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A SPECTROPHOTOMETRIC STUDY OF MOLYBDENUM(VI)
AND MOLYBDENUM(V) IN HYDROBROMIC ACID

A THESIS

Presented to the
Faculty of the Graduate Division

by

Joe Frank Allen

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AND MOLYBDENUM(V) IN HYDROBROMIC ACID

Approved:

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Date Approved by Chairman: 12 Oct. 1962

DEDICATION

This work is justly dedicated to those whose sacrifices have made it possible;

Trent, who did not realize he had sacrificed,

Debby, who would not understand why Daddy went to night school, and

Doris, whose love has made it all worthwhile.

ACKNOWLEDGMENTS

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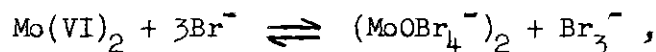
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SUMMARY

The absorption spectra of $(\text{NH}_4)_2\text{MoOBr}_5$, $\text{C}_9\text{H}_8\text{NMoOBr}_4$, and $\text{MoO}(\text{OH})\text{Br}_2 \cdot 4\text{H}_2\text{O}$ have been determined in organic solvents and, in the case of $(\text{NH}_4)_2\text{MoOBr}_5$, in a KBr pellet.

A large number of samples were prepared by adding Mo(VI) to constant boiling HBr (8.6M), giving solutions whose spectra showed the existence of the (MoOBr_4^-) ion and the presence of the tribromide ion, Br_3^- . This has been interpreted as being due to reduction of Mo(VI) to Mo(V) by the bromide ion in acid solution. The relative concentrations of the Mo(V) and Mo(VI) species in solution at equilibrium were shown to be well represented by the equation:



in which both the Mo(V) and Mo(VI) species are dimeric, giving an equilibrium constant,

$$K_1 = \frac{[(\text{MoOBr}_4^-)_2] [\text{Br}_3^-]}{[\text{Mo(VI)}_2]} = 2.27 \times 10^{-3} ,$$

over a range of molybdenum concentrations from 2×10^{-5} to 1×10^{-3} M. All these measurements were for solutions 8.6M in HBr, some of which contained a measured excess of tribromide ion.

Attempts to establish the nature of the Mo(VI) species have not been successful.

By comparison of the ultraviolet absorption spectra of aqueous HBr solutions of Mo(V) with the spectra of known compounds, it may be concluded that the MoOBr_5^- ion does not exist in hydrobromic acid solutions. Even when the bromide concentration is increased to 10.8M by adding LiBr to 8.6M HBr, the spectra show no indications of the formation of the MoOBr_5^- ion. Instead, the $(\text{MoOBr}_4^-)_2$ ion exists exclusively in the high acid concentrations, as is indicated by the identical spectra given by 8.6M HBr solutions and those containing added LiBr.

When the acid concentration is decreased below 8.0M, the changes occurring in the spectra lead to the conclusion that a substance containing Mo and Br in a ratio of 1:2, probably the $(\text{MoO}_2\text{Br}_2^-)_2$ ion, is present in solution in conjunction with $(\text{MoOBr}_4^-)_2$. This substance is also shown to be dimeric since a change in the molybdenum concentration has no effect on the relative peak heights, indicating that $(\text{MoO}_2\text{Br}_2^-)_2$ is of the same degree of condensation as the ion with which it is in equilibrium, in this case the dimer, $(\text{MoOBr}_4^-)_2$.

$(\text{MoO}_2\text{Br}_2^-)_2$ never exists alone in solution, for as the HBr concentration decreases below 6M a third species is indicated. This species, III, which absorbs at shorter wavelengths than $(\text{MoO}_2\text{Br}_2^-)_2$, must have a Mo:Br ratio of less than 1:2 and has been reasoned to be a dimeric cation such as $\text{Mo}_2\text{O}_3\text{Br}_2^{++}$. As the HBr concentration is decreased below 5M, the $(\text{MoO}_2\text{Br}_2^-)_2$ content becomes negligible and the concentration of the third species, III, decreases, indicating the formation of a fourth species which is possibly a bromide-free dimeric cation, such as $(\text{MoO}_2^+)_2$.

A study of the absorbance in the 700-900 m μ region verifies the presence of four species, as described above, and is in agreement as to the acid regions in which each exists.

CHAPTER I

INTRODUCTION

These studies were initiated in an attempt to further the knowledge and understanding of the chemistry of molybdenum in aqueous solutions. The chemistry of molybdenum(VI) in HCl, H₂SO₄, HNO₃ and HClO₄ solutions and the chemistry of molybdenum(V) in HCl, H₂SO₄ and HClO₄ solutions have been extensively studied; and the oxidation-reduction potential of the Mo(V)-Mo(VI) system in HCl solution has received some scrutiny, but the chemistry of molybdenum(VI) and molybdenum(V) in aqueous HBr solutions has received only limited attention.

These previous studies are presented in some detail following a description of the molybdenum(VI) and molybdenum(V) oxybromides that have been reported.

Oxybromides of molybdenum(VI).--A large amount of work was done in the latter half of the nineteenth century and the first decade of the twentieth century in preparing oxyhalides and oxyhalide complexes of molybdenum. This early work is well summarized in Gmelin's Handbuch der Anorganischen Chemie (1) and by Mellor (2).

The first oxybromide of molybdenum to be reported was MoO₂Br₂, prepared by Blomstrand (3) in two ways, by heating MoO₂ in a stream of dry, gaseous HBr and by heating a mixture of MoO₃, B₂O₃, and KBr. This substance sublimes readily to give yellow-red deliquescent crystals which dissolve in water to form essentially colorless solutions. The latter method was also used by Smith and Overholtzer (4) to prepare MoO₂Br₂.

A dark-red crystalline material, analyzed to be $\text{Mo}_2\text{O}_3\text{Br}_4$, was reported by Smith and Overholtzer (4) as a second product of the reaction of MoO_3 , B_2O_3 , and KBr. This compound, described as the color of potassium permanganate, and a yellow-brown needle-like compound, $\text{Mo}(\text{OH})_3\text{Br}_3$, were obtained by heating MoO_3 in a stream of dry, gaseous HBr. The yellow-brown substance was more volatile than the $\text{Mo}_2\text{O}_3\text{Br}_4$, allowing separation of the two by sublimation. The crystals of $\text{Mo}_2\text{O}_3\text{Br}_4$ slowly decomposed in air, but could be kept indefinitely in a carbon dioxide atmosphere, and they dissolved in water to form colorless solutions which turned blue upon standing. The $\text{Mo}(\text{OH})_3\text{Br}_3$ liquefied immediately upon exposure to air, but the yellow-brown crystals could be recovered by letting the liquid stand in a vacuum desiccator over sulfuric acid for a period of three or four days. Water solutions of $\text{Mo}(\text{OH})_3\text{Br}_3$ are pale yellow, becoming darker with time, and eventually depositing "molybdenum blue." ("Molybdenum blue" is the name normally given a wide variety of unidentified blue oxides of molybdenum.) This needle-like compound was also prepared by passing dry HBr gas over the oxybromide of Blomstrand, MoO_2Br_2 , yielding in addition small amounts of unidentified products.

The only complex oxybromide salts of molybdenum(VI) that have been reported (5) are $(\text{C}_9\text{H}_8\text{N})\text{MoO}_2\text{Br}_3 \cdot 2\text{H}_2\text{O}$ and $(\text{C}_5\text{H}_6\text{N})_2\text{MoO}_2\text{Br}_4 \cdot 2\text{H}_2\text{O}$. The quinolinium salt was prepared by passing the gaseous product which results when HBr reacts with MoO_3 into a solution of concentrated hydrobromic acid, adding bromine, and heating, followed by the addition of quinoline hydrobromide in the ratio of 1 mole quinoline to 3 moles of molybdenum.

Upon cooling, light yellow crystals of $(C_9H_8N)MoO_2Br_3 \cdot 2H_2O$ precipitated. The yellow dipyridinium salt was obtained in the same manner, using 20 per cent hydrobromic acid and 3 moles of pyridine hydrobromide to 1 mole of molybdenum.

Oxybromides of Molybdenum(V).--Souchay, Durand, and Schaal (6) found that by treating powdered molybdenum with bromine at 650-700°C a small amount of air sensitive black needles were formed, which analyses showed to be $MoOBr_3$. Blomstrand (3) had reported this compound to be $MoBr_4$. When air was passed through the reaction chamber with the bromine, MoO_2Br_2 was formed.

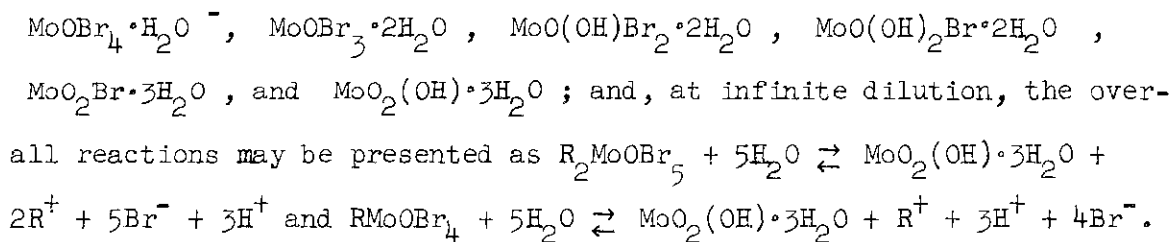
Weinland and Knoll (5) prepared $Mo(OH)Br_4 \cdot 2H_2O$ by dissolving the product of the reaction of gaseous HBr on MoO_3 in a 40 per cent hydrobromic acid solution, heating until no more bromine was evolved, then allowing the solution to stand over sulfuric acid until green, needle-like crystals formed. These needles were extremely hygroscopic, fuming in air. When an identical solution was allowed to stand over soda-lime, brown crystals of $MoO(OH)Br_2 \cdot 1-1/2 H_2O$ were formed. These prism-like crystals were very hygroscopic, dissolving in water to form brown solutions.

Complex oxybromide salts of the type R_2MoOBr_5 were prepared by Weinland and Knoll from solutions of molybdenum(V) in concentrated hydrobromic acid solution by adding an excess of the appropriate bromide to the solution. The Cs^+ , Rb^+ , K^+ , and NH_4^+ salts were red to brown in color, with the Mg^{++} , $C_9H_8N^+$, and $C_5H_6N^+$ salts being green. Complexes of the type $RMoOBr_4$ were prepared by using a limited amount of the component salt, with red salts of Li^+ , Ca^{++} , $C_9H_8N^+$, $C_5H_6N^+$ and a green salt

of K^+ being reported.

Rosenheim and Koss (7), and Angell, Wardlaw and James (8) also reported $(C_5H_6N)_2MoOBr_5$, $(C_9H_8N)_2MoOBr_5$, and $(C_5H_6N)MoOBr_4$, and Angell and co-workers prepared $(C_9H_8N)MoOBr_4$, which the former were unable to prepare. Angell and co-workers also verified the preparations of the K^+ , Rb^+ , and NH_4^+ salts of the type R_2MoOBr_5 , as well as $LiMoOBr_4$, reporting that they are all yellow to red when freshly prepared, but some of these rapidly turn green on exposure to air, most probably due to partial oxidation, which explains the green colors reported by Weinland and Knoll. Angell, et al., were not able to prepare $MgMoOBr_5$, $KMoOBr_4$, or $Ca(MoOBr_4)_2$ free from an excess of the corresponding metal bromide.

All the salts prepared by Angell, Wardlaw, and James dissolved in water to form yellow-brown solutions from which the salt could not be recovered. This behavior was attributed to hydrolysis, with the following species postulated as having at least transitory existence in solution:



These solutions were found to have an osmotic factor in water of 9 to 11 for R_2MoOBr_5 and 7 to 9 for $RMoOBr_4$, as would be predicted by the equations as written; and osmotic factors of about 3 and 2, respectively, in absolute ethanol, due to the simple ionization of the salt in this solvent. The preparation of a red, hygroscopic salt of formula $LiMoO_2Br_2 \cdot 6H_2O$ was taken as partial verification of the above scheme of hydrolysis, even though such salts could not be separated from the hydrolysis mixture.

Molybdenum(VI) in acid solutions.--Ion-exchange studies of molybdenum(VI) in HCl, HBr, and H₂SO₄ solutions (9, 10, 11) indicate that anionic species predominate at all acid concentrations greater than 1 M, apparently containing the anion from the acid present. Krauss and co-workers (9) assign the anionic species the general formula MoO₂Cl_n⁻ⁿ⁺², with n = 3 or 4 for the chloride solutions. At concentrations of about 1 M acid there is evidence for the presence of cationic forms, represented by MoO₂⁺⁺ or some polymeric form of MoO₂⁺⁺, but these are never the predominating form in these solutions. In solutions of HClO₄ or HNO₃, which are non-complexing acids, the cationic forms of molybdenum(VI) are the primary species present in acid concentrations greater than 1 M. In all acids below 1 M concentration the Mo(VI) appears to be present in the form of condensed molybdate anions. Babko (10) concluded that the cationic forms were present and monomeric to pH = 2, but Diamond (11) doubts the existence of any simple cations. Using solubility measurements, Jones (12) calculated the formula MoO₂⁺⁺·2MoO₃, but he ignored the formation of anionic complexes. Using spectrophotometric and solubility data, Souchay, Schaal, and Chauveaux (13) have shown that molybdenum(VI) exists as bicondensed cations in 10⁻² M molybdenum and 5 M HClO₄.

From the migration of Mo(VI) in electrolysis experiments in acid solutions, Babko (10) verified the predominance of anionic complexes in HCl and H₂SO₄ above 2 M in concentration, molybdate anions below 1 M acid, and in the 1-2 M acid region the coexistence of cationic and anionic species. However, Babko believed the anions existing in weak hydrochloric acid solutions to be due to chloride complexes rather than molybdate anions. When a solution of KCl, HCl, and ammonium molybdate at a pH of

3 was allowed to stand for over 20 hours, a white solid appeared. Analysis yielded a ratio of Mo:Cl of 5:2; and, upon further washing, a ratio of 8:1 was found. When potassium chloride and ammonium molybdate solutions of identical pH were mixed, the pH was found to increase, leading Babko to deduce that chloride was replacing hydroxide from the molybdate, thereby causing the pH increase.

Diamond (11, 14) studied the distribution of Mo(VI) between aqueous and organic solvents at various concentrations of hydrochloric and hydrobromic acids by using a radioactive molybdenum tracer. Using acid concentrations ≥ 2 M, extraction was very good into ethers, esters, and ketones, but poor into non-oxygenated solvents. Extraction was better from aqueous HBr than from aqueous HCl, with the maximum extraction occurring at lower acid concentrations for the HBr solutions. Analysis of the ether phases gave the ratios of Mo:Cl = Mo:Br = 1:2, indicating that the extracted species are of the formula $\text{MoO}_2\text{X}_2(\text{H}_2\text{O})_x(\text{ether})_y$, where X = Cl or Br. In HCl solutions greater than 6 M in concentration the distribution coefficient is not dependent upon the Mo(VI) concentration, showing that the species in both solvents must have the same degree of condensation. Below 6 M there was some evidence of polymeric species, with these becoming appreciable for 10^{-4} M molybdenum(VI) in 2 M HCl and in 4.4 M HBr. At higher molybdenum concentrations the polymeric forms are important at even greater acid concentrations. The conductivity of the substance extracted from aqueous HCl solution into β,β' -dichlorodiethyl ether indicated that ionization had occurred, whereas in other solvents, such as 2-ethylhexanol, the extracted substance appeared to be electrically neutral. Diamond concluded, therefore, that the extracted species was a very

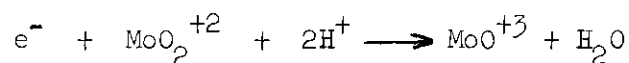
strong acid which ionized in β,β' -dichlorodiethyl ether but did not ionize in some of the other solvents used. No conductivity studies were made for the HBr solutions.

Neumann and Cook (15) compared the absorption spectra of known compounds in ether solution with aqueous HCl solutions of molybdenum(VI) and to the ether extracts of these HCl solutions. The spectra in 1 to 11 M HCl showed the presence of a species having a Mo:Cl ratio of 1:2, with this form becoming most prominent in 6 M HCl, at which concentration about 93 per cent of the molybdenum appeared in the form of the 1:2 complex. Above 6 M HCl a species with Mo:Cl ratio of 1:3 was found to be present, becoming more prominent as the acid concentration increased. The abundances of the 1:2 and 1:3 complexes were calculated at various HCl concentrations. The absorption characteristics and elemental analysis of the ether extracts confirmed that the 1:2 complex was the form extracted, in agreement with the work of Nelidow and Diamond (14). Comparison of the abundance of the 1:2 species with the exchange studies of Krauss and co-workers (9) suggested that the 1:2 complex was the form bound to the anion exchange resin.

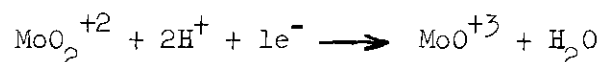
Molybdenum(V) in acid solutions.--A number of workers (16, 17, 18, 19) noted the variety of colors formed by Mo(V) in hydrochloric acid solutions of different concentrations. Hiskey and Meloche (18) describe these as amber in 0.5 - 3.5 M HCl, changing to brown in 3.5 - 7.3 M HCl, and becoming green in solutions above 7.3 M in HCl. Tourky and El-Shamy (20) indicated that "molybdenum blue" formation became a problem below 2 M HCl. These color changes led to a variety of investigations on the species of molybdenum existing in acid solution.

The absorption spectra of molybdenum(V) in hydrochloric acid was used by El-Shamy and El-Aggan (21) to suggest that at least three ionic species existed in these colored solutions at different acid concentrations, with a variety of absorption maxima in the ultraviolet and visible range of the spectrum. No attempt was made to identify these species.

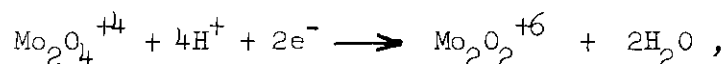
Foerster, Fricke, and Hausswald (16) assigned the equation



to the electrolytic reduction of Mo(VI) to Mo(V) at all HCl concentrations. El-Shamy and co-workers (20, 21) show that such could not be the case, for in their studies in dilute acid the changes in electromotive force as the HCl and molybdenum concentrations were varied indicated that condensation to polymeric forms occurred. It was felt that only cationic species took part in the reduction, although the probable presence of complex neutral or anionic species was accepted, and these were assumed to be in rapid equilibrium to give a sufficient supply of cationic Mo(VI) for reduction to occur at the cathode. The reduction was then assumed to occur as shown by the equations



and



for 7-8 M HCl and 2-4 M HCl, respectively.

Magnetic studies (22, 23, 24) on a number of solid molybdenum(V) oxyhalo complexes indicate the presence of one unpaired electron, as

would be expected for Mo(V) species, which are d^1 systems. However, Klemm and Steinberg (24) show that in the dimeric Mo(V) complexes $(C_5H_6N)_2 Mo_2O_4Cl_4$ (aqueous), $(C_5H_6N)_4 Mo_2O_4(SCN)_6$, and $Ba Mo_2O_4(C_2O_4)_2 \cdot 5H_2O$, only very weak paramagnetism is exhibited, indicating electron pairing between the molybdenum atoms in the complex. Sacconi and Cini (25) used the magnetic moment of solutions of Mo(V) in hydrochloric acid to establish the exclusive presence of monomers in HCl concentrations above 9.5 M and the complete formation of spin-paired polymers in acid concentrations below 2.5 M, with simultaneous existence of monomers and polymers in the 2.5 - 9.5 M HCl range. Jakob and co-workers (26) also noted the decreasing paramagnetism of Mo(V) solutions with a decrease in hydrochloric acid concentration. Upon heating, the paramagnetism returned, and, upon cooling, decreased once again, indicating the increased stability of the monomeric form at higher temperatures. Jakob verified the existence of dimeric species in low HCl concentrations by polarographic studies.

Souchay and Simon (27) believed that the spectrum of the emerald-green solutions of Mo(V) in concentrated HCl was that of the $MoOCl_5^-$ ion because the spectra of these solutions do not vary when the HCl concentration is varied above 7.5 M and the solution is the same color as the salt, $(NH_4)_2MoOCl_5$. In dilute HCl (up to 1.6 M) there exist no chloro complexes, for the spectra of these solutions are identical to those in 1-6 M solutions of non-complexing acids. The absorption characteristics of the solutions in the 2-7 M HCl range vary continuously with an increase of HCl concentration, and the evidence indicates ionic species containing chlorine. The spectral evidence strongly supports the existence of a chloride free tetramer, possibly $(MoO_2^{++})_4$, at low acid concentrations, a chloro

containing dimer, given the formula $\text{Mo}_2\text{O}_3\text{Cl}_2^{++}$ or $\text{Mo}_2\text{O}_3\text{Cl}_4$, at intermediate acidities, and a monomer, $\text{MoOCl}_5^=$, in concentrated HCl, with the dimeric species always existing in conjunction with one or both of the other forms.

In similar but less detailed experiments, Babko and Getman (28) used spectrophotometry in the ultraviolet and visible regions to study the species of Mo(V) in HCl solution and to study the equilibria between these species. With the aid of electrophoretic experiments it was determined that at least three species existed, a cationic form in 2 M HCl and neutral or anionic forms in 5 and 8 M HCl. Extraction into isoamylalcohol verified these conclusions, with no extraction of molybdenum from 2 M HCl, considerable extraction from 5 M HCl, and almost complete extraction from 8 M HCl. These data were used to justify the existence of MoO_2^+ in 2 M HCl, MoO^{+3} in 3 M HCl, MoOCl_3 in 5 M HCl, and $\text{MoOCl}_5^=$ in 8 M HCl, with no indication of polymers given. (These data could have been explained equally as well by using the species and domains of stability given by Souchay and Simon (27)). The equilibrium constant for each of the transformations between these species were approximated.

Spectral studies have also been made of a soluble "molybdenum blue" formed from mixtures of Mo(V) and Mo(VI) in dilute acids (29, 30, 31), and of the molybdates in solutions of pH greater than 1 (32).

Plan of attack.--Measurements of the ultraviolet and visible absorption spectra appeared to provide a suitable method of attack to determine the species of molybdenum(VI) and molybdenum(V) that exist in hydrobromic acid solutions. In the initial stages of work known compounds of molybdenum and bromine would be prepared and their spectra determined. A comparison

of these spectra with the spectra of solutions of molybdenum in aqueous HBr should make it possible to identify some of the species in solution and to exclude the presence of certain others.

It was expected that further conclusions could be drawn regarding the formulation of the species in solution and their domains of stability by observing the spectral changes resulting from independently varying the concentrations of molybdenum, hydrogen ion, and bromide ion.

It is expected that the complexes that exist in HBr will be quite analogous to those existing in HCl, probably forming monomeric anionic species at high acid concentrations and polymeric cationic or neutral species in the low and intermediate acid ranges.

CHAPTER II

EXPERIMENTAL

Chemicals.--The aqueous hydrobromic acid used in these investigations was distilled from a mixture of powdered red phosphorus and A.R. 47% hydrobromic acid, yielding constant boiling acid of 8.66 M concentration. This acid was stored in a polyethylene bottle and was found to be stable for at least two weeks, as noted by the lack of an absorption peak at about 267 μ . The primary impurity in aged HBr is the tribromide ion, Br_3^- , which results from air oxidation and which shows an absorption maximum at 267 μ .

The lithium bromide solutions were prepared from A.R. $\text{LiBr} \cdot x \text{H}_2\text{O}$. These solutions were passed through a Dowex-1 ion-exchange resin to remove traces of colored impurities, probably small amounts of transition metal bromides. The resulting LiBr solutions were spectrophotometrically clear in the visible and near ultraviolet regions of the spectrum.

The calcium bromide solutions were prepared from A.R. CaCO_3 by slowly adding constant boiling HBr to the solid CaCO_3 until the solid was completely dissolved. This solution was then passed through a Dowex-1 ion-exchange resin to remove a trace of a colored impurity.

The MoO_2 was from a sample prepared by Nancy Cook (15).

All other chemicals used were C.P. or A.R. grade. The organic solvents showed no absorbance in the visible and near ultraviolet regions of the spectrum, either before or after shaking with aqueous HBr.

Analytical procedures.--The bromide analysis was a variation of the potentiometric method of analysis for chloride as given by Pierce and Haenisch (33). An accurately weighed sample of about 0.3 g. of the material to be analyzed was dissolved in 50 ml. of cold 1 N HNO_3 . As soon as solution was effected, the bromide content was determined by titrating with standard 0.1 N AgNO_3 using the potentiometric method of end point detection. The potentiometer used was a Beckmann Zeromatic pH meter, using a silver electrode, and with the glass electrode being employed as the reference electrode.

The 1 N HNO_3 was used to prevent the formation of molybdenum blue when the compounds were added to water and to prevent the precipitation of Ag_2MoO_4 during the titration. If the solutions were allowed to stand for long periods, the odor of bromine could be detected, possibly due to the slow oxidation of bromide by HNO_3 . No bromine could be detected within the first hour after preparation if the solutions were kept cool.

The procedure outlined above was tested by dissolving samples of $\text{NaBr}\cdot 2\text{H}_2\text{O}$ and $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$ in 1 N HNO_3 and titrating as described. The bromide analysis was accurate to within 7 parts per 1000.

Titration with AgNO_3 using eosin and dichlorofluorescein as indicators proved unsatisfactory for these analyses.

The analysis for elemental bromine was adapted from the iodine analysis described by Pierce and Haenisch (34). Thirty ml. of KOH solution, containing 40 g. of KOH per 100 ml. solution, was carefully added to 50 ml. of the unknown solution of Br_2 in 8.6 N HBr. The solution was cooled and solid NaHCO_3 was added slowly with swirling until effervescence ceased. Twelve g. of iodate-free KI was added and the solution

diluted to 250 ml. with distilled water.

About 0.1 g. of reagent grade As_2O_3 was accurately weighed and placed in an Erlenmeyer flask. Fifty ml. of water and 10 ml. of 1 N NaOH were added and the solution was warmed to hasten solution of the As_2O_3 . One drop of methyl red solution was added and 1 N HBr was added slowly until a color change was noted. Solid NaHCO_3 was slowly added until effervescence ceased, then 2 g. in excess were placed in the solution to act as a buffer. Three ml. of starch solution were added and this solution was titrated using the unknown bromine solution as prepared above.

Two qualitative methods for analyzing for molybdenum have been used. The very sensitive method given by Feigl (35) employs methylene blue as a redox indicator and hydrazine sulfate as the reducing agent, with molybdenum acting as a catalyst. Two drops of solution containing the unknown were added to six drops of acidified 0.0012% methylene blue solution in a small test tube. The tube was placed in hot water and about 1 ml. of saturated hydrazine in 8.6 N HBr solution was added. Molybdenum was indicated by the fast disappearance of the blue color.

Boiling hydrazine solutions do not reduce methylene blue to colorless methylene white, but a trace of molybdate is sufficient to cause the disappearance of the blue color in a warm solution. This action is due to the rapid reduction of Mo(VI) to Mo(V) by hydrazine in warm acid solutions, followed by reduction of the methylene blue by the Mo(V), which is reoxidized to Mo(VI). The Mo(VI) is then available to be reduced again by the hydrazine, and so on, until all the methylene blue is destroyed. This method is useful for either Mo(V) or Mo(VI), but cannot be

used to distinguish between these oxidation states.

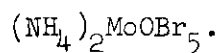
Mo(V) can be detected by the emerald-green color developed when this substance is added to concentrated HCl solution (8, 22, 28). This green color has been adapted into a quantitative method for analyzing for both Mo(V) and Mo(VI). An accurately weighed sample of about 0.3 g. of unknown was dissolved in 20 ml. of 6.5 M HCl and placed into a 50 ml. volumetric flask. One ml. of 8.6 M HBr was added, so that by swamping the bromide that was present in the unknown sample, all the samples would contain the same bromide concentration, and 6.5 M HCl was used to dilute to the mark. The absorbance was then measured at 700 m μ using 1 cm. pyrex cells and a Beckmann Model D.U. Spectrophotometer, using a slit width of 0.60 mm. The concentration of Mo(V) was determined from a previously prepared graph of known Mo(V) concentration plotted against absorbance.

(The graph is necessary because these solutions show a slight deviation from the Beer-Lambert Law.) To determine the total molybdenum concentration [Mo(V) + Mo(VI)], 0.25 ml. of saturated hydrazine in 6.5 N HCl was added to the flask. The solution was then heated in a water bath or at a low temperature on a hot plate until effervescence ceased, or, alternatively, the solution was allowed to stand for twelve hours at room temperature. The hydrazine reduced the Mo(VI) to Mo(V), evolving nitrogen. The solution was then cooled and the absorbance measured at 700 m μ . The total molybdenum concentration was taken from the graph and the Mo(VI) concentration could be obtained by subtracting the concentration of Mo(V) from the total concentration of molybdenum. This method gave an accuracy of about 9 parts per 1000 when run on solutions of known molybdenum concentration.

The ammonia analysis was performed by dissolving a carefully weighed quantity of the unknown sample in 100 ml. water, to which was added 10 grams of NaOH in 25 ml. water. About one-half of this solution was distilled from a round bottom flask into a beaker containing an excess of standard 0.1 M HCl, with care being taken to prevent the ammonia gas from escaping into the atmosphere. The excess HCl was titrated with standard 0.1 M NaOH using methyl red indicator.

Preparation of compounds.-- $(\text{NH}_4)_2 \text{MoOBr}_5$ was prepared by dissolving 15 g. of ammonium paramolybdate, $(\text{NH}_4)_6 \text{Mo}_7 \text{O}_{24} \cdot 4\text{H}_2\text{O}$, in 100 ml. of fuming HBr. The solution was evaporated on a hot plate until dark crystals began to appear. The solution was then allowed to cool and the dark crystals were filtered through a sintered glass filter. The solid was then redissolved in a minimum of hot fuming HBr and allowed to recrystallize, yielding brown crystals which darkened rapidly upon exposure to air. They were dried over H_2SO_4 and KOH in a vacuum desiccator.

The appearance of this solid was in agreement with the description given by Weinland and Knoll (5) for the compound of formula



	Analysis		
	<u>NH₃</u>	<u>Mo</u>	<u>Br</u>
Theoretical	6.5%	17.5	72.9
Found	6.5%	17.0	72.7

$\text{C}_9\text{H}_8\text{N MoOBr}_4$ was prepared using a variation of the method described by Weinland and Knoll (5). Twenty g. of MoO_3 was added to 100 ml. of fuming HBr. Heating was required to effect solution and to accelerate

the reduction of the Mo(VI) to Mo(V) by the hydrobromic acid. Dropwise addition of a solution of 10 g. of quinoline in fuming HBr to the hot solution, with constant stirring, gave an immediate formation of dark red, needle-like crystals. These crystals were recrystallized from fuming HBr, yielding a set of bright red needles which turned orange upon drying over H_2SO_4 and KOH in a vacuum desiccator. These crystals correspond to those described by earlier investigators (6, 8).

Analysis

	<u>Mo</u>	<u>Br</u>
Theoretical	17.1	56.9
Found	17.4	57.3

$MoO(OH)Br_2 \cdot 4H_2O$ was prepared by heating 20 grams of MoO_3 in contact with fuming HBr until solution was effected. After the solution was allowed to evaporate at room temperature for about a month, a dark solid precipitate was formed. The prism-like solid was recrystallized from HBr, requiring several days for reprecipitation to occur, with no change in the appearance of the solid.

Attempts to dry the solid over H_2SO_4 and KOH led to the formation of a "molybdenum blue." After air drying for two days on a fritted glass plate, the solid was found to be dark only on the exposed surface, with the freshly crushed solid having a brown appearance which quickly darkened upon exposure to air. Analysis was made on large crystals so that relatively little of the dark surface was used.

This compound is similar to that reported by Weinland and Knoll (5) as $MoO(OH)Br_2 \cdot 1-1/2 H_2O$, which was reported to be hygroscopic. The

air drying procedure possibly explains the higher number of water molecules and the nonhygroscopic nature of the presently reported compound.

	Analysis	
	<u>Mo</u>	<u>Br</u>
Theoretical	26.6	44.4
Found	26.7	45.6

Absorption spectra measurements.--The absorption spectra reported in the present work were taken on the Beckmann Model D.U. Spectrophotometer and on the Beckmann Model D.K.-1 Recording Spectrophotometer. The Model D.U. was used at specific wavelengths for gathering the more accurate data that is required for the calculations reported, while the curves covering a wide range of the spectrum were obtained using the Model D.K.-1.

Three sets of Beckmann silica absorption cells were used, allowing a choice of 10 cm., 1 cm., and 0.1 cm. path length. The 0.1 cm. path length was obtained by inserting matched 0.9 cm. silica plugs into the 1 cm. cells. The values of absorbance reported are for a 1 cm. light path unless otherwise specified.

The KBr pellet technique was used for verification of the spectrum of a solid compound whose spectrum could not be definitely ascertained in organic solvents. A small amount of the solid of interest was ground with a large amount of dry, solid KBr in an agate mortar; then the mixture was pressed into a disc 0.5 cm. in diameter and about 0.02 cm. in thickness. A number of pellets were pressed before attaining ones whose visual appearance showed a uniform distribution of the compound in a clear pellet. The blank was a KBr pellet pressed in the manner described above,

without the added compound, and selected to have roughly the same clarity as the sample pellet. Extra care was necessary to prevent the absorption of moisture by the pellet since moisture invariably caused the pellet to become opaque.

Notation.--In discussions of spectrophotometry the following notations will be used.

The optical density or absorbancy, A , is defined by the equation

$$A = \log I_0/I ,$$

in which I_0 is the intensity of light of wavelength λ , transmitted by a reference solution, and I is the intensity of the light transmitted through the solution of interest.

The Beer-Lambert law expressing the relationship between the absorbance and the molarity, C , of the absorbing species is

$$A = \epsilon C d ,$$

in which d is the path length of the cell and ϵ is the molar absorbancy index of the absorbing species.

Because of the marked tendency for molybdenum to appear in condensed forms, and because the extent of condensation is often unknown, the true molarity is often unknown and it is impossible to apply this equation. For this reason it is convenient to use a modified equation

$$A = \alpha f d$$

where f is the formal concentration of molybdenum; i.e., the number of moles of molybdenum atoms per liter of solution, and the proportionality

constant α may be called the formal absorbancy index.

Since it has become standard practice to use the symbol "[X]" to stand for the "molar concentration of X," it would be convenient to have a similar symbol for the "formal concentration of X." For this purpose {X} will be used.

Spectra of compounds.--The orange needles of $C_9H_8N MoOBr_4$ were found to dissolve in N,N-dimethylformamide, ethyl acetate, acetonitrile, and chloroform, forming orange solutions when concentrated and yellow solutions when dilute. The absorption spectra (Figures 1 and 2) show a broad weak band at about 700 μ , a shoulder at 480 μ , and peaks at 414, 380, and 305 μ . The 414 μ peak is about 30 per cent greater than that at 380 μ . The 305 μ peak was shown to be due to the quinolinium ion, $C_9H_8N^+$, by observing the spectrum of quinoline in hydrobromic acid solution. In the ethyl acetate solutions, some decomposition of the $MoOBr_4^-$ ion was indicated by the spectra since the 380 μ peak was displaced to about 376 μ and was found to be greater than the 414 μ peak.

The KBr pellet technique was attempted with this compound, but no satisfactory pellets were obtained.

The brown solid $MoO(OH)Br_2 \cdot 4H_2O$ dissolved in chloroform and ethyl acetate to form yellow solutions, showing a broad band at about 670 μ and a peak at 370 μ . A second broad band was found at 460 μ in chloroform and at about 445 μ in ethyl acetate, with no absorption peak in the 414 μ region for either solution (Figures 1, 2).

The addition of small amounts of tetraethylammonium bromide to the ethyl acetate solution of $MoO(OH)Br_2 \cdot 4H_2O$ caused a considerable shift in the spectrum. The 370 μ peak shifted to 380 μ with little

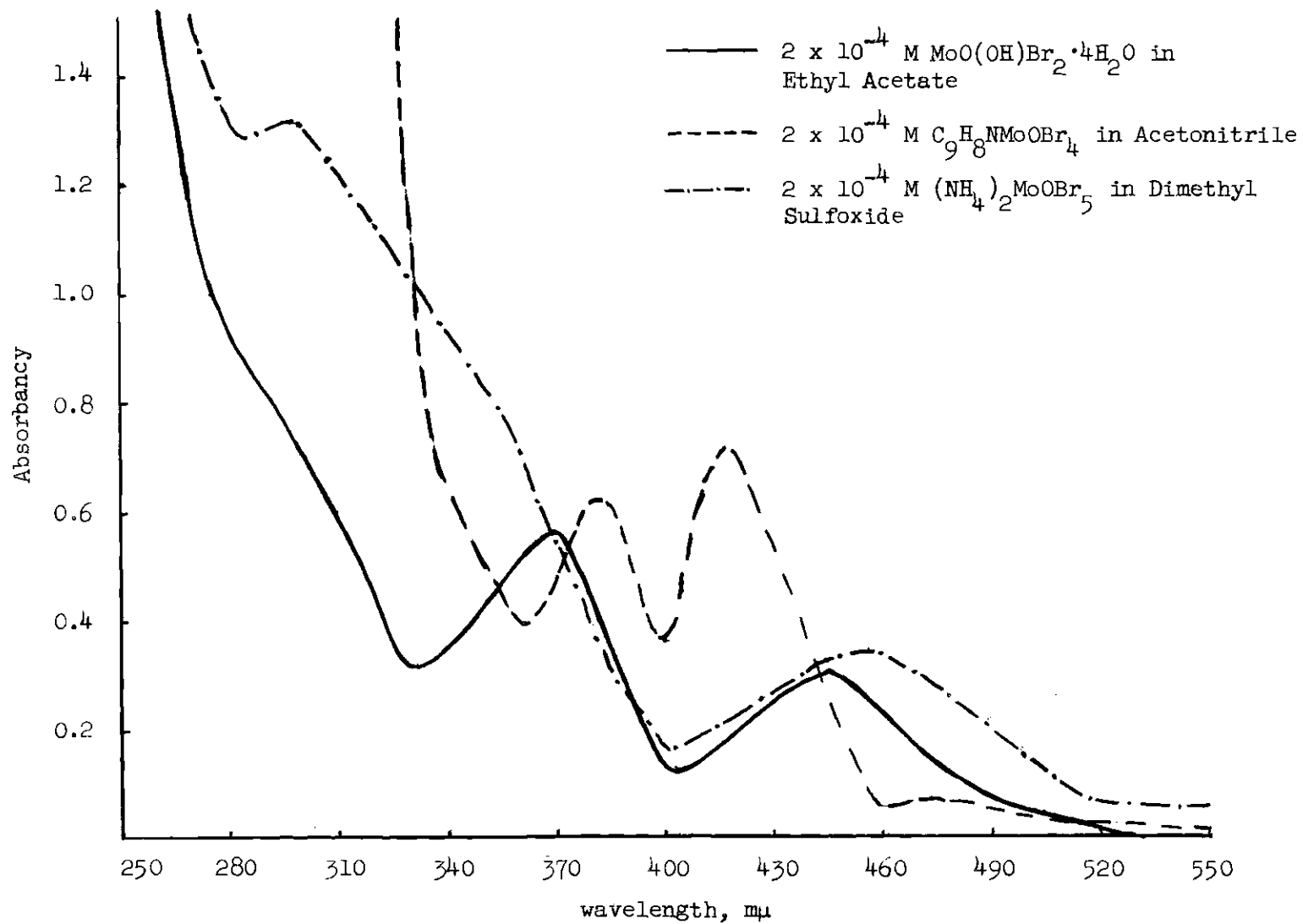


Figure 1. Ultraviolet and Visible Spectra of Molybdenum(V) - Bromide Compounds in Organic Solvents.

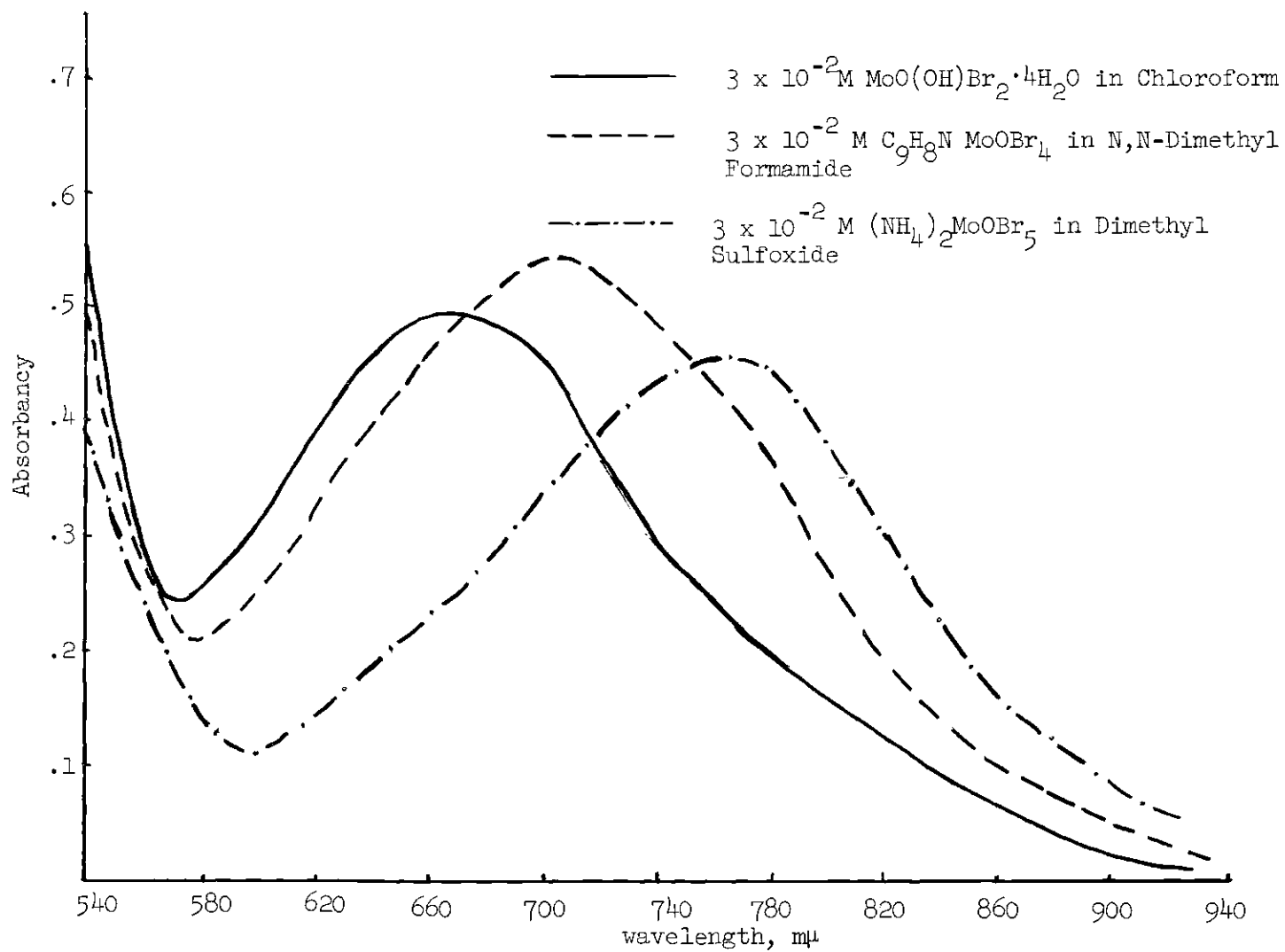
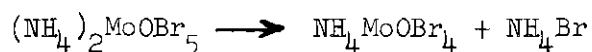


Figure 2. Visible and Near Infrared Spectra of Molybdenum(V) - Bromide Compounds in Organic Solvents.

change in peak height, a peak became prominent at 414 μ , and the 445 μ band decreased to a shoulder, causing this spectrum to become identical with the spectrum of the MoOBr_4^- ion in ethyl acetate. There is no doubt that the MoO(OH)Br_2 is converted to MoOBr_4^- by the addition of excess bromide ion to the solution.

Solid $(\text{NH}_4)_2\text{MoOBr}_5$ was added to several organic solvents, i.e., diethyl ether, ethyl acetate, N,N-dimethylformamide, and acetonitrile, in which the dark brown solid changed to a waxy yellow appearance. The solvents took on a yellow color, and the absorption spectra (Figure 3) showed peaks at 376 and 414 μ , shoulders at about 300 and 450 μ , and a broad band at about 700 μ (not shown in Figure 3). It should be noted that the 376 μ peak is slightly greater than that at 414 μ .

A careful measurement of the weight of solid remaining after addition of $(\text{NH}_4)_2\text{MoOBr}_5$ to ethyl acetate showed the decomposition



to be essentially complete. NH_4Br was the insoluble material, gaining its yellow appearance from small amounts of the undissolved molybdenum compound. The spectra observed in these solvents correspond to a mixture of MoOBr_4^- and MoO(OH)Br_2 , indicating further decomposition of the $\text{NH}_4\text{MoOBr}_4$, possibly due to solvolysis, or to reaction with slight amounts of dissolved water.

Further evidence for the identification of the species in the ethyl acetate solution was obtained by the addition of small quantities of tetraethylammonium bromide. The 376 μ peak shifted to 380 μ with no change in peak height, the 450 μ shoulder shifted to longer wave-

lengths, and the 414 μ peak increased, indicating that the $\text{MoO}(\text{OH})\text{Br}_2$ -like species is changed to MoOBr_4^- by the excess bromide (Figure 3). The previously noted decomposition of the quinolinium salt of MoOBr_4^- was also easily reversed by the addition of a small amount of tetraethylammonium bromide.

When dimethyl sulfoxide was employed as the solvent, $(\text{NH}_4)_2\text{MoOBr}_5$ dissolved with no apparent decomposition, forming a yellow solution. The spectrum of this solution showed a broad weak band at 770 μ , broad absorption at 460 μ and a large peak at about 300 μ , with no absorption in the 350-420 μ region. These bands decreased with time, disappearing within 24 hours, probably due to solvolysis (Figures 1 and 2).

In order to verify that this is the spectrum of undecomposed $(\text{NH}_4)_2\text{MoOBr}_5$, a small amount of the brown solid was finely ground with dry KBr and pressed into a pellet. The pellet showed absorption bands at 470 and 300 μ , agreeing quite well with the spectrum of the MoOBr_5^- ion in dimethylsulfoxide.

Molybdenum(V)-Molybdenum(VI) equilibrium in hydrobromic acid.--Solutions

2×10^{-4} f in molybdenum(VI) were prepared in HBr of various concentrations from a stock solution of ammonium paramolybdate in water. The spectra were found to change with time, becoming stable in about five days. The spectra after this time are shown in Figure 4. The spectra show a large amount of absorption below 250 μ , which is the limit of study because of absorption by hydrobromic acid.

The 8.6 M HBr solution shows a large peak at about 266 μ , a shoulder at 290 μ , maxima at 376 and 414 μ , and a plateau at about 470 μ .

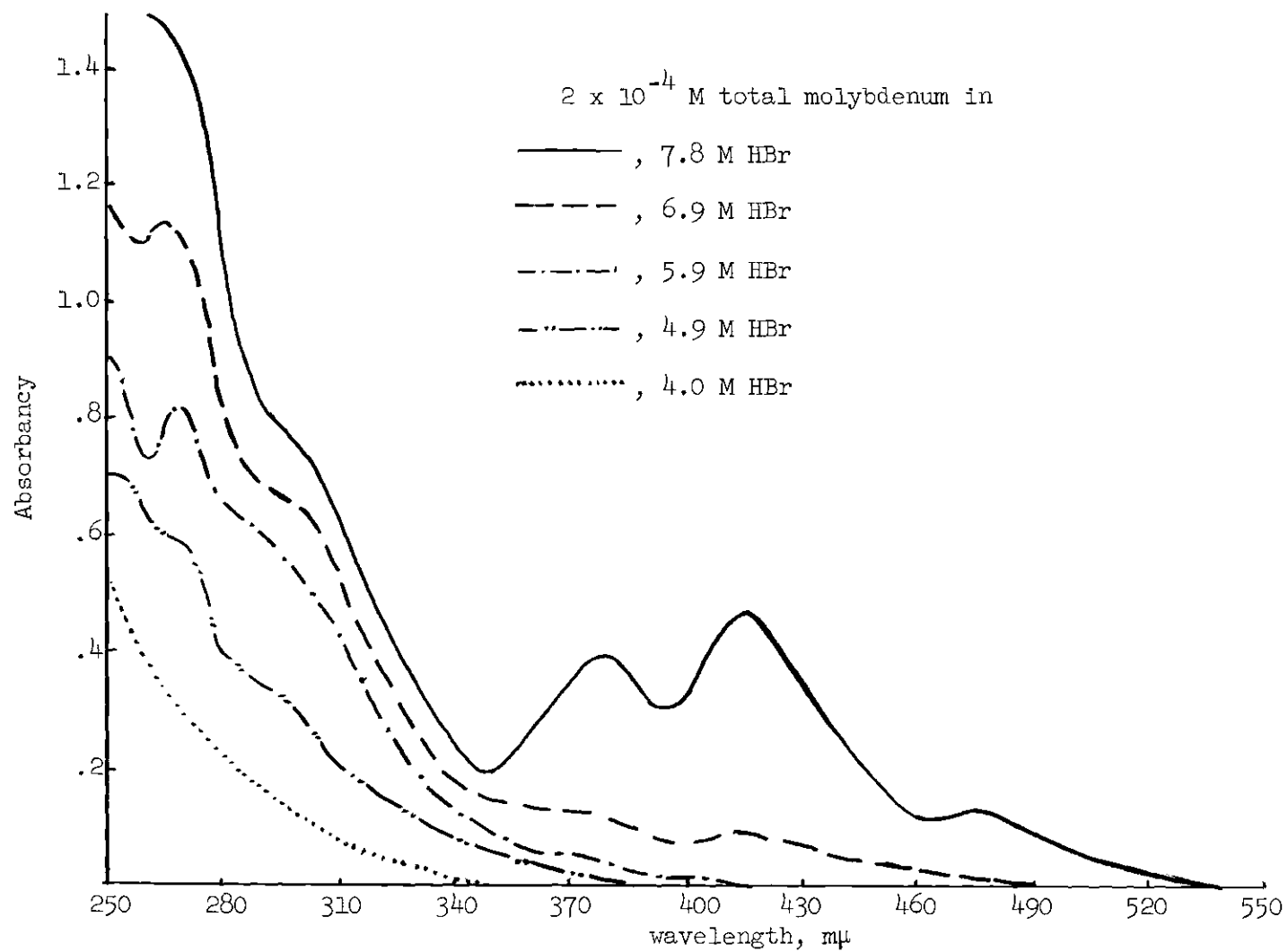
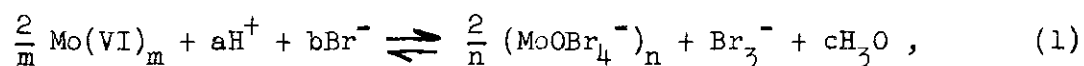


Figure 4. Spectra of Molybdenum(VI) in Hydrobromic Acid Solution.

The 414 μ peak was observed to be about 30 per cent greater than that at 376 μ . At higher concentrations of molybdenum (up to $5 \times 10^{-3} M$) and using 10 cm. cells, a broad band was observed at 700 μ which was much weaker than the other bands that have been observed. The absorption at 266 μ corresponds to the wavelength at which the tribromide ion, Br_3^- , absorbs (36) and, by comparison with spectra of known compounds, the 376, 414, and 470 μ absorptions indicate the presence of a Mo(V) species, specifically the $MoOBr_4^-$ ion. This evidence indicates that bromide ion has reduced Mo(VI) to Mo(V). The intensity of the absorption is such that not all the Mo can be present as $MoOBr_4^-$, and since it will be shown in a later section that there is no evidence of Mo(V) species other than $MoOBr_4^-$ in 8.6 M HBr, the conclusion is drawn that an equilibrium between Mo(V) and Mo(VI) exists. However, none of the bands in the observable spectrum can be attributed to the Mo(VI) species.

It appeared that a study of this equilibrium would yield information on the nature of the species involved. From the stoichiometry of the oxidation-reduction part of the reaction, one Br_3^- must be formed when two Mo(VI) atoms are reduced. In its most general form, the equilibrium can be written as



with equilibrium constant

$$K = \frac{\left\{ (MoOBr_4^-)_n \right\}^{\frac{2}{n}} [Br_3^-]}{\left\{ (Mo(VI))_m \right\}^{\frac{2}{m}} [H^+]^a [Br^-]^b} \quad (2)$$

The values of m and n were investigated in experiments in which the hydrobromic acid concentration was maintained constant at 8.6 M, and

the molybdenum concentration was varied.

Since the hydrogen ion and bromide ion concentrations are constant, equation 2 may be expressed as

$$K(n)^{\frac{2}{n}} \left(\frac{1}{m}\right)^{\frac{2}{m}} [H^+]^a [Br^-]^b = K_1 = \frac{\left\{(\text{MoOBr}_4^-)_n\right\}^{\frac{2}{n}} [Br_3^-]}{\left\{\text{Mo(VI)}_m\right\}^{\frac{2}{m}}} \quad (3)$$

From the stoichiometry of equation (1),

$$[Br_3^-] = \frac{n}{2} \left[(\text{MoOBr}_4^-)_n \right] = \frac{1}{2} \left\{ (\text{MoOBr}_4^-)_n \right\} \quad (4)$$

when the solutions are prepared from molybdenum(VI) and hydrobromic acid only. Substitution of equation 4 into equation 3 yields

$$K_1 = \frac{\frac{1}{2} \left\{ (\text{MoOBr}_4^-)_n \right\}^{\left(\frac{2}{n} + 1\right)}}{\left\{ \text{Mo(VI)}_m \right\}^{\frac{2}{m}}} \quad (5)$$

Using the absorbance at 414 $m\mu$ ($\alpha = 3860$) and at 700 $m\mu$ ($\alpha = 17.0$) as a measure of the $(\text{MoOBr}_4^-)_n$ concentration, the following relationships arise:

$$\left\{ (\text{MoOBr}_4^-)_n \right\} = \frac{A}{\alpha d} \quad , \quad (6)$$

and

$$\left\{ \text{Mo(VI)}_m \right\} = f - \frac{A}{\alpha d} \quad , \quad (7)$$

where f is the total molybdenum concentration. Substitution of these relationships into equation 5 yields

$$K_1 = \frac{\frac{1}{2} \left(\frac{A}{\alpha d} \right)^{\frac{2}{n} + 1}}{\left(f - \frac{A}{\alpha d} \right)^{2/m}} \quad (8)$$

The values of K_1 obtained from equation 8 are listed in Table 1. It can be seen that the data are satisfied by $n=m=2$, but not by $n=m=1$. It can also be shown that no other values of m and n are suitable.

To verify this result, it was deemed advisable to observe the equilibrium with an added amount of tribromide ion, Br_3^- . A stock solution was prepared by adding a small amount of liquid bromine to 8.6 M HBr. The Br_3^- content was determined by an iodometric titration. An aliquot was added to the flask containing molybdenum in hydrobromic acid to give a suitable Br_3^- concentration, X . After several days were allowed for equilibration, the spectra of these solutions were measured.

K_1 has been expressed as

$$K_1 = \frac{\left\{ (\text{MoOBr}_4)_n \right\}^{\frac{2}{n}} [\text{Br}_3^-]}{\left\{ \text{Mo(VI)}_m \right\}^{\frac{2}{m}}} \quad (3)$$

It has been shown that $n=m=2$, so equations 6 and 7 may be represented as

$$\left[(\text{MoOBr}_4^-)_2 \right] = \frac{A}{\epsilon d}$$

and

Table 1. Equilibrium Constants for Mo(V)-Mo(VI)

Equilibrium in 8.6M HBr

$\{Mo\}_{total} \times 10^3$	A_{414} ($\alpha=3860$)	A_{700} ($\alpha=17.0$) (b)	$K_1 \times 10^3$ for $m=n=2$		$K \times 10^3$ for $m=n=1$	
			λ_{414}	λ_{700}	λ_{414}	λ_{700}
2.50	0.628 (a)	0.278	1.52	1.99	2.85	2.85
2.50	0.630 (a)	0.282	1.53	2.09	2.86	2.90
2.50	0.654 (a)	-	1.77	-	3.68	-
2.50	0.659 (a)	-	1.84	-	3.83	-
2.00	0.590 (a)	-	2.47	-	8.11	-
2.00	0.595 (a)	-	2.59	-	8.63	-
2.00	0.592 (a)	0.238	2.51	1.63	8.11	3.81
2.00	0.610 (a)	0.240	2.97	1.69	11.2	4.05
1.00	0.304 (a)	-	1.47	-	5.45	-
1.00	0.294 (a)	-	1.22	-	3.91	-
1.00	0.295 (a)	-	1.25	-	4.06	-
1.00	0.328 (a)	0.135	2.41	1.53	13.6	5.96
1.00	0.345 (a)	0.139	3.77	1.84	32.	8.25
0.200	0.730	-	1.66	-	28	-
0.200	0.750	-	3.24	-	101	-
0.100	0.376	-	1.82	-	68	-
0.100	0.374	-	1.30	-	51	-

(a) 0.1 cm path length

(b) All 700 μ readings were made with a 10 cm. path length.

$$[\text{Mo(VI)}_2] = C - \frac{A}{\epsilon d} ,$$

since the degree of condensation has been established. The equilibrium value for the Br_3^- ion becomes

$$[\text{Br}_3^-] = X + [(\text{MoOBr}_4^-)_2] = X + \frac{A}{\epsilon d} .$$

Substitution into equation 3 yields

$$K_1 = \frac{\left(\frac{A}{\epsilon d}\right) \left(X + \frac{A}{\epsilon d}\right)}{\left(C - \frac{A}{\epsilon d}\right)} \quad (9)$$

The values of K_1 calculated using equation 9 are found in Table 2.

The average value for the equilibrium constant K_1 taken over all the data listed in Tables 1 and 2 is

$$K_1 = 2.27 (\pm .56) \times 10^{-3} .$$

In order to obtain some insight into the composition of the Mo(VI) species present in these solutions, the hydrogen ion concentration was varied while maintaining the bromide ion concentration and ionic strength* constant. Experimentally this was done by using mixtures of LiBr and HBr,

*The ionic strength, μ , is defined as

$$\mu = \sum_i c_i Z_i^2 ,$$

in which c_i is the concentration of the i^{th} ion and Z_i is the charge on that ion.

Table 2. Equilibrium Constants for Mo(V)-Mo(VI)

Equilibrium in 8.6M HBr with Br_3^- Added.

Initial $[\text{Br}_3^-] = 1.83 \times 10^{-3}\text{M}$.

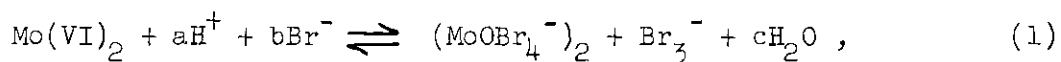
$\{\text{Mo}\}_{\text{total}} \times 10^3$	A_{414} ($\epsilon = 7720$)	A_{700} ($\epsilon = 34.0$) (b)	$K_1 \times 10^3$ for $m=n=2$	
			λ_{414}	λ_{700}
5.00	-	0.438	-	3.26
5.00	-	0.434	-	3.21
1.09	0.240 (a)	-	2.84	-
1.09	0.250 (a)	-	3.12	-
0.872	0.195 (a)	-	2.97	-
0.545	0.120 (a)	-	2.84	-
0.545	0.125 (a)	-	2.92	-
0.436	0.930	-	2.41	-
0.436	0.935	-	2.93	-
0.200	0.412	-	2.15	-
0.200	0.450	-	2.62	-
0.100	0.212	-	2.27	-
0.100	0.213	-	2.29	-

(a) 0.1 cm. path length

(b) All 700 m μ readings were made with a 10 cm. path length.

with the HBr concentration kept high in order to maintain all the Mo(V) in the form of the $(\text{MoOBr}_4^-)_2$ ion. The 414 μ peak was used as a direct measure of the $(\text{MoOBr}_4^-)_2$ concentration.

Using equation 1,



and keeping the bromide ion concentration constant, equation 2 becomes

$$K [\text{Br}^-]^b = K_2 = \frac{[(\text{MoOBr}_4^-)_2] [\text{Br}_3^-]}{[\text{Mo(VI)}_2] [\text{H}^+]^a}.$$

It may also be noted that equation 4 with $n=2$ applies to these solutions, giving

$$K_2 = \frac{[(\text{MoOBr}_4^-)_2]^2}{[\text{Mo(VI)}_2] [\text{H}^+]^a}. \quad (10)$$

Taking logarithms,

$$\log K_2 = 2 \log [(\text{MoOBr}_4^-)_2] - \log [\text{Mo(VI)}_2] - a \log [\text{H}^+],$$

equating for two different H^+ concentrations, $[\text{H}^+]_1$ and $[\text{H}^+]_2$, and solving for a yields

$$a = \frac{2 \log \frac{[(\text{MoOBr}_4^-)_2]_2}{[(\text{MoOBr}_4^-)_2]_1} - \log \frac{[\text{Mo(VI)}_2]_2}{[\text{Mo(VI)}_2]_1}}{\log \frac{[\text{H}^+]_2}{[\text{H}^+]_1}} \quad (11)$$

Since the degree of condensation has been established, equations 6 and 7 become

$$\left[(\text{MoOBr}_4^-)_2 \right] = \frac{A}{\epsilon d} ,$$

and

$$\left[(\text{Mo(VI)})_2 \right] = C - \frac{A}{\epsilon d} ,$$

Substituting into equation 11 gives

$$a = \frac{2 \log \frac{A_2}{A_1} - \log \frac{C - \frac{A_2}{\epsilon d}}{C - \frac{A_1}{\epsilon d}}}{\log \frac{[\text{H}^+]_2}{[\text{H}^+]_1}} \quad (12)$$

Values for a are given in Table 3, showing $a = 3$.

Similarly, holding the hydrogen ion and ionic strength constant while allowing the bromide ion concentration to vary, equation 13 may be derived.

$$b = \frac{2 \log \frac{A_2}{A_1} - \log \frac{C - \frac{A_2}{\epsilon d}}{C - \frac{A_1}{\epsilon d}}}{\log \frac{[\text{Br}^-]_2}{[\text{Br}^-]_1}} \quad (13)$$

where the subscripts refer to values of the absorbance obtained for Br^- concentrations of $[\text{Br}^-]_1$ and $[\text{Br}^-]_2$.

Table 3. The $[H^+]$ Dependence, a , of the Mo(V)-Mo(VI)Equilibrium $[Br^-] = 8.6M$, $\lambda = 414 \text{ m}\mu$,

$$\{Mo\}_{total} = 1.96 \times 10^{-4}M$$

$[H^+]_1$	$[H^+]_2$	A_1	A_2	a
8.24	7.56	0.674	0.658	2.6
8.24	7.21	0.674	0.648	2.7
7.90	7.21	0.672	0.648	3.4
7.56	6.86	0.658	0.632	3.2

$$a_{ave} = 3.1 \pm .3$$

Table 4. The $[Br^-]$ Dependence, b , of the Mo(V)-Mo(VI)Equilibrium $[H^+] = 8.3M$, $\lambda = 414 \text{ m}\mu$,

$$\{Mo\}_{total} = 2.00 \times 10^{-4}M$$

$[Br^-]_1$	$[Br^-]_2$	A_1	A_2	b
7.28	6.59	0.630	0.690	-7.0
7.28	5.89	0.630	0.734	-8.6
6.93	5.89	0.652	0.734	-8.4
6.93	4.85	0.652	0.764	-8.5

$$b_{ave} = -8.1 \pm 0.6$$

Such experimental studies of the bromide dependence, b, require the use of HBr in combination with another strong acid. The requirements on the acid are rather stringent; it must be a strong acid, its anion must not complex with Mo(V) in competition with Br^- , and it should not affect the system via oxidation or reduction. Two acids were considered, trifluoroacetic acid and perchloric acid. The former was found unsatisfactory because it caused the formation of a colloidal suspension when added to a molybdenum solution.

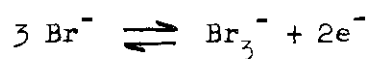
The disadvantage of perchloric acid is its possible action as an oxidizing agent. In solutions of HBr and HClO_4 containing no other substances there was no indication of Br_3^- formation within three days. However when HClO_4 is added to a solution of Mo(V) in HBr there is evidence in the spectrum that oxidation to Br_3^- has occurred within a few hours. There is a decrease in the Mo(V) concentration at the same time. The net effect of added HClO_4 is thus equivalent to the addition of a small amount of Br_3^- , with this amount increasing with time of standing.

In equilibrium experiments starting with Mo(VI), equation 13 will then only be valid to the extent that equation 4 is correct. In spite of this limitation there appeared to be no better way to proceed, and the experiments were performed. The results are given in Table 4. It is evident that the bromide dependence obtained in this way is not a realistic figure, because the Mo(VI) species would thereby have a Mo:Br ratio of about 1:9.

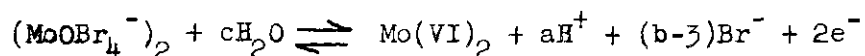
The observed trend is seen to be that the solutions with more HClO_4 and less HBr have the greater amount of Mo(V). This is the reverse of what would be expected if the oxidation effect were the dominating factor.

The conclusion to be drawn is that maintenance of constant ionic strength in these HBr - HClO₄ mixtures does not lead to a constancy of the activity of water or of the activity coefficients of the ions involved in the equilibrium.

The molybdenum(V) - molybdenum(VI) oxidation potential. -- The equilibrium redox equation may be expressed in terms of the half-reactions



and



An estimate of the potential for the latter reaction can be made from the equilibrium data.

The net oxidation potential, E_{net}° , for the equilibrium reaction may be stated as

$$E_{\text{net}}^{\circ} = \frac{RT}{nF} \ln K$$

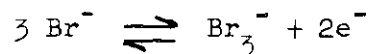
which, at 25°C and using log₁₀, becomes

$$E_{\text{net}}^{\circ} = \frac{0.0591}{2} \log K = \frac{0.0591}{2} \log \frac{K_1}{[\text{H}^+]^a [\text{Br}^-]^b} \quad (14)$$

Since $K_1 = 2.27 \times 10^{-3}$ when $[\text{H}^+] = [\text{Br}^-] = 8.6$, and taking $a = 3$ and $b = -8$,

$$E_{\text{net}}^{\circ} = +0.06$$

Latimer (37) gives a value of $E_{\text{Br}}^{\circ} = -1.05$ for the half-reaction



and, since

$$E_{\text{net}}^{\circ} = E_{\text{Br}}^{\circ} - E_{\text{Mo}}^{\circ}$$

the value, E_{Mo}° , for the molybdenum half-reaction is found to be -1.11.

This value for E_{Mo}° is an estimation due to the use of concentrations of the species rather than their activities, and to the uncertainties in the values of a and b. The estimate is not as crude as it might appear on first sight, though, because E_{net}° will never be large (e.g., $E_{\text{net}}^{\circ} = -0.24$ for a = 3 and b = +3), and E_{Mo}° certainly must be within a few tenths of a volt of E_{Br}° .

Molybdenum(V) in hydrobromic acid.--A series of investigations was made concerning the Mo(V) species which exist in aqueous HBr. A stock solution of about 1×10^{-2} M Mo(V) in 8.6M HBr was prepared by adding 1 ml. of saturated hydrazine in concentrated HBr to a 50 ml. flask containing ammonium paramolybdate, $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$, in 8.6M HBr. The solution was heated until nitrogen was no longer expelled from the solution, indicating that the reduction was completed. From the stock were prepared five solutions which were 8.6M, 6.5M, 5.0M, 3.5M, and 1.1M in HBr respectively, and each of which was 4×10^{-4} M in Mo(V). The spectra of these solutions are shown in Figures 5 and 6. These spectra can best be interpreted in terms of four Mo(V) species. The 8.6M HBr solutions show the familiar spectrum of the $(\text{MoOBr}_4^{-})_2$ ion, to be designated as I, which exists exclusively at this acid concentration. Excess bromide, in the

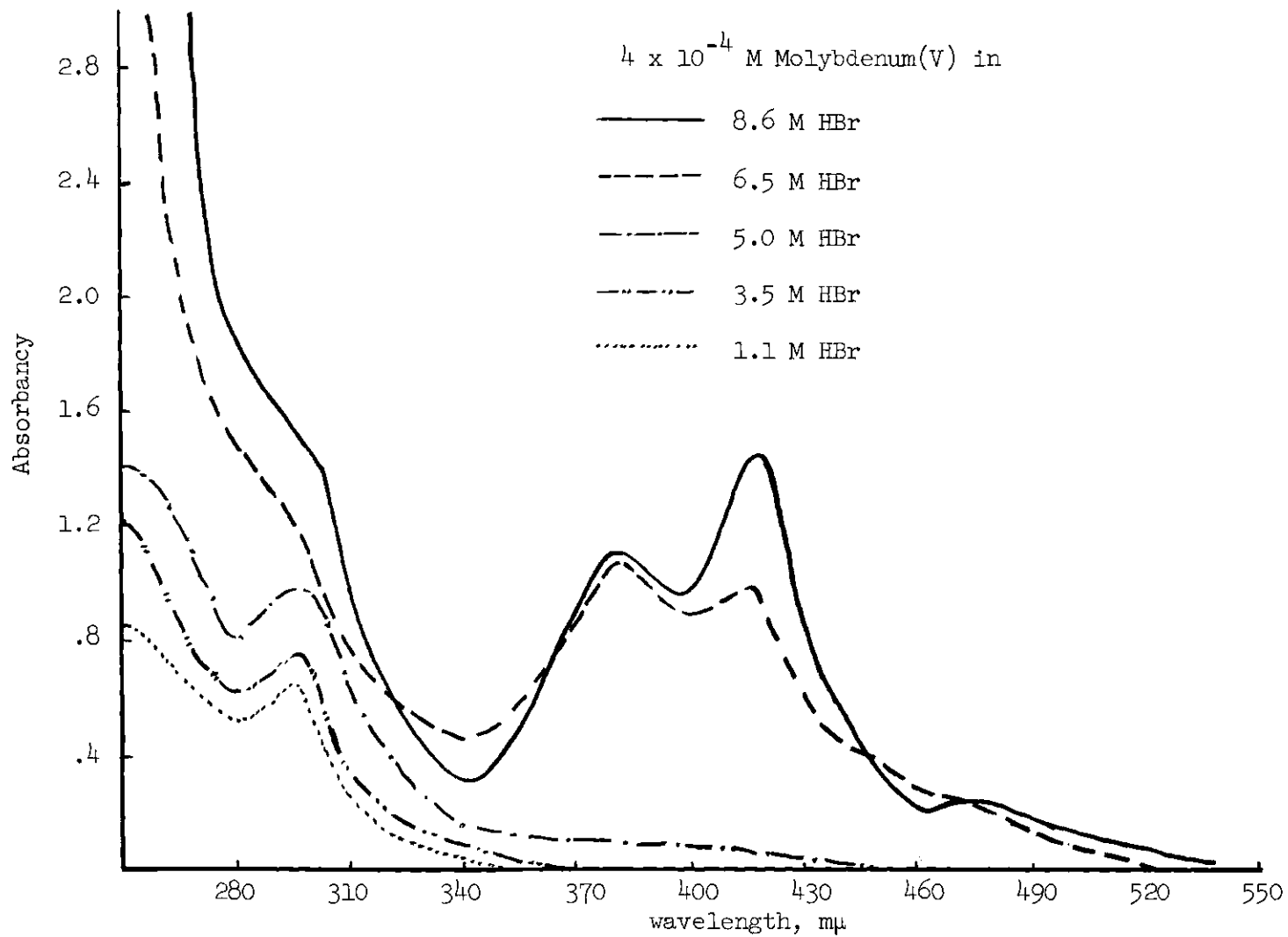


Figure 5. Spectra of Molybdenum(V) in Hydrobromic Acid Solutions.

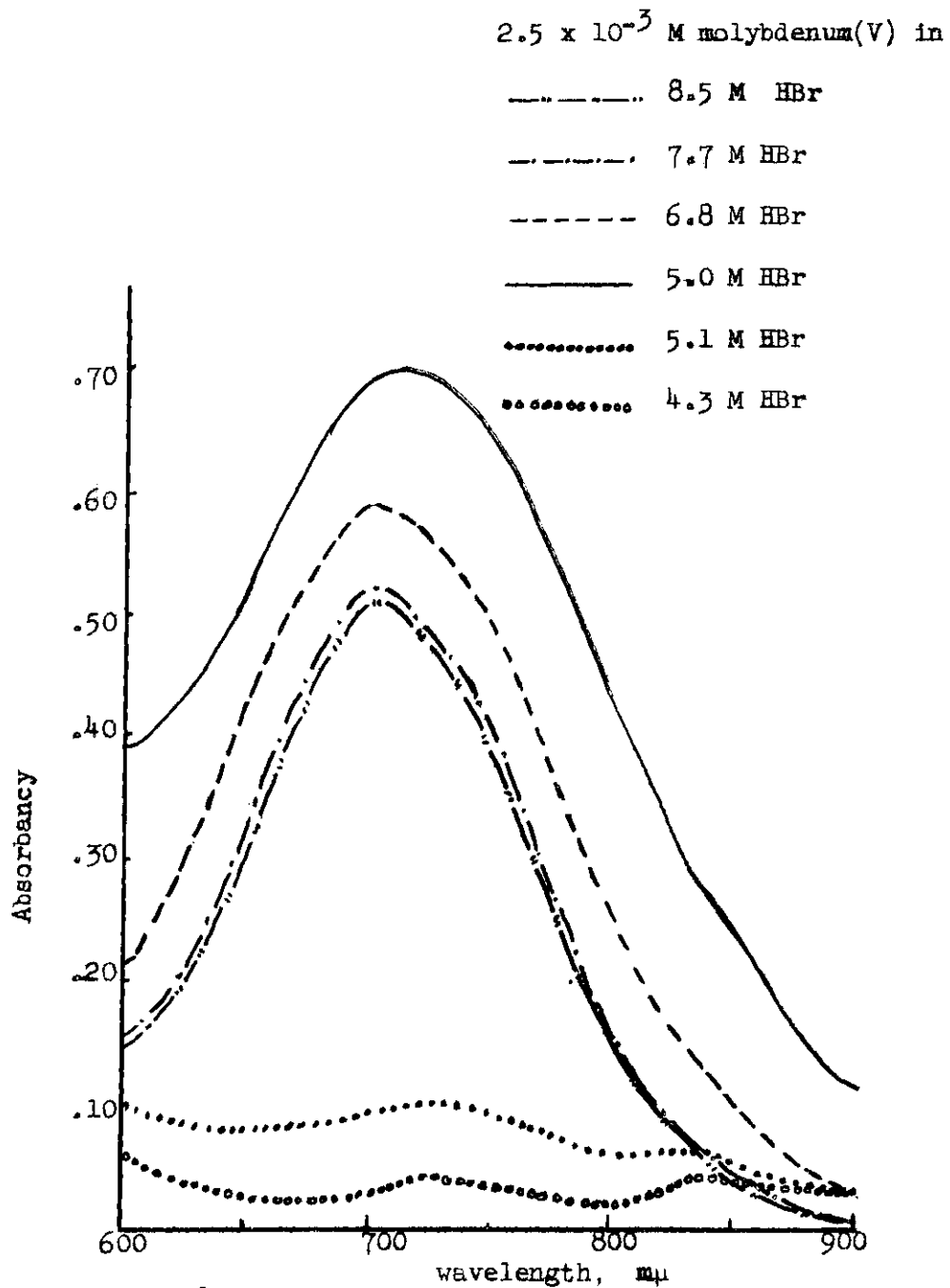


Figure 6. Visible and Near Infrared Absorption Spectra of Molybdenum(V) in Hydrobromic Acid Solutions.

form of LiBr, was added to this solution in an attempt to change the $(\text{MoOBr}_4^-)_2$ ion to MoOBr_5^- . However, in solutions having 8.6M HBr and 2.2M LiBr, there was no change from the solution having no LiBr, establishing the fact that the MoOBr_5^- ion does not exist in more than negligible amount in hydrobromic acid solutions.

The 6.5M solution shows a deviation from the spectrum of I, with a shift in the 475 μ shoulder to shorter wavelengths and a decrease in the 414 μ peak, without a subsequent decrease in the 376 μ peak. This spectrum shows that I is in equilibrium with a species, II, which shows the spectrum of the compound $\text{MoO}(\text{OH})\text{Br}_2$.

In the solutions of 1-5M HBr there was only a trace of the complexes absorbing in the 350-500 μ region, showing instead a large maximum at about 295 μ . This maximum was found to decrease as the acid concentration decreased. It may be concluded that these solutions contain a species, III, which is in equilibrium simultaneously with a small amount of II and a fourth substance, IV, in the 3-5M HBr solutions, and that III and IV coexist in the low acid range. Substance IV does not show an absorption maximum at wavelengths greater than 250 μ but probably absorbs at about 240 μ as reported by Simon and Souchay (27) in HClO_4 or dilute HCl solutions.

Other conclusions may be drawn regarding the species II, III, and IV. The 6.5, 5.0, and 1.1M HBr solutions were found to follow the Beer-Lambert law (Tables 5 and 6) when the molybdenum(V) concentration was varied, so I, II, III, and IV, must all have the same degree of condensation. Since I, $(\text{MoOBr}_4^-)_2$, has been shown earlier to be dimeric, then the other species, II, III, and IV, must also be dimeric.

Table 5. Beer-Lambert Law Data for the
Mo(V) System in 6.2M HBr

$\{\text{Mo(V)}\}_{\text{total}}$	A_{414}	A_{376}
5×10^{-5}	0.150	0.142
1×10^{-4}	0.318	0.294
2×10^{-4}	0.634	0.594
4×10^{-4}	1.22	1.15

Table 6. Beer-Lambert Law Data for the
Mo(V) System in 5.2M HBr and 1.0M HBr

$\{\text{Mo(V)}\}_{\text{total}}$	A_{295}	
	<u>5.2M HBr</u>	<u>1.0M HBr</u>
5×10^{-5}	0.124	0.083
1×10^{-4}	0.242	0.162
2×10^{-4}	0.482	0.326
4×10^{-4}	0.955	0.646

Substance II shows considerable extraction into ethyl acetate and isopropyl ether, with very little extraction into carbon tetrachloride or chloroform. It is reasonable that the correct formulation for this species is $(\text{MoO}_2\text{Br}_2^-)_2$.

Neumann (15) has shown that complexes having few halide atoms usually have absorption maxima at shorter wavelengths than those with a greater number of halides. This leads to the conclusion that the formulation of III would be a dimeric species having fewer than two bromides per molybdenum, probably $\text{Mo}_2\text{O}_3\text{Br}_2^{++}$, in analogy to the species suggested by Souchay and Simon (27) for the Mo(V)-HCl system.

Extraction studies made from 5M and 1.1M HBr solutions indicated no extraction of the species absorbing in the 290 μ region into any organic solvent, verifying that III is cationic.

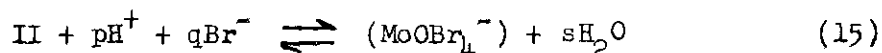
Substance IV would likely be a bromide-free cation, as suggested by other investigators (13, 14, 27, 28) for dilute acid solutions.

A study of the spectra in the 700 μ region also lends evidence to the existence of three bromide containing species and a fourth species which is presumably bromide-free (Figure 6). In 8.6M HBr the peak is at 700 μ , but as the acid concentration was dropped to 6.0M, the peak rose, broadened, and shifted to about 720 μ , showing a small shoulder at about 840 μ . A further decrease in acid concentration led to a very sharp decrease in the 720 μ peak, which shifted to 740 μ , and showed the presence of a distinct but very weak absorption band at 840 μ (extinction coefficient of about 1). Both the 840 μ peak and the remnant of the 740 μ peak fell as the HBr concentration was decreased below 5M, with the 740 μ band showing the greater drop.

These variations in the 700-900 μ region of the spectrum are quite satisfactorily explained by the species previously hypothesized. Species I, $(\text{MoOBr}_4^-)_2$, absorbs at 700 μ and is the only species present in 7.8-8.6M HBr; however, in 6-7.8M HBr this ion coexists with species II which absorbs at 740 μ , with an extinction coefficient greater than that substance absorbing at 700 μ . Even in 6M HBr there is evidence for the formation of a third species, III, which has a very weak absorption maximum at about 840 μ . In solutions of less than 6M HBr the drop in the 740 μ peak indicates only a trace of II in these solutions. As the acid concentration decreases further, both the 740 and 840 μ peaks drop, indicating the formation of a substance, IV, which does not absorb in this region of the spectrum.

The interpretation of the changes in two widely separated regions of the spectrum lends considerable confidence that the present interpretation, in terms of the existence of four species of Mo(V) in various hydrobromic acid solutions, is correct. An estimation of the relative concentrations of each of these species in various HBr concentrations is presented in Figure 7.

Attempts were made to study the equilibrium between species I and II by investigating the H^+ and Br^- dependence for the equation



The H^+ dependence was studied in HBr - LiBr mixtures, keeping the bromide concentration constant at 8.5M. In analogy to the derivation of equation 12 it can be shown that

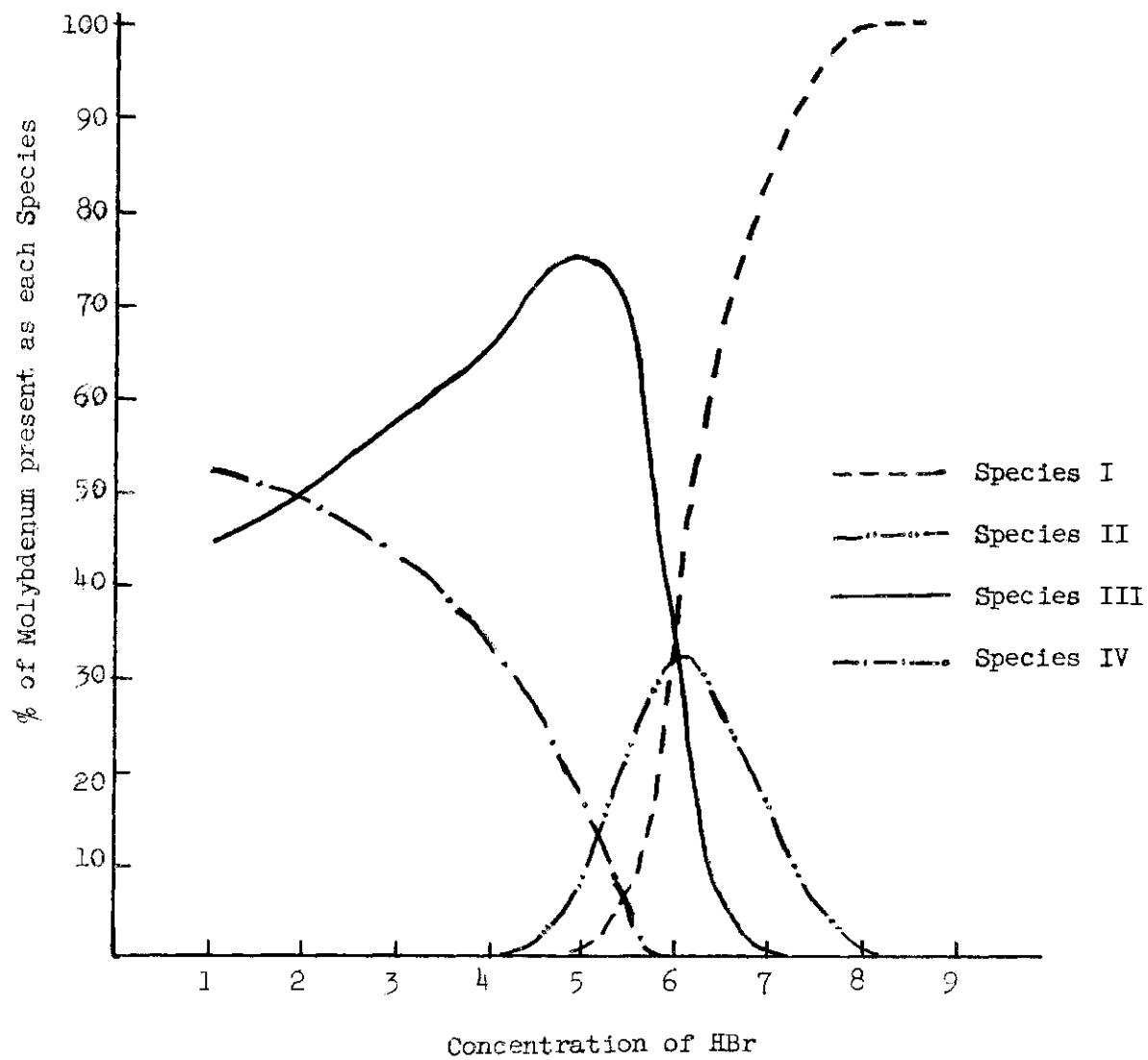


Figure 7. Relative Amounts of Molybdenum(V) Species in Hydrobromic Acid Solutions.

$$p = \frac{\log \frac{A_2}{A_1} - \log \frac{C - \frac{A_2}{\epsilon d}}{C - \frac{A_1}{\epsilon d}}}{\log \frac{[H^+]_2}{[H^+]_1}} \quad (16)$$

From Table 7, it is found that the hydrogen ion dependence is unity, and from the relative changes of the 376 and 414 $m\mu$ peaks, it is evident that the equilibrium involved is between species I and II.

Some experiments, with constant ionic strength and constant H^+ concentration, were performed in the hope of casting light on either the value of q or the activity effects. Preliminary experiments with HBr - $HClO_4$ mixtures showed the same type of difficulties as mentioned on page 36. Experiments were then attempted using HBr-LiBr and HBr- $CaBr_2$ mixtures. The H^+ concentration was kept constant by using constant HBr concentration while the bromide concentration was varied by adding $CaBr_2$ or LiBr to the HBr solutions. Use of two positive ions with different charge allowed the bromide ion concentration to be varied while the ionic strength was kept constant. The data obtained are listed in Table 8. The bromide dependence obtained from these data yields values ranging from negative to positive and are, therefore, not presently interpretable.

The principle effect to be observed is the greater effect of Ca^{++} at any given $[Br^-]$ or μ , in giving greater amounts of $(MoOBr_4^-)_2$. It is probable that this effect is exerted by Ca^{++} having the greater ability to decrease the activity of water.

Table 7. The $[H^+]$ Dependence, p , of the Equilibrium
 Between $(MoOBr_4^-)_2$ and $(MoO_2Br_2^-)_2$.
 $[Br^-] = 8.53M, \lambda = 414 m$

$\{Mo(V)\}_{total}$	$[H^+]_1$	$[H^+]_2$	A_1	A_2	p
2×10^{-4}	2.58	1.72	0.532	0.464	1.14
2×10^{-4}	3.44	1.72	0.570	0.464	0.91
4×10^{-4}	2.58	1.72	1.03	0.940	0.75
4×10^{-4}	3.44	1.72	1.15	0.940	0.96

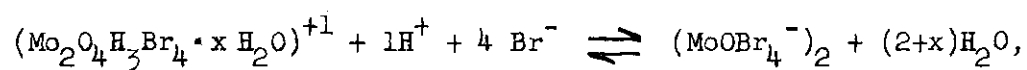
ave. $p = 0.94 \pm .11$

Table 8. Absorbance Data for the Mo(V) System
 in HBr-LiBr and HBr-CaBr₂ Mixtures

$$\{Mo(V)\}_{total} = 1.96 \times 10^{-4}M, [HBr] = 5.20M$$

$[LiBr]$	$[CaBr_2]$	μ	$[Br^-]$	A_{414}	A_{376}
-	0.692	7.27	6.58	0.526	0.520
2.07	-	7.27	7.27	0.404	0.376
-	0.866	7.78	6.92	0.576	0.545
2.58	-	7.78	7.78	0.501	0.448
-	1.04	8.32	7.28	0.590	0.532
3.12	-	8.32	8.32	0.648	0.552

Taking the hydrogen dependence at face value, and assuming a value of $q = 4$, as required for the conversion of II into I, the equilibrium can be represented as



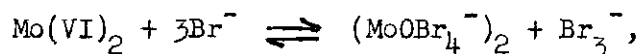
where the cation containing molybdenum is species II, which has previously been referred to as $(\text{MoO}_2\text{Br}_2^-)_2$. Contrary to this the extraction of this species into polar solvents suggests that it is anionic rather than cationic. The evidence that the species is anionic is judged to be stronger, and hence the results from the HBr-LiBr mixtures must reflect an activity dependence rather than a concentration dependence.

CHAPTER III

CONCLUSIONS AND RECOMMENDATIONS

The absorption spectra of $(\text{NH}_4)_2\text{MoOBr}_5$, $\text{C}_9\text{H}_8\text{NMoOBr}_4$, and $\text{MoO}(\text{OH})\text{Br}_2 \cdot 4\text{H}_2\text{O}$ have been determined in organic solvents and, in the case of $(\text{NH}_4)_2\text{MoOBr}_5$, in a KBr pellet.

A large number of samples were prepared by adding Mo(VI) to constant boiling HBr (8.6M), giving solutions whose spectra showed the existence of the $(\text{MoOBr}_4^-)_2$ ion and the presence of the tribromide ion, Br_3^- . This has been interpreted as being due to reduction of Mo(VI) to Mo(V) by the bromide ion in acid solution. The relative concentrations of the Mo(V) and Mo(VI) species in solution at equilibrium were shown to be well represented by the equation:



in which both the Mo(V) and Mo(VI) species are dimeric, giving an equilibrium constant,

$$K_1 = \frac{[(\text{MoOBr}_4^-)_2] [\text{Br}_3^-]}{[\text{Mo(VI)}_2]} = 2.27 \times 10^{-3}$$

over a range of molybdenum concentrations from 2×10^{-5} to 1×10^{-3} M. All these measurements were for solutions 8.6M in HBr, some of which contained a measured excess of tribromide ion.

Attempts to establish the nature of the Mo(VI) species have not been successful.

By comparison of the ultraviolet absorption spectra of aqueous HBr solutions of Mo(V) with the spectra of known compounds, it may be concluded that the MoOBr_5^{\equiv} ion does not exist in hydrobromic acid solutions. Even when the bromide concentration is increased to 10.8M by adding LiBr to 8.6M HBr, the spectra show no indications of the formation of the MoOBr_5^{\equiv} ion. Instead, the $(\text{MoOBr}_4^-)_2$ ion exists exclusively in the high acid concentrations, as is indicated by the identical spectra given by 8.6M HBr solutions and those containing added LiBr.

When the acid concentration is decreased below 8.0M, the changes occurring in the spectra lead to the conclusion that a substance containing Mo and Br in a ratio of 1:2, probably the $(\text{MoO}_2\text{Br}_2^-)_2$ ion, is present in solution in conjunction with $(\text{MoOBr}_4^-)_2$. This substance is also shown to be dimeric since a change in the molybdenum concentration has no effect on the relative peak heights, indicating that $(\text{MoO}_2\text{Br}_2^-)_2$ is of the same degree of condensation as the ion with which it is in equilibrium, in this case the dimer, $(\text{MoOBr}_4^-)_2$.

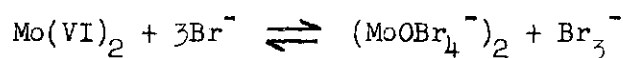
$(\text{MoO}_2\text{Br}_2^-)_2$ never exists alone in solution, for as the HBr concentration decreases below 6M a third species is indicated. This species, III, which absorbs at shorter wavelengths than $(\text{MoO}_2\text{Br}_2^-)_2$, must have a Mo:Br ratio of less than 1:2 and has been reasoned to be a dimeric cation such as $\text{Mo}_2\text{O}_3\text{Br}_2^{++}$. As the HBr concentration is decreased below 5M, the $(\text{MoO}_2\text{Br}_2^-)_2$ content becomes negligible and the concentration of the third species, III, decreases, indicating the formation of a fourth species which is possibly a bromide-free dimeric cation, such as $(\text{MoO}_2^+)_2$, which

does not appear to be a tetramer as suggested by Simon and Souchay (27). However, the solutions used by Simon and Souchay contained much higher concentrations of molybdenum than the solutions used in the present work.

A study of the absorbance in the 700-900 μ region verifies the presence of four species, as described above, and is in agreement as to the acid regions in which each exists.

It is suggested that a correlation of the magnetic properties of these solutions with the absorption spectrum at different HBr concentrations would be profitable. Mo(V) is a d^1 system and would be expected to show a magnetic moment corresponding to one unpaired electron. However, Sacconi and Cini (25) have shown that spin-pairing occurs with Mo(V) in hydrochloric acid as the acid concentration was decreased below 8M, with the spin-free species decreasing from 90 to 30 per cent as the HCl concentration decreased from 6.8 to 4.8M. It might be suggested, therefore, that a corresponding decrease in magnetic moment would occur in this approximate range in HBr, and that such a decrease might be related to the conversion of $(\text{MoOBr}_4^-)_2$ and $(\text{MoO}_2\text{Br}_2^-)_2$, which could be presumed to be spin-free, to species III and IV, which would be expected to be spin-paired. Thus a sharp drop in the magnetic moment as the hydrobromic acid concentration was dropped from 6M to 5M would strongly substantiate the existence of the species described in the present study.

Molybdenum(VI) is a d^0 system and would, therefore, be expected to show no magnetic moment. Should the $(\text{MoOBr}_4^-)_2$ ion prove to be spin-free in solution, the equilibrium



could also be studied, using the magnetic moment as a measure of the $(\text{MoOBr}_4^-)_2$ concentration.

Klemm and Steinberg (24) have shown the solid salts $(\text{C}_5\text{H}_6\text{N})_2\text{MoOBr}_5$, $(\text{C}_5\text{H}_6\text{N})\text{MoOBr}_4$, $(\text{C}_9\text{H}_8\text{N})_2\text{MoOBr}_5$, and $(\text{C}_9\text{H}_8\text{N})\text{MoOBr}_4$ to be spin-free, so the MoOBr_4^- salts may not be dimeric in the solid state. An X-ray examination would be quite helpful in the determination of the degree of condensation of these salts.

The solvent extraction studies made in hydrobromic acid solutions by Diamond (11, 14) need to be reinvestigated in view of the reduction of the molybdenum which occurs in these solutions. In the present work, it was found that $(\text{MoOBr}_4^-)_2$ and $(\text{MoO}_2\text{Br}_2^-)_2$ are extracted to a considerable degree into polar organic solvents. It seems unlikely that the extraction data of Diamond was for Mo(VI) species, but a reinvestigation using the absorption spectra of the extracted solution would easily establish this point. There is a possibility that the extracted solution would yield some useful information about the Mo(VI) species present, but the favorable extraction of Br_3^- into these solvents makes such a possibility seem unlikely.

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VITA

Joe Frank Allen was born June 3, 1934, near Hogansville, Georgia, the sixth of seven children of Grady W. and Sallie (nee Shanks) Allen. He attended school in the Hogansville system, graduating from Hogansville High School in June, 1951. He entered Berry College in 1951, receiving the Bachelor of Arts degree at that institution in May 1955. From 1955 to 1957 he attended the University of Mississippi, obtaining the Master of Science degree in May, 1959. He entered the Graduate Division of the Georgia Institute of Technology in September, 1957, where he served as an Instructor in Chemistry from 1957 to 1961.

On August 26, 1955, he married the former Doris Tarvin, daughter of Mr. and Mrs. Walter C. Tarvin, of Rocky Face, Georgia. He is the father of two children, Deborah Jean and Robert Trent.

He has accepted employment with the Radioisotopes Division of Union Carbide Nuclear Corporation and has established residence at 125 Amherst Lane, Oak Ridge, Tennessee.