thermal data presently available for high temperature species are derived from statistical calculations based on these measurements. Greatly improved instrumentation and experimental techniques (particularly vacuum and inert atmosphere techniques) provide the basis for a series of experiments designed to yield selective evidence for updating the available thermal data. Among the systems which might yield useful information to a spectroscopic study are the metal-metal halide systems of Ga, Sn, Pb, Sb, and Ba, and the As-AsX_3 and Se-SeX_4 systems. In each of these systems the metal has a significant vapor pressure at low temperatures making static pressure measurements impossible and transpiration studies difficult.

The strong chloride ion affinity of aluminum trichloride and the remarkable volatility of the vapor complexes formed by aluminum trichloride and various metal halides suggest that further studies of metal-metal halide-aluminum trichloride systems should be made. The combination of an ionic salt studied at low temperature is most likely to yield significant results. Since the reaction of aluminum trichloride with chloride ion provides one of the main dirving forces for the formation of the vapor complexes, increasing the covalency of the metal-chlorine bond in the salt is expected to be detrimental to the formation of the complexes. In addition, the formation of the complexes will generally involve a decrease in entropy which will cause the complexes to become less stable with respect to the reactants as the temperature is increased. The effect of covalency and high temperature is seen in the relative instability of $BiClCl_4(g)$ with respect to $BiCl(g)$ and $AlCl_3(g)$. Nickel and cobalt offer the most promising possibilities for studies in this area. Both have very low vapor pressures above the metal and metal chloride at intermediate temperatures (500-800°). The addition of aluminum trichloride to these systems would perhaps yield volatile MCl_2-$AlCl_3$ vapor complexes so that M(II) concentration could be used as a variable in a study of the formation of M(I) species.

During the course of this study, two problems arose which deserve additional study. The first is an analysis of the BiCl(g) bands in the near infra-red spectrum. These bands defy assignment on the basis of vibrational and/or rotational structure of an electronic transition. A more thorough study designed to elucidate the nature of the transitions is likely to yield spectroscopically interesting results. The -OH overtone which appears on the high energy side of this spectrum may be minimized by the use of optical grade fused silica for the end windows which are presently Ames Lab issue quartz.

An investigation of the Te-$TeCl_4$ systems at high temperatures should be performed in order to determine the nature of the second equilibrium. The vapor pressure of tellurium is comparable to that of zinc and it appears likely that a study of the all vapor system in the 700 to 1000° range, experimentally similar to the study of the Zn-$ZnCl_2$ system (2), would be possible. Two problems which must be circumvented are the presence of significant amounts of dimer in the tellurium vapor at these temperatures, and the extensive tellurium tetrachloride absorption in the ultraviolet region.

No modifications to the equipment appear necessary for the continuation of these high temperature spectroscopic studies. I will emphasize, though, the primary importance, to this and future studies, of the ability to weigh air sensitive reactants accurately. Most of the systems mentioned above for possible study will contain condensed metal and gaseous salt reactants. The weight of the salt, then, is the only variable from run to run, and for significant results it will be necessary to use as wide a range of salt weights as possible. Since the size of the cells is rather small, the amount of salt that can be added without salt condensation is apt to be fairly small ($\lesssim$ 0.05 g). An accurate method of weighing very small samples in an inert atmosphere using direct measurements, rather than the weighing bottles and transfers used in this study, would be very desirable. The use of a microbalance in a nitrogen or argon-filled glovebag should be considered before further studies are begun.

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APPENDIX

Table 4. Bi-$BiCl_3$-$AlCl_3$, high temperature data (650-900°)

Run	Temp °K	$P_{BiCl} \times 10^2$ atm	$P_{AlCl_3} \times 10$ atm	Absorbance (723 mμ, 10.0-cm path)
33	923	1.93	5.23	.143
	971	3.76	6.27	.149
	1023	7.36	7.22	.161
	1075	13.4	8.00	.157
	1122	21.7	8.59	.147
34	923	1.99	4.39	.121
	972	3.99	5.21	.127
	1022	7.50	5.63	.127
	1073	13.5	6.47	.128
	1123	22.6	6.94	.119
	1173	35.8	7.35	.115
35	924	2.31	4.81	.158
	973	4.69	5.77	.162
	1026	9.21	6.60	.162
	1074	1.61	7.22	.160
	1125	2.71	7.78	.146
	1172	4.16	8.22	.139

Table 5. $Bi\text{-}BiCl_3\text{-}AlCl_3$, low temperature data (400-700°)

Run	Temp °K	P_{BiCl} x 10^2 atm	P_{AlCl_3} x 10 atm	Absorbance (723 mμ, 10.0-cm path)
13	774	.199	3.64	.027
	823	.531	6.28	.096
	873	1.32	9.17	.235
	922	2.81	1.28	.470
	975	5.99	1.70	.544
14	774	.182	3.51	.054
	825	.508	5.90	.136
	873	1.20	8.80	.248
	923	2.61	1.24	.452
	974	5.54	1.64	.498
18	774	.130	.830	.023
	824	.355	1.21	.037
	873	.857	1.56	.049
	924	1.89	1.86	.050
	973	3.78	2.08	.051
20	674	.0127	.581	.004
	723	.0455	1.14	.013
	775	.149	2.09	.037
	825	.412	3.36	.085
	875	.993	4.85	.167
	928	2.29	6.53	.208
	975	4.47	7.91	.215
30	774	.141	3.28	.050
	873	.936	8.19	.222
	927	2.16	11.7	.344
	974	4.25	14.9	.360
31	775	.193	2.27	.036
	872	1.25	5.29	.199
	925	2.82	7.20	.276
32	774	.180	2.49	.037
	875	1.22	6.05	.216
	923	2.59	8.18	.288

Table 5 (Continued)

Run	Temp °K	$P_{BiCl} \times 10^2$ atm	$P_{AlCl_3} \times 10$ atm	Absorbance (723 mμ, 10.0-cm path)
33	773	.133	1.76	.033
34	773	.135	1.54	.033
	872	.895	3.39	.105
35	773	.159	1.66	.029

Table 6. Bi-$BiCl_3$, near I.R. data

Run	Temp °K	$[BiCl_3]$ mM	Absorbance (1495 mμ, 10.0-cm path)
4	1025	1.53	.059
	1128	1.17	.131
	1227	.686	.218
	1326	.252	.275
5	1029	5.28	.092
8	1026	13.0	.120
9	1027	1.74	.065
	1127	1.41	.136
	1224	.887	.224
	1321	.374	.270
33	923	5.42	.031
	1023	5.21	.086
	1121	4.71	.185
34	923	5.89	.036
	1024	5.68	.091
	1124	5.16	.187
	1173	4.74	.241
35	924	9.27	.039
	1026	9.01	.106
	1125	8.39	.218
	1172	7.93	.282

Table 7. Molecular data for entropy estimates

	Sources
BiCl(g)	
mass - 244.43 amu	
moment of inertia (10^{40} I) - 304.46 g cm^{2}	(13, 57)
symmetry number - 1	
vibrational frequency - 304.5 cm^{-1}	(13, 57)
$AlCl_3(g)$	
mass - 133.33 amu	
moment of inertia ($10^{120} I_A I_B I_C$) - 1.3218 x 10^{8} g cm^{2}	(42)
symmetry number - 6	
vibrational frequencies - 610 cm^{-1} (2)	(42)
400 cm^{-1} (1)	
245 cm^{-1} (1)	
150 cm^{-1} (2)	
$BiAlCl_4(g)$	
mass - 377.76 amu	
moment of inertia ($10^{120} I_A I_B I_C$) - 4.94 x 10^{8} g cm^{2} (estimate)	
symmetry number - 3	
vibrational frequencies - 250 cm^{-1} (12) (estimate)	
$BiCl_3(g)$	
vibrational frequencies 320 cm^{-1} (1)	(58, 59, 60, 61, 62)
265 cm^{-1} (2)	
120 cm^{-1} (1)	
[90] cm^{-1} (2)	

Table 8. Te-$TeCl_4$; absorbance data

Run	Temp °K	$P^{o}_{TeCl_4} \times 10^2$ atm	Absorbance (10.0-cm path)					
			560 mμ	600 mμ	640 mμ	660 mμ	680 mμ	720 mμ
9	548	3.47	.446	.371	.514	.536	.504	.354
	573	3.64	.492	.400	.529	.555	.526	.382
	598	3.81	.528	.418	.530	.553	.526	.394
	623	3.97	.555	.430	.525	.544	.510	.400
	648	4.13	.582	.446	.524	.539	.520	.399
	673	4.29	.598	.467	.524	.534	.522	.400
11	548	5.83	.590	.502	.709	.750	.710	.504
	573	6.08	.660	.548	.753	.800	.759	.547
	598	6.35	.717	.584	.776	.829	.785	.581
	623	6.62	.771	.610	.780	.828	.787	.607
	648	6.89	.812	.638	.785	.827	.795	.611
	673	7.15	.865	.675	.798	.830	.805	.631
14	548	4.24	.470	.387	.555	.591	.556	.400
	573	4.43	.527	.429	.594	.635	.606	.448
	598	4.62	.547	.438	.590	.626	.603	.457
	623	4.81	.568	.453	.584	.613	.595	.457
	648	5.01	.601	.469	.581	.608	.593	.465
	673	5.18	.687	.540	.626	.649	.635	.501
15	548	11.55	.818	.674	.961	1.024	.969	.700
	573	12.08	1.114	.920	1.243	1.316	1.276	.935
	598	12.57	1.295	1.050	1.339	1.425	1.396	1.086
	623	13.13	1.410	1.149	1.410	1.492	1.473	1.181
	648	13.64	1.505	1.219	1.441	1.512	1.495	1.223

Table 8 (Continued)

Run	Temp °K	$P^{o}_{TeCl_4} \times 10^2$	Absorbance (10.0-cm path)					
			560 mμ	600 mμ	640 mμ	660 mμ	680 mμ	720 mμ
19	548	10.02	.778	.650	.920	.986	.938	.685
	573	10.48	.975	.810	1.100	1.178	1.136	.857
	598	10.92	1.071	.904	1.176	1.252	1.223	.948
	623	11.39	1.155	.960	1.200	1.285	1.261	1.017
	648	11.84	1.201	1.016	1.233	1.309	1.290	1.050
	673	12.27	1.255	1.048	1.237	1.306	1.292	1.070
	698	12.75	.950	.760	.872	.904	.882	.710
	723	13.24	.684	.539	.591	.608	.577	.463
22	548	8.15	.668	.573	.804	.855	.820	.599
	573	8.51	.807	.685	.918	.975	.948	.727
	598	8.88	.886	.746	.970	1.034	1.014	.803
	623	9.24	.937	.777	.977	1.036	1.024	.835
	648	9.62	.966	.802	.974	1.036	1.026	.832
	673	10.00	1.012	.840	.977	1.028	1.017	.843
	698	10.37	.873	.710	.809	.838	.819	.670

Table 9. Entropy (eu) of some gaseous group IV, V, VI and VII chlorides, temperature 600°K[a]

$SiCl$ 62.8			
$SiCl_4$ 95.3	PCl_3 87.2	SCl_2 76.5	Cl_2 59.2
$GeCl$ 65.3			
$GeCl_4$ 99.9	$AsCl_3$ 91.5	$SeCl_2$ 80.7[b]	$BrCl$ 63.4
$SnCl$ 66.2		$TeCl$ 65.5[b]	
$SnCl_4$ 104.3	$SbCl_3$ 94.0	$TeCl_2$ 82.7[b]	ICl 65.2
		$TeCl_4$ 104[b]	

[a] Source (42, 53, 54, 55)

[b] Estimated.

Table 10. Te-$TeCl_4$-$AlCl_3$; sample data

Run	wt. Te g	wt. $TeCl_4$ g	wt. $AlCl_3$ g	cell vol. ml. 10-cm path
23	0.17434	0.01735	0.05132	27.46
24	0.0	0.01845	0.04153	27.90