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THE ASSOCIATION OF PENTAVALENT MOLYBDENUM

IN AQUEOUS HYDROCHLORIC AND HYDROBROMIC ACIDS

A DISSERTATION

Presented to

The Faculty of the Graduate Division

by

Claybourne Claude Snead

In Partial Fulfillment
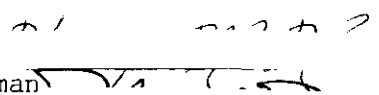
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IN AQUEOUS HYDROCHLORIC AND HYDROBROMIC ACIDS

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SUMMARY

The association of pentavalent molybdenum in aqueous HCl and HBr has been studied using the techniques of ultraviolet and visible spectrophotometry and magnetic susceptibility measurements utilizing the Gouy method.

The solutions studied were prepared by dissolving $(NH_4)_2MoOCl_5$ in various HCl solutions and $(NH_4)_2MoOBr_5$ in HBr. Concentrations ranged from about 0.001 to 0.1-0.2 F in HBr in total molybdenum concentration. The magnetic susceptibility experiments required the more concentrated solutions.

In each concentrated acid the magnetic susceptibility of the molybdenum (V) had the characteristic values, $1255 \times 10^{-6} (gm\ atom)^{-1}$ in HCl, and $1360 \times 10^{-6} (gm\ atom)^{-1}$ in HBr. These values are attributed to $MoOCl_5^=$ and $MoOBr_5^=$, respectively. The magnetic susceptibilities of solutions containing a fixed molybdenum concentration were found to decrease to very small values in dilute acids with the major decreases occurring in 7 to 4 F HCl and 8 to 5.5 F HBr. This reduction in paramagnetism had been previously attributed to the formation of diamagnetic dimers.

An equation,

$$A/C_o = \varepsilon_D/2 - \frac{1}{2}\sqrt{\frac{\varepsilon_D - 2\varepsilon_M}{K}}\ z^{1/2}/C_o\ ,$$

which holds for a monomer in equilibrium with any number of dimers, was derived for treatment of the spectrophotometric data. In this equation,

A is the absorbance of a solution at a given wavelength; C_o is the total concentration of molybdenum, expressed as monomer, $MoOBr_5^=$ or $MoOCl_5^=$; ε_M is the extinction coefficient of the monomer(s); K is the overall dimerization (the sum of the equilibrium constants for all of the individual dimerizations); ε_D is a weighted extinction coefficient for all of the associated species, considered to be dimers; and Z is defined as $A - C_o$. Absorbances of the solutions of Mo(V) in 5-12 F HCl and in 5 to 8.7 F HBr are described by this equation, as verified by the linearity of a plot of A/C_o versus $Z^{1/2}/C_o$. In such a plot the intercept is $\varepsilon_D/2$ and the slope is

$$-\frac{1}{2}\sqrt{\frac{\varepsilon_D - 2\varepsilon_M}{K}} \ ,$$

from which K and ε_D can be obtained. The results obtained are: 7.01 F HCl, K = 0.80, ε_D = 50; 6.49 F HCl, K = 1.44, ε_D = 110; 5.96 F HCl, K = 2.02, ε_D = 312; 4.98 F HCl, K = 48, ε_D = 244; 4.01 F HCl, K = 7.0 x 10^3, ε_D = 60; 6.99 F HBr, K = 7.2, ε_D = 149; 6.50 F HBr, K = 42, ε_D = 182; 6.11 F HBr, K = 235, ε_D = 88.

The magnetic and spectrophotometric results suggest that there are a series of three or more dimers involved in each media as the acidity is lowered from 12 to 5 F HCl and from 8.7 to 5 F HBr. In each case, the first dimer is paramagnetic and it first obtains a detectable concentration around 7.5 to 7 F HCl and 8 F HBr. The second dimer encountered in each of the systems always occurs in equilibrium with the preceding dimer; however, it obtains its maximum concentration in 5—6.5 F HCl and 5 to 7 F HBr. The second dimer is responsible for the large

increase in absorption intensity observed with decreasing acidity at the wavelengths used in this study and is diamagnetic. This is reflected in the large increase in intensity observed in these solutions. The decreases in ϵ_D observed in the 5.98 and 4.01F HCl and 6.11F HBr solutions are due to the occurrence of dimers, also diamagnetic, that do not absorb at the two wavelengths. In solutions of 5F HBr and below 4F HCl, the Beer-Lambert Law is obeyed, indicating no further polymerization. All species present at these lower acidities are diamagnetic.

There has been considerable uncertainty about the nature of the species present in concentrated HBr and since the results of the absorbance and magnetic measurements strongly suggest the existence of monomeric and dimeric species analogous to those in HCl, efforts were made to establish definitely the nature of the molybdenum species in concentrated HBr. Attempts to determine the ultraviolet and visible spectrum of $(NH_4)_2MoOBr_5$ in a KBr pellet were unsuccessful due to the extreme hygroscopicity of the compound. The relatively non-hygroscopic compound, $(C_9H_8N)_2MoOBr_5$ was prepared and its spectrum determined. The spectra of solid $(C_9H_8N)_2MoOBr_5$, in KBr, was found to be virtually identical with that of Molybdenum (V) in 8.7F HBr.

It was observed that the compounds, $(NH_4)_2MoOCl_5$ and $(NH_4)_2MoOBr_5$, reacted with ethanol and acetone to yield solutions containing molybdenum and chloride, or bromide, ions, and a tan solid. In the acetone solution, it has been established that there are four chlorides per molybdenum atom. The solids have been identified as NH_4Cl or NH_4Br, obtaining their discoloration due to small amounts of occluded molybdenum. The solutions contain molybdenum in a paramagnetic state. This behavior has been

interpreted in terms of the existence in these solutions of $(MoOCl_4)_2^=$

or $(MoOBr_4)_2^=$ which would be paramagnetic dimers.

These dimers could arise in the following manner:

$$2NH_4^+ + MoOX_5^= \rightleftharpoons (MoOX_4)_2^= + 2NH_4X(s)$$
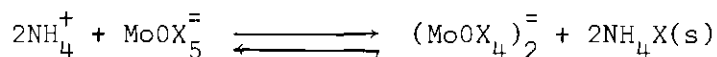
in which X is either Cl or Br. The possibility of the species being

monomeric, $MoOX_4^-$ or $MoOX_4(solvent)^-$, arising from the reaction,

$$NH_4^+ + MoOX_5^= + solvent \rightleftharpoons MoOX_4(solvent)^- + NH_4X(s) ,$$
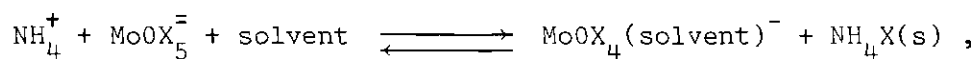
cannot be entirely discounted.

It was possible to show further that the species, $MoOBr_5^=$, in

fact, is the predominant species present in 8.7 F HBr by examination of

the intensities of the absorption spectrum of $(C_9H_8N)_2MoOBr_5$ in acetone

and comparing them with those of Mo(V) in concentrated HBr. This was

made possible by the lack of decomposition of $(C_9H_8N)_2MoOBr_5$ in acetone.

It is concluded, therefore, that the association of Molybdenum(V)

in HCl and HBr involves several equilibria in the range, 12 to 5 F HCl

and 8.7 to 5 F HBr, with the first two equilibria being postulated as

$$2MoOX_5^= \rightleftharpoons (MoOX_4)_2^= + 2X^-$$

$$(MoOX_4)_2^= + H_2O \rightleftharpoons (MoOX_4)_2O^{-4} + 2H^+ .$$
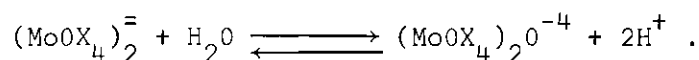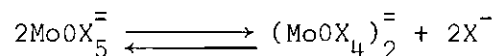
The sum of the two reactions yields the equation representing the second

dimerization step,

$$2MoOX_5^= + H_2O \rightleftharpoons (MoOX_4)_2O^{-4} + 2H^+ + 2X^- .$$
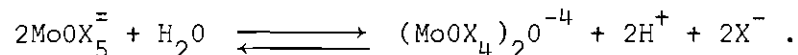
Equilibrium constants, expressed in concentrations, for the two dimerizations are expressible as

$$K_1 = \frac{[(MoOX_4)_2^=]}{[(MoOX_5)^=]^2}$$

and

$$K_2 = \frac{[(MoOX_4)_2O^{-4}]}{[MoOX_5^=]^2}$$

for given HCl or HBr concentrations. The dimeric $(MoOX_4)_2^=$ ion is paramagnetic and the $(MoOX_4)_2O^{-4}$ is diamagnetic. There are also other species involved in 5 F HCl and 5 F HBr and still others at even lower acid concentrations. No effort was made to study these.

Combining the magnetic and absorbance data, and in the case of Mo(V) in HCl, activity data, it was possible to obtain estimates of the equilibrium constants, K_1 and K_2: 5 HCl, K_1 = 12, K_2 = 33; 6 F HCl, K_1 = 3.5, K_2 = 2.6; 6.5 F HCl, K_1 = 2.4, K_2 = 1.2; 7 F HCl, K_1 = 1.1, K_2 = 0.21; 8 F HCl, K_1 = 0.35, K_2 = 0.02; 9 F HCl, K_1 = 0.12, K_2 = 0.00; 6.99 F HBr, K_1 = 3.9, K_2 = 3.3; 6.50 F HBr, K_1 = 10, K_2 = 32; 6.11 F HBr, K_1 = 20, K_2 = 215.

The structure of the $(MoOX_4)_2^=$ ion is postulated to involve bridging through the halogens, with an electron distribution around the molyb-

denum atoms being very similar to that of the monomer, $MoOX_5^=$. The

$(MoOX_4)_2O^{-4}$ would contain an oxygen bridge, allowing for the observed

diamagnetism by way of a super exchange interaction through the

Mo-O-Mo linkage.

CHAPTER I

INTRODUCTION

Interest in the nature of solutions of pentavalent molybdenum in HCl and HBr began with the observation that solutions of molybdenum (V) in HCl changed colors when the concentration of acid was changed (1,2, 3,4). The colors noted were amber in 0.5—3.5 F HCl, brown in 3.5 to 7.3 F HCl, and green in solutions above 7.3 F HCl (3).

These facts have been interpreted in terms of equilibria between a monomeric species, $MoOCl_5^=$, and a series of dimers which arise as the concentration of acid is lowered. The dimerization is reflected by a decrease in paramagnetism and increased absorption in the visible spectrum.

Molybdenum (V) solutions in hydrobromic acid also involve equilibria that are manifested by color changes as the acid concentration is changed; yellow in 7.5 to 8.7 F HBr, dark brown in 5 to 7 F HBr, and amber below 4 F HBr. The changes in the absorption spectra have not lent themselves so readily to interpretation as they have in HCl, and little is known about the magnetic behavior of such solutions, although there is a decrease in the paramagnetism of the molybdenum as the acidity is reduced.

Studies of the equilibria in 5 to 8.7 F HBr and 5—12 F HCl will be made in some detail using spectrophotometric and magnetic techniques.

James and Wardlaw (5) and Angell, James and Wardlaw (6), using

freezing point, osmotic, and conductivity data, postulated hydrolyses of the following type occurring in aqueous solutions:

$$R_2MoOX_5 + 5H_2O \longrightarrow MoO_2(OH)\cdot 3H_2O + 2R^+ + 3H^+ + 5X^-$$

$$RMoOX_4 + 5H_2O \longrightarrow MoO_2(OH)\cdot 3H_2O + R^+ + 3H^+ + 4X^- \; .$$
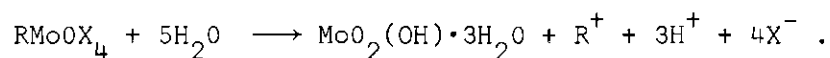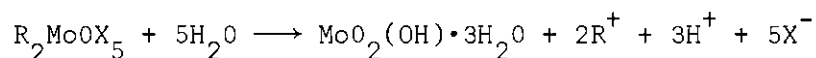
X can be either Cl or Br, and R is K, NH_4, Li, Rb, C_6H_5N, or C_9H_8N . Their data can be explained just as well, however, by postulating polymeric species instead of monomers as the hydrolysis products.

On the basis of the visible and ultraviolet spectrum of Mo(V) in HCl, El Shamy and others (7,8) postulated the existence of at least three species, some of them polymers, in the solutions.

Souchay and Simon (9) proposed that the species present in concentrated HCl was the $MoOCl_5^=$ ion. This ion was in equilibrium with a dimer, $Mo_2O_3Cl_2$, in the range, 3.5 to 7 F HCl, and this dimer was in equilibrium with a tetramer, $(MoO_2^+)_4$, in lower acid concentrations.

Magnetic measurements (10,11,12,15) on molybdenyl oxyhalide salts of type, R_2MoOX_5 and $RMoOX_4$, have indicated magnetic moments that are in accordance with the spin only formula for an atom containing one d electron. The various values for the magnetic moments are tabulated in Table 1.

Since the pentavalent state of molybdenum is paramagnetic, Sacconi and Cini (13) studied the paramagnetism of Molybdenum (V) in hydrochloric acid solutions as a function of HCl concentration. The value of the atomic magnetic susceptibility of the molybdenum in concentrated HCl, 8

Table 1. Tabulated Values for Magnetic Moments
of Molybdenyl Oxyhalides.

Compound	Magnetic Moment (B.M.)	Temp. (°K)	Compound	Magnetic Moment (B.M.)	Temp. (°K)
R_2MoOCl_5:			$RMoOCl_4$:		
K_2MoOCl_5	1.74[a,d]	300	$RbMoOCl_4$	1.74[b]	300
$(NH_4)MoOCl_5$	1.71[a,d]	300	$CsMoOCl_4$	1.63[b]	300
$(C_9H_8N)_2MoOCl_5$	1.74[a,d]	300	$C_6H_5NMoOCl_4$	1.73[b]	300
	1.70[b]	300	$C_9H_8NMoOCl_4$	1.73[b]	300
Rb_2MoOCl_5	1.68[c]	300	$(C_2H_5)NH_3MoOCl_4$	1.74[b,d]	300
	1.69[b,d]	300			
$(C_6H_5N)_2MoOCl_5$	1.75[c]	300			
	1.74[a,d]	300			
Cs_2MoOCl_5	1.72[b]	300			
$((CH_3)NH_3)MoOCl_5$	1.74[b]	300			
$((CH_3)_2NH_2)MoOCl_5$	1.72[b]	300			
R_2MoOBr_5:			$RMoOBr_4$:		
$(C_6H_5N)_2MoOBr_5$	1.80[c]	300	$(C_6H_5N)MoOBr_4$	1.78[c]	300
	1.82[a,d]	300		1.76[a,d]	300
	1.67[b]	300	$(C_9H_8N)MoOBr_4$	1.77[c]	300
$(C_9H_8N)_2MoOBr_5$	1.72[c]	300		1.76[a,d]	300
	1.80[a,d]	300			
$(NH_4)_2MoOBr_5$	1.72[a,d]	300			
Cs_2MoOBr_5	1.73[b]	300			
Rb_2MoOBr_5	1.73[b]	300			

[a]Reference (15).

[b]Reference (12).

[c]Reference (10).

[d]Measured over the temperature range, 90—300°K.

to 12 F, was very close to the values for molybdenum in solid compounds. In the concentration range of 8 to 2.5 F HCl they observed a sharp decrease in susceptibility. Below 2.5 F HCl all of the paramagnetism had disappeared. These data were interpreted in terms of a paramagnetic monomer, $MoOCl_5^=$, existing alone in 12 to 8 F HCl and in equilibrium with a diamagnetic dimer in 2.5 to 8 F HCl. The reduction in paramagnetism was caused by "pairing of the spins" of the molybdenum atoms as they coupled together to form the dimer. In the acid concentrations below 2.5 F HCl all of the monomer had disappeared and only diamagnetic species were present.

Babko and Getman (14) used spectrophotometric, electrophoretic, and extraction data to study the equilibria in HCl. They postulated the existence of only monomers throughout the HCl concentration range and estimated equilibrium constants for the various reactions. Their results, however, could be interpreted in the same manner as Souchay and Simon's (9).

Garside (15) studied solutions of Mo(V) in HCl and HBr in the same manner as Sacconi and Cini (13). Results analogous to those of Sacconi and Cini (13) were obtained (the susceptibility of the molybdenum at the highest acidities being very near the value for Mo(V) in solids, and a large decrease occurring between 8 and 6 F HBr and 7 and 3 F HCl, with negligible values at lower acidities). No concentrations of Mo(V), however, were specified. He also reported values of the magnetic susceptibilities of various solids containing the $MoOCl_5^=$ and $MoOBr_5^=$ ions over a temperature range.

Jakob (16) and others also observed that the paramagnetism of

Mo(V) solutions decreased when the concentration of HCl was lowered. Changing the temperature of the solutions resulted in a shift of the equilibria as manifested by changes in the observed paramagnetism. Polarographic studies confirmed the presence of dimers at low HCl concentrations.

Haight (17) believed that the large increase in absorption intensity of Mo(V) in 5—7 F HCl at the wavelength of 450 mµ could be explained by a monomer-dimer equilibrium. Using absorbance data at that wavelength he calculated values for the equilibria in 5 to 6 F HCl. He proposed an oxygen bridged structure, formulated as $(MoOCl_4)_2O^{-4}$, as the dimer in equilibrium with $MoOCl_5^=$. Other dimeric forms were involved as the concentration of HCl was lowered below 5 F.

Gray and Hare (18) showed that the spectrum of molybdenum (V) in 9 to 12 F HCl was essentially the same as the reflectance spectrum of solid $(NH_4)_2MoOCl_5$. They accounted for the visible and ultraviolet spectrum of the $MoOCl_5^=$ ion using semi-empirical molecular orbital calculations based on a C_{4v} symmetry model. Using this scheme, absorption maxima in the visible region occurring near 14,000 cm^{-1} (720mµ) and 23,000cm^{-1}(435mµ) were assigned to the transitions $B_2 \longrightarrow E$ and $B_2 \longrightarrow B_1$, respectively. Three prominent transitions in the ultraviolet region near 26,700 cm^{-1}(375mµ), 32,100cm^{-1}(312mµ), 35,700$cm^{=1}$(280mµ) were assigned as charge transfer bands. The transitions in the visible region increase profoundly in intensity as the concentration of HCl is lowered from 12 F to 5—6 F.

Hare and co-workers (19) studied solutions of Mo(V) in HCl by means of electron spin resonance. Combining their results with those of

Sacconi and Cini (13), they established the presence of a second para-
magnetic species (dimeric) in the 8 to 2 F HCl range. It must be noted,
however, that they used solutions of concentration, 0.03 F Mo(V), con-
siderably more dilute than the concentration, 0.34 F, used by Sacconi
and Cini (13), and hence the amounts of various species they reported
are actually rather crude estimates. It was concluded that the para-
magnetic dimer was the same one studied by Haight (17). This work also
reported values of the magnetic susceptibility of solid $(NH_4)_2MoOCl_5$
over a temperature range.

Wentworth and Piper (20) studied spectra of the ions, $MoOX_5^=$ in
which X is Cl, Br, or F, in various host crystals. They directed their
attention, however, mostly to the $MoOCl_5^=$ ion. They observed that the
band near $14,000 cm^{-1}$ was electronic in origin, and the band near 25,000
cm^{-1} was vibronically allowed.

The nature of the molybdenum species in concentrated HBr has been
subject to some controversy. J. F. Allen and Neumann (21) indicated that
the predominant species in concentrated HBr was dimeric, $(MoOBr_4)_2^=$, by
interpretation of absorbance data for the equilibrium between Mo(VI) and
Mo(V) in HBr (HBr reduces hexavalent molybdenum to pentavalent molyb-
denum) and by the observation that the ultraviolet and visible spectrum
of solid $(NH_4)_2MoOBr_5$, in KBr, bore little resemblance to that of
solutions of Mo(V) in concentrated HBr. Other absorbance data indicated
that all of the species in HBr were dimeric. On the other hand, E. A.
Allen and others (12) also asserted that the spectrum of Mo(V) in con-
centrated HBr was that of the $MoOBr_5^=$ ion by reason of its analogy to
the spectrum of $MoOCl_5^=$ in concentrated HCl.

Mitchell studied the chemical, magnetic, and spectrophotometric properties of various dipyridyl complexes of Mo(V), $MoO_2Cl(dipy)$, $Mo_2O_3Cl_4(dipy)_2$, $MoOCl_3(dipy)$ (22), and of $K(MoO_2C_2O_4)2.5H_2O$ and $Ba(MoO_2C_2O_4)_25H_2O$ (23). The atomic susceptibility of the molybdenum in $MoOCl_3(dipy)$ corresponded to that of the spin only formula for one electron; however, the magnetic moments of the other two pyridyl complexes were unusually low, a result he attributed to polymerization. The two oxalate complexes were diamagnetic; a fact which led him to propose that the compounds should be formulated as a dimer, $[Mo_2O_4(C_2O_4)_2(H_2O)_2]^{-2}$, containing two oxygen bridges.

The X-Ray studies of Sands and Zalkin (24) revealed that the paramagnetic molecule, $MoCl_5$, is dimeric in the solid state, although it exists as a monomer in the vapor. Bridging occurs through the chlorines,
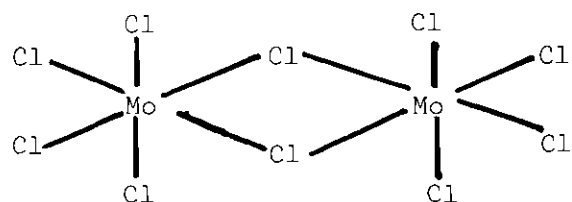
Other X-ray structural work (25,26) on diamagnetic compounds containing pentavalent molybdenum has established the presence of oxygen bridges. Cotton and others (25) determined the presence of a single, linear, oxygen bridge of length, 3.72 angstroms, between the two molybdenum atoms in $[(C_2H_5OCS_2)_2MoO]_2O$,
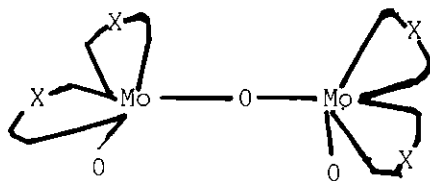
X represents the $C_2H_5OCS_2$ group. Cotton and Morehouse (26) found a double oxygen bridge in the $(MoO(C_2O_4)H_2O)_2O_2^=$ ion,
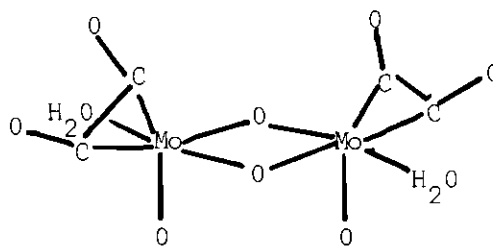
The Mo-Mo distance was 2.541 angstroms. The diamagnetism apparently resulted from a Mo-Mo bond in the latter case and a Mo-O-Mo interaction in the former case.

CHAPTER II

EXPERIMENTAL

A. Magnetic Measurements

The Gouy method was employed in determining the magnetic sus-
ceptibilities. In the Gouy technique the experimentally determined
quantity is a force, f, that is measured on a balance of suitable sen-
sitivity and is related to the susceptibility per unit volume, χ_v, of
the material under investigation as

$$f = \frac{1}{2} \chi_v A (H^2 - H_o^2)$$

where the additional quantities are: A, the cross sectional area of
the sample and H and H_o which are the field strengths at the center of
the space between the magnet poles and at the upper extremity of the
sample when the sample is inserted in the field, respectively. Usually,
the sample is of such length that H_o is negligible; however, in these
experiments H_o was about 800 gauss. The force is measured as the differ-
ence in weights of the sample, suspended between the magnet poles, when
the magnetic field is off and when the magnet is excited.

Since the quantity that is related to molecular structure is the
molar susceptibility, χ_M, it is necessary to convert the susceptibility
per unit volume to the molar susceptibility through the following rela-
tionships:

$$\chi_M = FW \cdot \chi_S = FW \cdot \chi_V d$$

where χ_S, the specific susceptibility or susceptibility per unit mass, is related to χ_V by the density, d. FW is the formula weight of the sample.

Since it is difficult to measure the magnetic field strength accurately, the usual procedure is to calibrate the system with a material of known susceptibility. The modified equation is now

$$f = \chi_V \alpha$$

where α is the quantity, $\frac{1}{2}A(H^2 - H_0^2)$. As long as the sample has the same area and the same field strength is employed, the simplified equation may be used.

Since the sample under investigation was placed in a glass tube it was necessary to allow for the effect of the glass on the force. This was done by measuring the force on the tube when empty and then measuring the force on the tube when filled with the sample to a fiducial mark. The difference in the two forces will give a value for the force on the sample that includes a contribution from the air in the empty sample tube. The effect of the air was calculated from Soné's data (27) by the equation,

$$f_{air} = \chi_S^a \cdot d_a \cdot \alpha$$

where χ_S^a is the specific susceptibility of the air and d_a is the density

of air.

The apparatus for the magnetic studies consisted of two Newport electromagnets, four inches in diameter, wired in series and mounted on a yoke. The pole faces were conical in shape, with faces two and one-half inches in diameter. Power was delivered to the magnet assembly by a Newport Type B Mark II Power Supply.

Operating conditions involved a direct current of about nine amperes which produced a field of about 11.9 kilogauss when the gap between the pole faces was set at about 25 millimeters. Current control was achieved by measuring with a potentiometer the voltage drop across a precision resistor inserted in one branch of the output circuit. In practice the output of the power supply would be adjusted until the galvanometer registered no deflection from a predetermined setting.

The sample container for solutions was a single ended tube constructed from a piece of Fischer Porter precision bore tubing, three-eighths of an inch in diameter. The sample container was calibrated with deaerated, distilled water (28) and occasionally with a 10.10 per cent (weight) $NiCl_2$ solution (29).

A much smaller diameter tube, which was calibrated with $HgCo(SCN)_4$ (30), was used for measurements on solids. It was constructed of pyrex tubing, about one-eighth inch in diameter.

The forces on the sample tubes were measured with either a Christian-Becker or a Mettler automatic reading semi-micro balance.

The densities of the solutions used in the magnetic measurements were determined in a pycnometer that had been calibrated with boiled, distilled water. The densities of the solids were determined directly

from the weight of material required to fill the sample tube to the reference mark.

B. Absorbance Data

The absorbance data used for quantitative measurements were obtained on a Beckman Model DU Spectrophotometer, using either a hydrogen or tungsten source. Silica cells of path length 1, 5, and 10 centimeters were used.

Qualitative spectra were obtained on a Cary 14 Recording Spectrophotometer.

Spectra of solids were obtained by forming a KBr pellet containing the compound. The pellets pressed involved small amounts (usually fractions of a milligram) of the compound of interest in about 150 milligrams of KBr. The resulting pellet was about 0.5 cm in diameter and 0.02 cm in thickness. To minimize the absorption of moisture, the KBr was kept in an oven and the grinding was done in an agate mortar.

C. Synthesis of Compounds

$(NH_4)_2MoOCl_5$ was prepared by the reduction of ammonium paramolybdate, $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$, with hydrazine. Specifically, 17.7 grams of ammonium paramolybdate was dissolved in 100 cc of concentrated HCl to which was added 3.5 cc of 64 per cent (weight) hydrazine solution. The solution was heated until evolution of nitrogen stopped. Upon conclusion of the reduction, 5.35 grams, 0.1 mole, of NH_4Cl was added and the mixture cooled. Green crystals of $(NH_4)_2MoOCl_5$ precipitated. The material was recrystallized from hot water that had been saturated with hydrogen chloride gas. The $(NH_4)_2MoOCl_5$ was stored in a vacuum desic-

cator over potassium hydroxide. Analysis of the crystals showed:

	NH_4	Mo	Cl
Theoretical	11.11%	29.49%	54.48%
Found	11.62%	29.9%	54.29%

$(NH_4)_2MoOBr_5$ could be prepared merely by heating a solution of $(NH_4)_6Mo_7O_{24} \cdot 4 H_2O$ in concentrated HBr since it has been shown that Mo(VI) is reduced to Mo(V) by HBr (21). Fifteen grams of ammonium paramolybdate were dissolved in 100 cc of concentrated HBr and the solution was evaporated until dark brown crystals began to appear. The dark brown $(NH_4)_2MoOBr_5$ is very hygroscopic and the crystals darkened rapidly upon exposure to air. It was stored in a vacuum desiccator over both KOH and H_2SO_4. The analysis showed the following:

	Mo	Br
Theoretical	17.52%	72.97%
Found	17.8 %	72.25%

$(C_9H_8N)_2MoOBr_5$ was prepared by dissolving 16 grams of MoO_3 in 100 cc of concentrated HBr. The solution was heated for several hours. Upon addition of 35 cc of quinoline in 100 cc of boiling, concentrated HBr, yellow-brown crystals precipitated. These crystals were washed with concentrated HBr and air-dried on a fritted plate. The crystals are only slightly hygroscopic. The material was stored over KOH and H_2SO_4 in a vacuum desiccator. Analysis of the material showed the following:

	Mo	Br
Theoretical	12.43%	51.77%
Found	12.3 %	50.32%

The rather low value for the analysis for the bromide content probably reflects a difficulty in the analysis rather than the presence of an impurity. It was impossible to prevent the precipitation of molybdenum blue when the compound was dissolved and some of the bromide ion was probably occluded to the solid.

D. Analytical Procedures

The ammonia was determined by the Kjeldahl procedure in which a weighed sample is dissolved in concentrated NaOH and the ammonia is distilled off into a trap containing 0.1F HCl. The HCl was back titrated with standard NaOH.

A spectrophotometric technique was used to determine the molybdenum. A weighed sample was dissolved in 6.5 F HCl and the absorbance measured at a wavelength of 7000 angstroms. The concentration was read from a previously prepared calibration curve. The analyses were similar for the chloride and bromide compounds except that the 6.5 F HCl solution also contained two per cent by volume concentrated HBr in the latter case.

The chloride and bromide analysis was based on a potentiometric titration with 0.1000F $AgNO_3$ solution using a silver electrode against a glass electrode. The sample was dissolved in chilled 1F HNO_3 and titrated as soon as possible.

E. Solvents

Hydrobromic acid, unlike hydrochloric acid, is oxidized by the air and must be distilled before use. The product of the air oxidation is the tribromide ion, Br_3^-, which has a characteristic absorption peak near 267 millimicrons. The hydrobromic acid, Baker AR grade, was distilled over powdered red phosphorous. The constant boiling mixture had a concentration of about 8.6 to 8.8F, depending on the barometric pressure at the time of distillation. It was stored in a polyethylene bottle and was stable for at least two to three weeks, as noted by the absence of the peak at 267 millimicrons.

The acetone that was used was Baker Reagent grade which was purified by storage over $CaCl_2$, and then $CaSO_4$. It was distilled from $CaSO_4$ and used immediately.

All other solvents were either Reagent grade or Analyzed Reagent grade and were used without further purification.

CHAPTER III

THEORETICAL

A. Treatment of Absorbance Data

Consider an equilibrium situation characterized by a monomer, M, in equilibrium with dimers, D_1, D_2, ..., D_n as formulated by the equilibrium constants,

$$K_1 = [D_1]/[M]^2, \qquad K_2 = [D_2]/[M]^2, \qquad K_n = [D_n]/[M]^2, \qquad (1)$$

in which all concentrations are expressed in formula weights per liter. The total concentration expressed in terms of monomer is

$$C_o = [M] + 2[D_1] + 2[D_2] \ldots + 2[D_n] \qquad (2)$$

and the absorbance of such a solution, for a light path of one centimeter, is given by

$$A = \epsilon_M[M] + \epsilon_1[D_1] + \epsilon_2[D_2] \ldots + \epsilon_n[D_n] . \qquad (3)$$

Equation (2) may be rewritten as

$$C_o = [M] + 2K_1[M]^2 + 2K_2[M]^2 \ldots + 2K_n[M]^2 \qquad (4)$$

$$= [M] + 2[M]^2(K_1 + K_2 \ldots + K_n)$$

$$= [M] + 2[M]^2 K$$

where K is the sum of the equilibrium constants,

$$K = K_1 + K_2 \ldots + K_n \tag{5}$$

Similarly, Equation (3) may be rewritten as

$$A = \epsilon_M[M] + \epsilon_1 K_1[M]^2 + \epsilon_2 K_2[M]^2 \ldots + \epsilon_n K_n[M]^2 \tag{6}$$

$$= \epsilon_M[M] + [M]^2 (\epsilon_1 K_1 + \epsilon_2 K_2 \ldots + \epsilon_n K_n)$$

Now multiply the second term by K/K;

$$A = \epsilon_M[M] + [M]^2 K(\epsilon_1 \frac{K_1}{K} + \epsilon_2 \frac{K_2}{K} \ldots + \epsilon_n \frac{K_n}{K})$$

we obtain

$$A = \epsilon_M[M] + [M]^2 K \epsilon_D \tag{7}$$

where the expression in parenthesis is defined as ϵ_D,

$$\epsilon_D = (\epsilon_1 \frac{K_1}{K} + \epsilon_2 \frac{K_2}{K} + \ldots + \epsilon_n \frac{K_n}{K}) \tag{8}$$

Dividing Equation (7) by (4), the following is obtained:

$$A/C_o = \frac{\epsilon_M[M] + [M]^2 K\epsilon_D}{[M] + 2K[M]^2} = \frac{\epsilon_M + [M]K\epsilon_D}{1 + 2K[M]} \ . \tag{9}$$

Rearranging and solving for [M],

$$[M] = \frac{A - C_o\epsilon_M}{K(\epsilon_D C_o - 2A)} = \frac{Z}{K(\epsilon_D C_o - 2A)}$$

in which Z is defined as the quantity, $A - \epsilon_M C_o$. Inserting this equation in Equation (4), we obtain

$$C_o = \frac{Z}{K(\epsilon_D C_o - 2A)} + \frac{2Z^2}{K(\epsilon_D C_o - 2A)^2}$$

which, after multiplying through by $K(\epsilon_D C_o - 2A)^2$, yields

$$KC_o(C_o\epsilon_D - 2A)^2 = Z(C_o\epsilon_D - 2A + 2Z) \tag{10}$$

$$= Z(C_o\epsilon_D - 2A + 2A - 2\epsilon_M C_o)$$

$$= ZC_o(\epsilon_D - 2\epsilon_M) \ .$$

Doing the indicated cancellation,

$$(C_o\epsilon_D - 2A)^2 = Z(\epsilon_D - 2\epsilon_M)/K \tag{11}$$

appears. Taking the square root, we obtain

$$C_o\varepsilon_D - 2A = (\frac{\varepsilon_D - 2\varepsilon_M}{K})^{1/2} Z^{1/2} \tag{12}$$

and after some more rearranging, the final result obtained is

$$A/C_o = \varepsilon_D/2 - \frac{1}{2}(\frac{\varepsilon_D - 2\varepsilon_M}{K})^{1/2} Z^{1/2}/C_o \tag{13}$$

Hence, for any number of dimers in equilibrium with a monomer, Equation (13) should hold and a graph of A/C_o against $Z^{1/2}/C_o$ should be linear with a slope of $-\frac{1}{2}(\frac{\varepsilon_D - 2\varepsilon_M}{K})^{1/2}$ and intercept $\varepsilon_D/2$. To obtain a value for Z, it is necessary to determine ε_M, which is evaluated by measuring the absorbance of a solution in which the monomer is the only absorbing species. The value of K obtained by this treatment, of course, is the sum of all the individual equilibrium constants unless there is only one monomer-dimer equilibrium.

An equation similar to (13) holds for the case in which Z is negative; in this case, one obtains

$$A/C_o = \varepsilon_D/2 - \frac{1}{2}(\frac{2\varepsilon_M - \varepsilon_D}{K})^{1/2} (-Z)^{1/2}/C_o , \tag{14}$$

B. Susceptibility Data

For liquids and solids, the relation,

$$f = \chi_V \alpha ,$$

is used as it stands in computing the susceptibility; however, in calculating the susceptibility of a solute in solution, the effect of the solvent must be determined and subtracted from the observed force on the solution. For a solution, the force, f_s, that it experiences is given by

$$f_s = \chi_V^{\text{sol'n}} \alpha \ , \tag{15}$$

where $\chi_V^{\text{sol'n}}$ is the susceptibility per unit volume of the solution. Assuming the magnetic effect to be a molecular property, the following equation holds:

$$\chi_V^{\text{sol'n}} = \chi_M^A [A] + \chi_M^B [B] \tag{16}$$

in which χ_M^A and χ_M^B are the molar susceptibilities of the solute and solvent, respectively, and [A] and [B] are their concentrations as formula weights per cubic centimeter of solution. Equation (16) may also be written as:

$$\chi_V^{\text{sol'n}} = \chi_S^A ([A] \cdot FW_A) + \chi_S^B ([B] \cdot FW_B) \tag{17}$$

$$= \chi_S^A w_a + \chi_S^B w_b$$

in which χ_S^A, χ_S^B are now the specific susceptibilities of the solute and solvent, respectively; FW refers to their formula weights, and w_a and

w_b are their respective concentrations, expressed now as grams per cc of solution. Since

$$w = d \cdot p \qquad (18)$$

where d is the density of the solution and p is the weight fraction of the component of interest, then

$$\chi_V^{sol'n} = \chi_S^A \cdot p_A \cdot d + \chi_S^B \cdot p_B \cdot d \quad . \qquad (19)$$

Hence, the contribution of the solvent to the force is

$$f' = \chi_S' \, p' d\alpha \qquad (20)$$

where the primes now refer to the solvent. The susceptibility per unit volume of the solute in solution, χ_V'', may be obtained, therefore, from the equation

$$\chi_V'' = \frac{f_s - f'}{\alpha} \quad . \qquad (21)$$

The molar susceptibility of the solute is, therefore,

$$\chi_M = \frac{\chi_V''}{c} \qquad (22)$$

where c is the concentration of the solute in formula weights per cc of solution.

CHAPTER IV

RESULTS

A. Magnetic Measurements

In the measurements on solutions the value of the constant, α,

for the Gouy Balance underwent some variation, since the measurements

were made over a period of a year and one half. Its value was on the

order of 44.00×10^6 mg cc. It was checked very frequently during a

given series of measurements.

The calibration constant for the measurement on solid $(NH_4)_2MoOBr_5$

was 7.212×10^6 mg cc.

All magnetic measurements were carried out at a temperature of

23 ± 2 degrees Centigrade.

The susceptibilities of the molybdenum in solution are presented

as the atomic susceptibility of pentavalent molybdenum and were calcu-

lated on the basis of all the molybdenum being monomer. The values for

the specific susceptibilities of the various HCl and HBr solutions were

taken from Cini and Percione (31) or determined in this laboratory. The

diamagnetic increments used for determining the atomic susceptibility,

χ_{Mo}, of the molybdenum were: Mo $- 12 \times 10^{-6}$; $Cl^- - 22.9 \times 10^{-6}$;

$Br^- - 36 \times 10^{-6}$; $O^= - 12 \times 10^{-6}$; $NH_4^+ - 11.5 \times 10^{-6}$ (32). The sum of the

diamagnetic corrections for $(NH_4)_2MoOCl_5$ and $(NH_4)_2MoOBr_5$ is $- 173.5$ and

$- 227$ ($\times 10^{-6}$), respectively. By subtracting these from the molar sus-

ceptibility, χ_M, of the compound, a value for the atomic susceptibility

of the molybdenum, χ_{Mo}, is obtained.

1. $(NH_4)_2MoOCl_5$ in HCl

The susceptibilities of the following hydrochloric acid solutions of Mo(V) were obtained: 10.66F, 9.50F, 8.01F, 7.01F, 5.96F, 4.98F, 4.01F, 2.98F, 1.93F, 0.98F. Three concentrations of molybdenum were used, 0.01003 F, 0.05108F, 0.1003F, all concentrations expressed as monomer, $MoOCl_5^=$.

The specific susceptibilities of the solutions, the specific susceptibilities of the HCl solutions, and the apparent atomic susceptibilities of the molybdenum are presented in Table 2.

In Figure 1 is displayed the specific susceptibilities of solutions of Mo(V) of concentration, 0.05108F, as a function of HCl concentration. The large increase in diamagnetic susceptibility of the solutions between 7.5 and 3 F HCl may be attributed to the formation of diamagnetic dimers. The apparent linear behavior outside this region reflects the presence of only paramagnetic species in the range, 12 to 7.5 F HCl, and only diamagnetic species in the 1 to 3 F HCl solutions.

The atomic susceptibility of the molybdenum, all calculated as monomer, is presented in Figure 2. The data for the most dilute solutions, 0.01003 F Mo(V), is the least reliable as the differences in deflections due to the solute are of the same order of magnitude as the experimental error. The apparent atomic susceptibility in the more concentrated solutions (8-12 F) is essentially constant with an average value of $1250 \times 10^{-6}(gm\ atom)^{-1}$ in good agreement with the values, $1195 \times 10^{-6}(gm\ atom)^{-1}$ (19), and $1229 \times 10^{-6}(gm\ atom)^{-1}$ (15) obtained by measurements on solid $(NH_4)_2MoOCl_5$. The decrease in the apparent atomic

Table 2. Magnetic Susceptibility Data for Mo(V) in Hydrochloric Acid

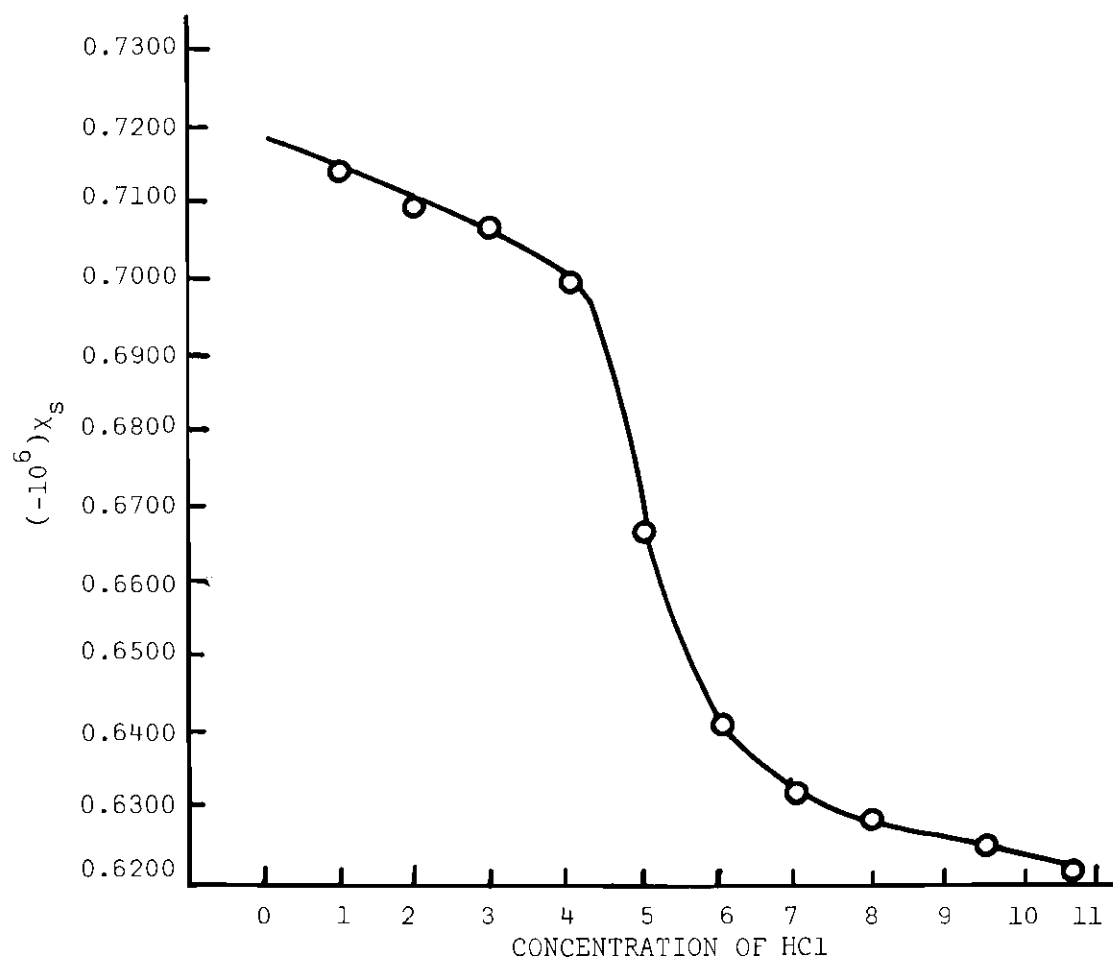| [HCl]	$-\chi_s^{HCl}$ [a]	$C_o = 0.01003$		$C_o = 0.05108$		$C_o = 0.1003$	
		$-\chi_s^{sol'n}$ [a]	χ_{Mo} [a]	$-\chi_s^{sol'n}$ [a]	χ_{Mo} [a]	$-\chi_s^{sol'n}$ [a]	χ_{Mo} [a]
10.66	0.6802	0.6685	1292	0.6220	1288	0.5694	1259
9.50	0.6839	0.6710	1429	0.6256	1266	0.5772	1191
8.01	0.6887	0.6792	1155	0.6284	1293	0.5759	1237
7.01	0.6920	0.6793	1360	0.6324	1257	0.5813	1196
6.50	0.6937	0.6809	1360				
5.96	0.6956	0.6838	1247	0.6415	1119	0.5832	1198
5.31	0.6978					0.6053	954
4.98	0.6989	0.6918	721	0.6664	645	0.6381	612
4.01	0.7028	0.6978	64	0.7000	5	0.6824	165
2.98	0.7070	0.7047	34	0.7078	-71	0.6958	
1.93	0.7114			0.7093	-13	0.7012	48
0.98	0.7156	0.7150		0.7138	-23	0.7050	48

[a] Times factor 10^{-6}.

Figure 1. Specific Susceptibility of Solutions of Mo(V) as
Function of HCl Concentration for
C_O = 0.05108F.
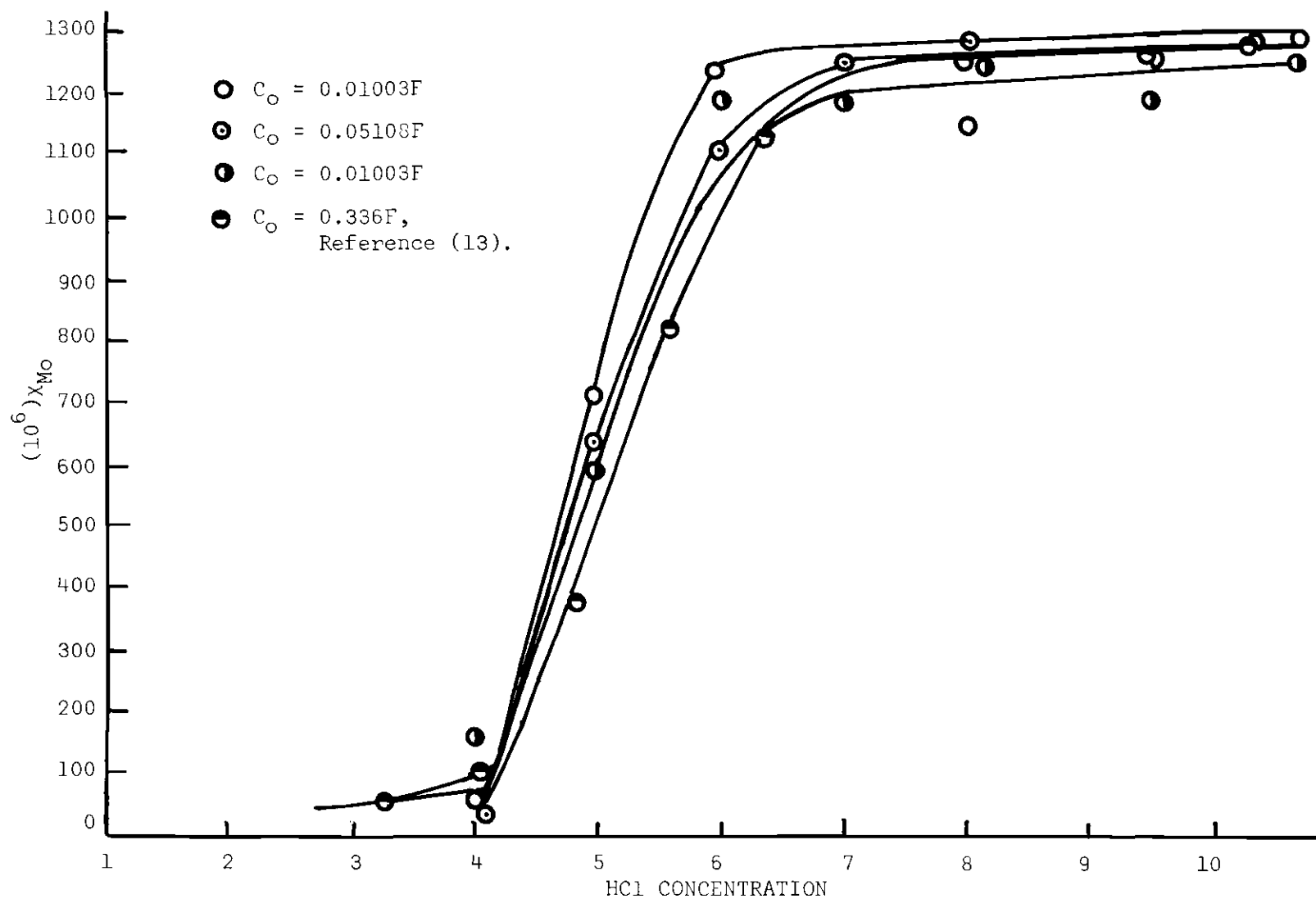
Figure 2. Apparent Atomic Susceptibility of Mo(V) as Function of HCl Concentration.

susceptibility in 7 to 4 F HCl is, of course, due to the formation of diamagnetic dimers. The effect of the dimerization on the molybdenum susceptibility in the range, 7-6 F HCl, is also apparent in Figure 2.

2. $(NH_4)_2MoOBr_5$ in HBr

The atomic susceptibility of molybdenum was determined in solid $(NH_4)_2MoOBr_5$. A value of 1278×10^{-6} (gm atom)$^{-1}$, which compares favorably with the value, 1247×10^{-6} (gm atom)$^{-1}$ determined by Garside (15), was obtained.

The susceptibilities of the following hydrobromic acid solutions of Mo(V) were determined: 8.63F, 7.94F, 6.99F, 6.50F, 6.11F, 5.27F, 4.06F, 2.93F, 1.50F. Some difficulty with the precipitation of molybdenum blue in the 4.06, 2.93, and 1.50 F HBr solutions was experienced. Data obtained from the experiments are presented in Tables 3 and 4, and in Figures 3 and 4. The atomic susceptibility of molybdenum, as determined in the 8.63F HBr solution, is 1360×10^{-6} (gm atom)$^{-1}$ which agrees quite well with the value, 1278×10^{-6} (gm atom)$^{-1}$ for solid $(NH_4)_2MoOBr_5$. The large increase in diamagnetic susceptibility of the solutions in 7.5 to 5F HBr, displayed in Figure 3, and the decrease in the apparent atomic susceptibility of the molybdenum occurring over the same range of acid, as seen in Figure 4, is due, as in the case of the solution in HCl, to the formation of diamagnetic species. The reduction in paramagnetism of the molybdenum occurs in the same range of HBr concentration that the pronounced changes in the absorption spectrum occur. Little reliability can be placed in quantitative interpretation of the data for atomic molybdenum below 6F HBr due to the fact that the diamagnetic contribution of the solvent is nearly as large as that of the solution, and that

Table 3. Susceptibilities of Mo(V) as Functions of HBr Concentration

[HBr]	$-\chi_s^{HBr}$ [a]	C_o	$-\chi_s^{sol'n}$ [a]	χ_{Mo}^a [a]
8.63	0.5679	0.01535	0.5525	1372
8.63	0.5679	0.03732	0.5312	1368
8.63	0.5679	0.07558	0.4963	1339
7.94	0.5763	0.0166	0.5625	1340
7.94	0.5763	0.0320	0.5563	1276
7.94	0.5763	0.0660	0.5485	1292
6.99	0.5887	0.0123	0.5761	1325
6.99	0.5887	0.0364	0.5541	1229
6.99	0.5887	0.07818	0.5227	1094
6.50	0.5955	0.00904	0.5884	971
6.50	0.5955	0.03814	0.5704	788
6.50	0.5955	0.07772	0.5467	772
6.11	0.6011	0.0169	0.5976	396
6.11	0.6011	0.04014	0.5928	325
6.11	0.6011	0.0736	0.5792	303
5.27	0.6138	0.01618	0.6114	116
5.27	0.6138	0.03598	0.6092	58
5.27	0.6138	0.07565	0.6012	105
4.06	0.6337	0.0240	0.6313	2
4.06	0.6337	0.0290	0.6266	173
4.06	0.6337	0.0730	0.6227	67
2.93	0.6545	0.0252	0.6482	155
2.93	0.6545	0.0396	0.6463	114
2.93	0.6545	0.0693	0.6383	146
1.50	0.6842	0.0255	0.6790	68
1.50	0.6842	0.0412	0.6779	31
1.50	0.6842	0.0736	0.6690	83

[a]Times factor 10^{-6}.

Table 4. Magnetic Susceptibility Data for Molybdenum (V)
in HBr Solutions

HBr	$C_o = 0.0665F$			$C_o = 0.0304F$		
	$-\chi_s^{sol'n}$ [a]	χ_{Mo}^a	Fraction Total[b] Paramagnetism	$-\chi_s^{sol'n}$ [a]	χ_{Mo}^a	Fraction Total[b] Paramagnetism
8.63	0.5048	1327		0.5384	1345	
7.94	0.5162	1230	0.905	0.5496	1278	0.941
6.99	0.5342	1058	0.779	0.5619	1132	0.832
6.50	0.5586	665	0.489	0.5771	718	0.528
6.11	0.5802	325	0.239	0.5899	396	0.291
5.27	0.6048	70		0.6110	4	
4.06	0.6218	102		0.6291	71	
2.93	0.6408	122		0.6477	131	
1.50	0.6705	81		0.6785	57	

[a]Times factor, 10^{-6}.

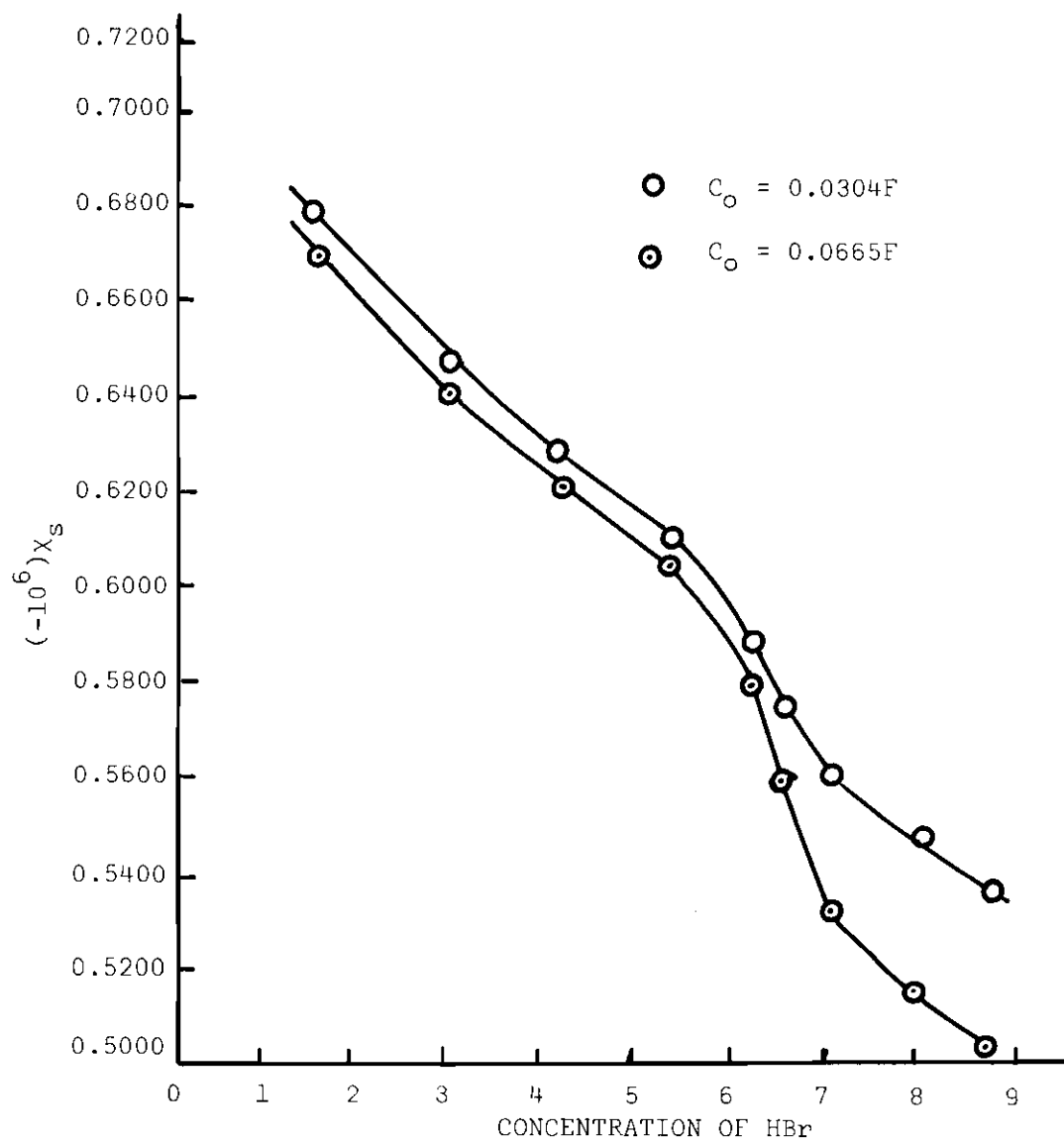[b]Based on $\chi_{Mo} = 1360 \times 10^{-6} (gm\ atom)^{-1}$.

Figure 3. Specific Susceptibility of Solutions of Mo(V)
as Function of HBr Concentration.
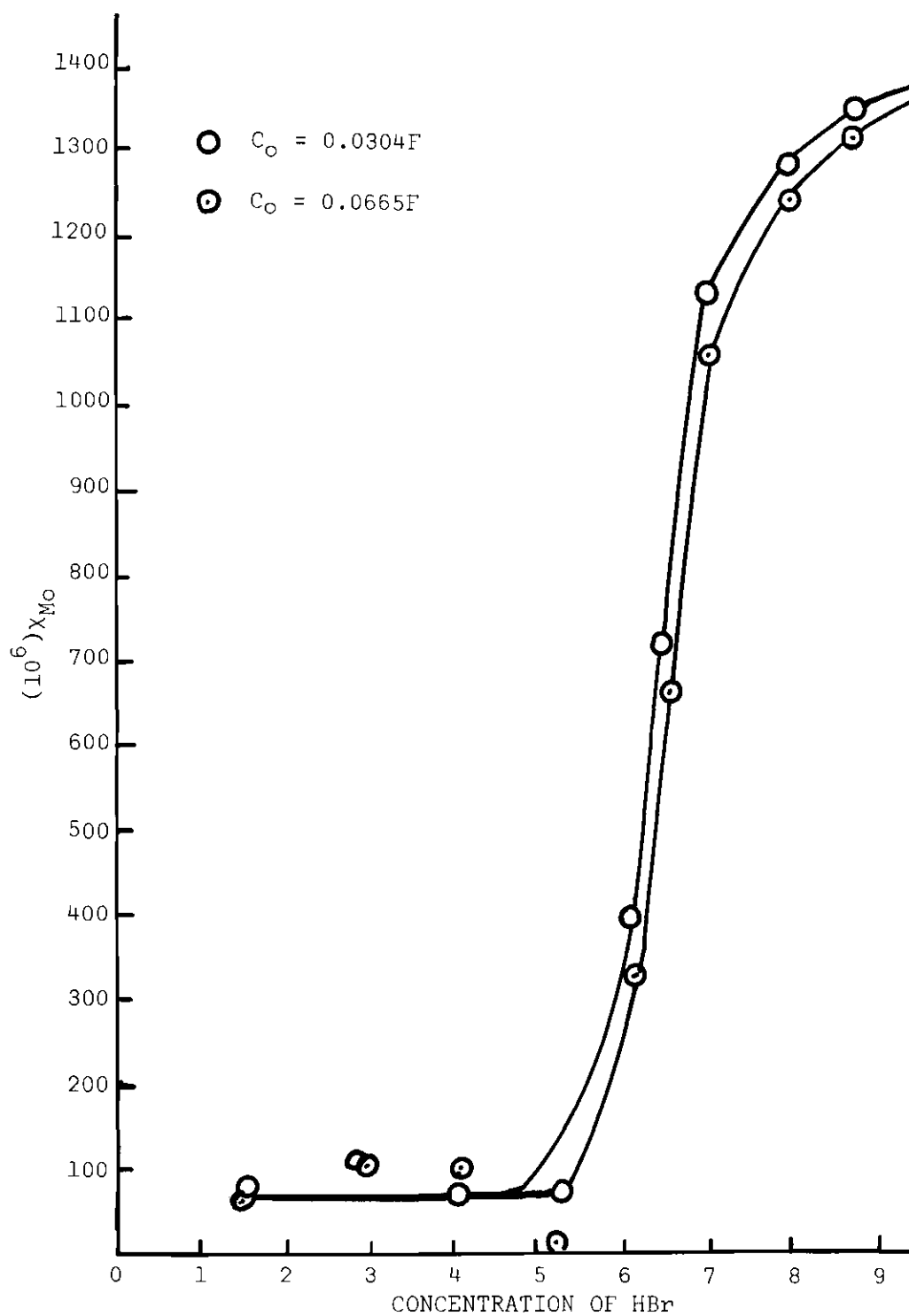
Figure 4. Apparent Atomic Susceptibility of Mo(V) in HBr.

molybdenum blue formation was a problem in the more dilute HBr solutions. As evidenced by the rapid drop off in the values of the atomic suscepti- bility as the HBr concentration is lowered below 8.6F, the range of existence of paramagnetic species is much smaller than in the chloride case.

B. Absorbance Measurements

1. $(NH_4)_2MoOCl_5$ in HCl

Solutions of Molybdenum (V) in HCl are known to follow the Beer- Lambert Law in 12 to 8F HCl, indicating the presence of only monomer, $MoOCl_5^=$.

The wavelength selected for study of the monomer-dimer equilibria was 520 millimicrons as the $MoOCl_5^=$ absorbs very weakly there. Any in- crease in intensity at this wavelength would be practically all due to the presence of other species. The value of ε_M at 520 mμ, evaluated in 12.05F HCl, was found to be 0.43 1/mole cm^{-1} (Table 5).

The absorbances of solutions of molybdenum (V) ranging in concen- tration from 0.002 to 0.1F in 7.01, 6.49, 5.96, 4.98, 4.01, 2.98, 1.93, 0.98F HCl were measured at this wavelength. The results are tabulated in Table 6 and shown in Figure 5. The results obtained through treat- ment of the data according to Equation (13) in Chapter 3 are shown in Table 6 and are consistent with the assumptions leading to Equation (13).

The changes in the values of ε_D as the concentration of HCl is lowered, Table 7, suggest that at least three dimers are involved in the 7 to 4F HCl range. The values of K are, of course, constant only

Table 5. Absorbance Data for Mo(V) in 12.05,
2.98, 1.93, and 0.98F HCl[a]

12.05F HCl			2.98F HCl		
C_o	A_{520}[b]	A/C_o	C_o	A_{520}	A/C_o
0.1025	0.0438	0.43 ± 0.005	0.04981	0.811	16.3 ± 0.2
0.08200	0.0342	0.42 ± 0.001	0.02490	0.408	16.4 ± 0.1
0.05012	0.0212	0.42 ± 0.002	0.01992	0.333	16.7 ± 0.3
0.02562	0.0100	0.39 ± 0.02	0.00996	0.165	16.6 ± 0.3
			0.00498	0.083	16.7 ± 0.5

1.93F HCl			0.98F HCl		
C_o	A_{520}	A/C_o	C_o	A_{520}	A/C_o
0.05463	0.711	13.0 ± 0.1	0.05255	0.623	11.9 ± 0.1
0.02732	0.359	13.2 ± 0.1	0.02628	0.315	12.0 ± 0.2
0.02185	0.293	13.4 ± 0.2	0.02102	0.258	12.3 ± 0.2
0.01093	0.146	13.4 ± 0.3	0.01051	0.128	12.2 ± 0.3
0.005463	0.074	13.6 ± 0.6			

[a]All data given for light path of 1 cm unless otherwise indicated.

[b]5 cm light path used.

Table 6. Absorbance Data for Molybdenum (V)
in HCl, λ = 520mμ

| HCl, conc'n (FW/L)	c_o	A	A/c_o	$\dfrac{1}{z^{2}}/c_o$	Light Path
7.01	0.1026	0.373	3.63	5.59	1 cm
7.01	0.08208	0.248	3.02	5.63	1 cm
7.01	0.05130	0.116	2.26	5.98	1 cm
7.01	0.02052	0.025[a]	1.22	6.14	5 cm
7.01	0.01026	0.0094[a]	0.916	6.96	10 cm
6.49	0.06534	0.526	8.05	10.69	1 cm
6.49	0.04081	0.239	5.85	11.50	1 cm
6.49	0.03265	0.151	4.62	11.35	1 cm
6.49	0.02614	0.105	4.01	11.75	1 cm
6.49	0.02040	0.066	3.23	11.72	1 cm
6.49	0.01143	0.0234[a]	2.05	11.91	5 cm
6.49	0.008162	0.0134[a]	1.64	12.26	5 cm
5.96	0.05303	1.29	24.3	21.2	1 cm
5.96	0.04945	1.14	23.0	21.4	1 cm
5.96	0.04242	0.875	20.6	21.8	1 cm
5.96	0.03950	0.785	19.8	22.1	1 cm
5.96	0.02652	0.376	14.2	22.7	1 cm
5.96	0.01061	0.0610[a]	5.75	22.4	1 cm
4.98	0.02539	1.63	64.1	50.1	1 cm
4.98	0.01990	1.14	57.2	53.4	1 cm
4.98	0.01523	0.810	53.2	58.9	1 cm
4.98	0.01433	0.767	53.5	60.8	1 cm
4.98	0.01270	0.619	48.7	61.7	1 cm
4.98	0.01016	0.466	45.9	66.9	1 cm
4.98	0.00995	0.443	44.5	66.6	1 cm
4.98	0.00716	0.275	38.5	72.8	1 cm
4.98	0.00508	0.155	30.5	77.0	1 cm
4.01	0.04046	1.21	29.9	26.9	1 cm
4.01	0.03237	0.92	28.4	29.5	1 cm
4.01	0.02428	0.701	28.8	34.2	1 cm
4.01	0.02023	0.571	28.2	37.2	1 cm
4.01	0.01618	0.453	28.0	41.3	1 cm
4.01	0.008092	0.220	27.2	57.6	1 cm

[a]Corrected to a path length of 1 cm.
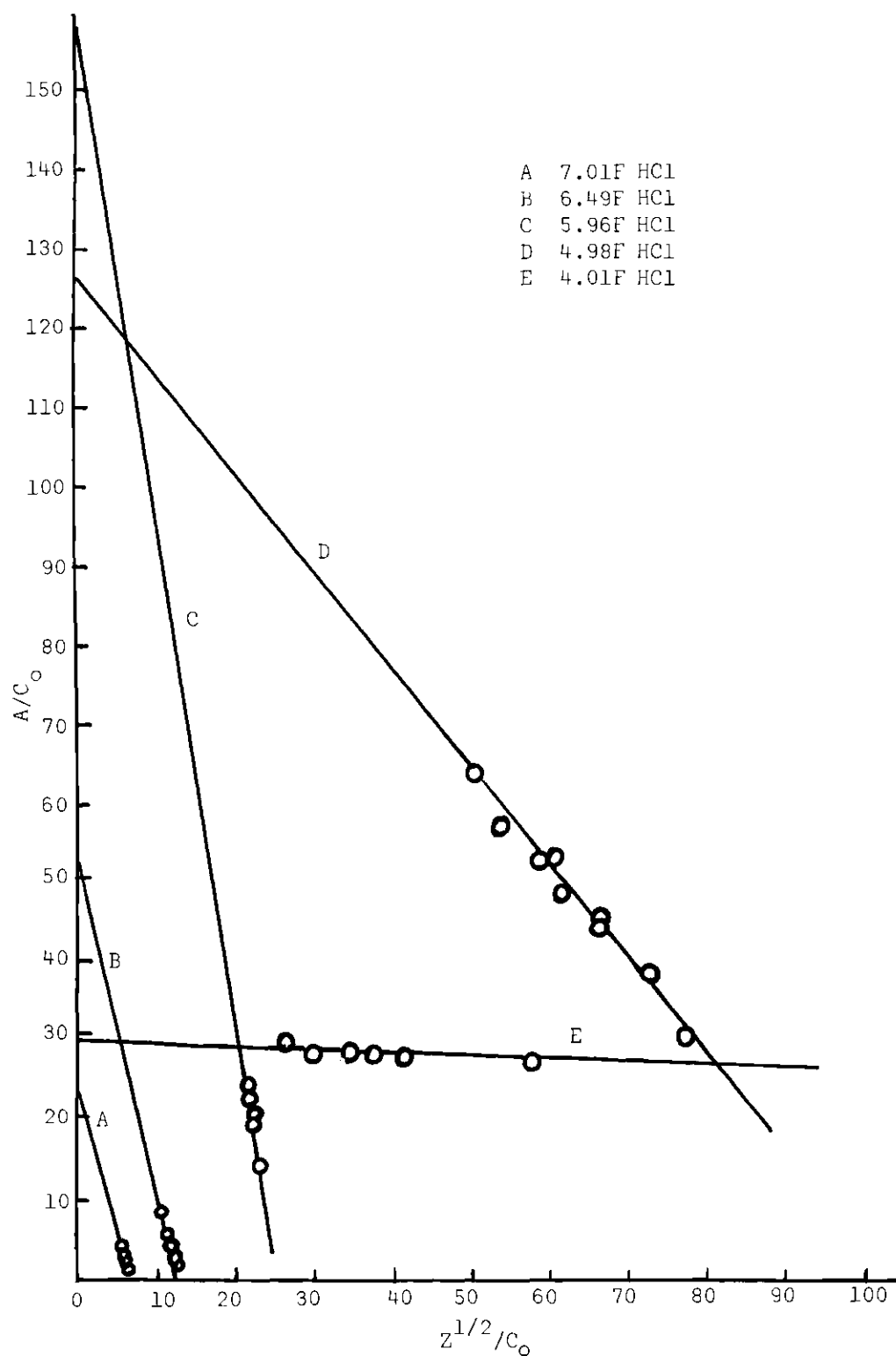
Figure 5. Graph of A/C_O vs. $Z^{1/2}/C_O$ for Mo(V) in HCl, at λ = 520mµ.

Table 7. Equilibrium Data for Molybdenum (V) in HCl

HCl, (FW/L)	K	ε_D	Color of Solution
7.01	0.80 ± 0.04	50 ± 5	Light Green
6.49	1.44 ± 0.16	110 ± 27	Yellow Green
5.96	2.02 ± 0.15	312 ± 25	Dark Brown
4.98	48 ± 2	244 ± 10	Dark Brown
4.01	$7.0(\pm 2.8) \times 10^3$	60 ± 6	Red Brown

for a fixed HCl concentration. The 7.01F HCl solution contains mostly just one dimer in equilibrium with the monomer. Increasing amounts of the second dimer in the 6.49 and 5.96F solutions are manifested by the large increase in ε_D. It is this second dimer that is responsible for the dark brown color in the solutions. The decrease in ε_D in the 4.98 and 4.01F solutions reflect the occurrence of dimers that have little or no absorption at this wavelength. As predicted by Equation (8) in Chapter 3, ε_D will decrease once the concentration of non-absorbing species has become appreciable. Since the 2.98, 1.93, 0.98F HCl solutions obey the Beer-Lambert Law (Table 5), there is no longer any $MoOCl_5^=$ in these solutions and no further polymerization of the molybdenum occurs. Since the apparent atomic susceptibility decreases in solutions of about 7 to 4F HCl, it may be concluded that the dimer responsible for the increased absorption and the brown color is diamagnetic. The dimer which appears first in the 8 to 7F HCl region is

paramagnetic since the apparent atomic susceptibility shows no pronounced
decrease until the HCl concentration is below 7F where the concentration
of the second dimer becomes appreciable. All of the other species in
HCl are diamagnetic.

2. $(NH_4)_2MoOBr_5$ in HBr

An earlier spectrophotometric study of Mo(V) in HBr (21) reported
that solutions in 6.2F, 5.2F, and 1.0F HBr follow the Beer-Lambert Law.
However, the solutions had relatively low concentrations of Mo(V), the
highest concentration being 4×10^{-4}F. It was decided to examine solu-
tions at higher molybdenum concentrations. Solutions in 5.01, 5.27,
7.94, and 8.72F HBr followed the Beer-Lambert Law (see Table 8). How-
ever, solutions in 6.99, 6.50, and 6.11F HBr do not follow the Beer-
Lambert Law, thus indicating that some sort of association is occurring
in this region of acidity.

It was decided to collect and treat the absorbance data in the
same manner as in the HCl solutions. The solutions studied were 6.99,
6.50, and 6.11F HBr. It was not possible to find a wavelength at which
the species characteristic of the highest acidity had negligible absorp-
tion while the associated species had appreciable absorption at the same
wavelength. Nevertheless the wavelength, 700mμ, was selected. The value
of ε_M, determined in 8.72F HBr, was found to be 18.5 1/mole cm^{-1} (Table
8). The results in Tables 9 and 10, and Figure 6, indicate that the
notion of dimerization-equilibria occurring in HBr is consistent with
the data.

The results in Tables 3, 4, and 10 indicate that the dimer re-
sponsible for the increased absorption intensity at that wavelength is

Table 8. Absorbance Data for Mo(V) in 8.72,
7.94, 5.27, and 5.01F HBr[a]

8.72F HBr			7.94F HBr		
C_o	A_{700}	A/C_o	C_o	A_{700}	A/C_o
0.04997	0.92	18.4 ± 0.2	0.05125	0.968	18.9 ± 0.2
0.03998	0.707	17.7 ± 0.1	0.04100	0.770	18.8 ± 0.1
0.02998	0.547	18.2 ± 0.1	0.03075	0.581	18.9 ± 0.1
0.01999	0.371	18.6 ± 0.2	0.02050	0.388	18.9 ± 0.1
0.00999	0.196	19.6 ± 0.3	0.01025	0.196	19.1 ± 0.4
			0.005125	0.098	19.1 ± 0.4

5.27F HBr[b]			5.01 F HBr		
C_o	A_{700}	A/C_o	C_o	A_{700}	A/C_o
0.09998	0.722	7.2	0.0562	0.180	3.2 ± 0.1
0.07998	0.498	6.2	0.0337	0.097	2.9 ± 0.1
0.03999	0.185	4.6	0.0281	0.081	2.9 ± 0.1
0.02000	0.085	4.5	0.0112	0.036	3.2 ± 0.2
0.009998	0.040	4.0	0.00562	0.017	3.0 ± 0.4

[a]All data given for light path of 1 cm unless contraindicated.

[b]The deviations from the Beer-Lambert Law at the highest concentrations of Mo(V) are apparent; the dimerization-hydrolysis of $MoOBr_5^-$ in these solutions results in the production of H^+ and Br^- ions which can increase the acidity markedly at the highest concentrations.

Table 9. Absorbance Data for Molybdenum (V) in HBr
$\lambda = 700m\mu$

HBr, (FW/L)	C_o	A	A/C_o	$z^{\frac{1}{2}}/C_o$	Light Path
6.99	0.02896	0.96	33.1	22.5	1 cm
6.99	0.02317	0.698	30.1	22.4	1 cm
6.99	0.01738	0.486	28.0	23.3	1 cm
6.99	0.01448	0.390	26.9	24.1	1 cm
6.99	0.01158	0.297	25.6	24.9	1 cm
6.99	0.007240	0.170	23.5	26.2	1 cm
6.99	0.005792	0.130	22.5	25.5	1 cm
6.50	0.02070	1.03	49.7	38.9	1 cm
6.50	0.1656	0.770	46.5	41.1	1 cm
6.50	0.01240	0.532	42.9	44.4	1 cm
6.50	0.01035	0.422	40.7	46.3	1 cm
6.50	0.00888	0.317	38.3	48.9	1 cm
6.50	0.00414	0.133	32.1	57.2	1 cm
6.11	0.02243	0.836	37.3	28.9	1 cm
6.11	0.01794	0.643	35.8	31.1	1 cm
6.11	0.01346	0.477	35.4	35.5	1 cm
6.11	0.01122	0.394	35.1	38.5	1 cm
6.11	0.008972	0.308	34.3	42.0	1 cm
6.11	0.004486	0.141	31.4	53.7	1 cm

Table 10. Equilibrium Data for Molybdenum (V) in HBr

[HBr]	ϵ_D	K	Color of Solution
6.99	149 ± 10	7.2 ± 0.2	Dark Brown
6.50	182 ± 4	42 ± 1	Dark Brown
6.11	88 ± 2	235 ± 6	Dark Brown

Table 11. Comparison of Amounts of Paramagnetic Species with Monomer in 6.99, 6.50, and 6.11F HBr

HBr	C_o = 0.0665F		C_o = 0.0304F	
	Fraction[a] Total Paramagnetism	Fraction[b] Monomer	Fraction[a] Total Paramagnetism	Fraction[b] Monomer
6.99	0.779 ± 0.053	0.621 ± 0.005	0.832 ± 0.054	0.752 ± 0.005
6.50	0.489 ± 0.057	0.343 ± 0.003	0.528 ± 0.048	0.461 ± 0.004
6.11	0.239 ± 0.055	0.164 ± 0.002	0.291 ± 0.064	0.231 ± 0.004

[a]See Table 4.

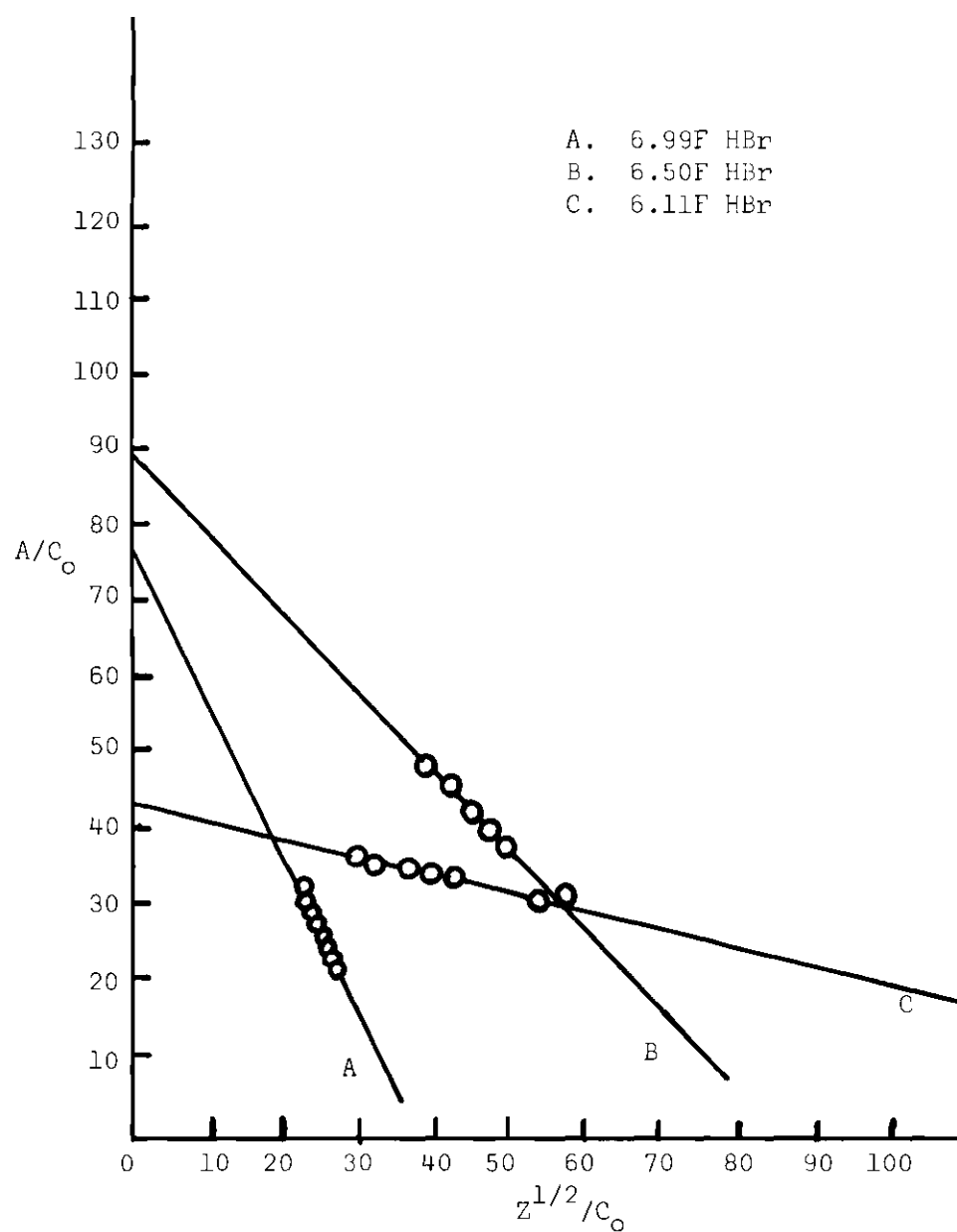[b]Computed using Equation (4) in Chapter III.

Figure 6. Graph of A/C_o vs. $Z^{1/2}/C_o$ for Mo(V) in HBr, at $\lambda = 700m\mu$.

diamagnetic. There is also a paramagnetic species present in the same solutions with the diamagnetic dimer since the paramagnetism in the solutions is greater than that corresponding to the monomer alone. This will be noted by an inspection of Table 11, in which the fractions of paramagnetic species and the fractions of monomer at each acidity studied are presented, along with their maximum errors. The decrease in ε_D in the 6.11F HBr solution indicates the presence of a third associated species that does not absorb at the wavelength. Solutions in 5F HBr or lower follow the Beer-Lambert Law, indicating no further polymerization, Table 8.

Since the absorbance and magnetic data suggest strongly the existence of monomeric $MoOBr_5^=$ in concentrated HBr, efforts were made to redetermine the spectrum of the material.

It was found to be impossible to obtain a KBr disc of $(NH_4)_2MoOBr_5$ that did not show signs of hydrolysis and molybdenum blue formation.

The relatively non-hygroscopic compound, $(C_9H_8N)_2MoOBr_5$, was examined in a KBr pellet. The ultraviolet and visible spectrum showed the following maxima: $14,290$ cm^{-1}($670m\mu$); $21,280$ cm^{-1}($470m\mu$); $23,530$ cm^{-1}($425m\mu$); $25,840$ cm^{-1}($387m\mu$). The spectrum is illustrated in Figure 7. The band near $14,000$ cm^{-1} has also been studied in solids, $(R)_2MoOBr_5$ where R is Rb, Cs, and C_5H_6N, by E. A. Allen and co-workers (12) who found it near $14,080$ cm^{-1}($710m\mu$), and by Wentworth and Piper (20) who found it centered near $14,400$ cm^{-1}($694m\mu$) in solid $(NH_4)_2MoOBr_5$. It is clear that the spectrum of solid $(C_9H_8N)_2MoOBr_5$ is virtually identical to the spectrum of molybdenum (V) in concentrated HBr in which
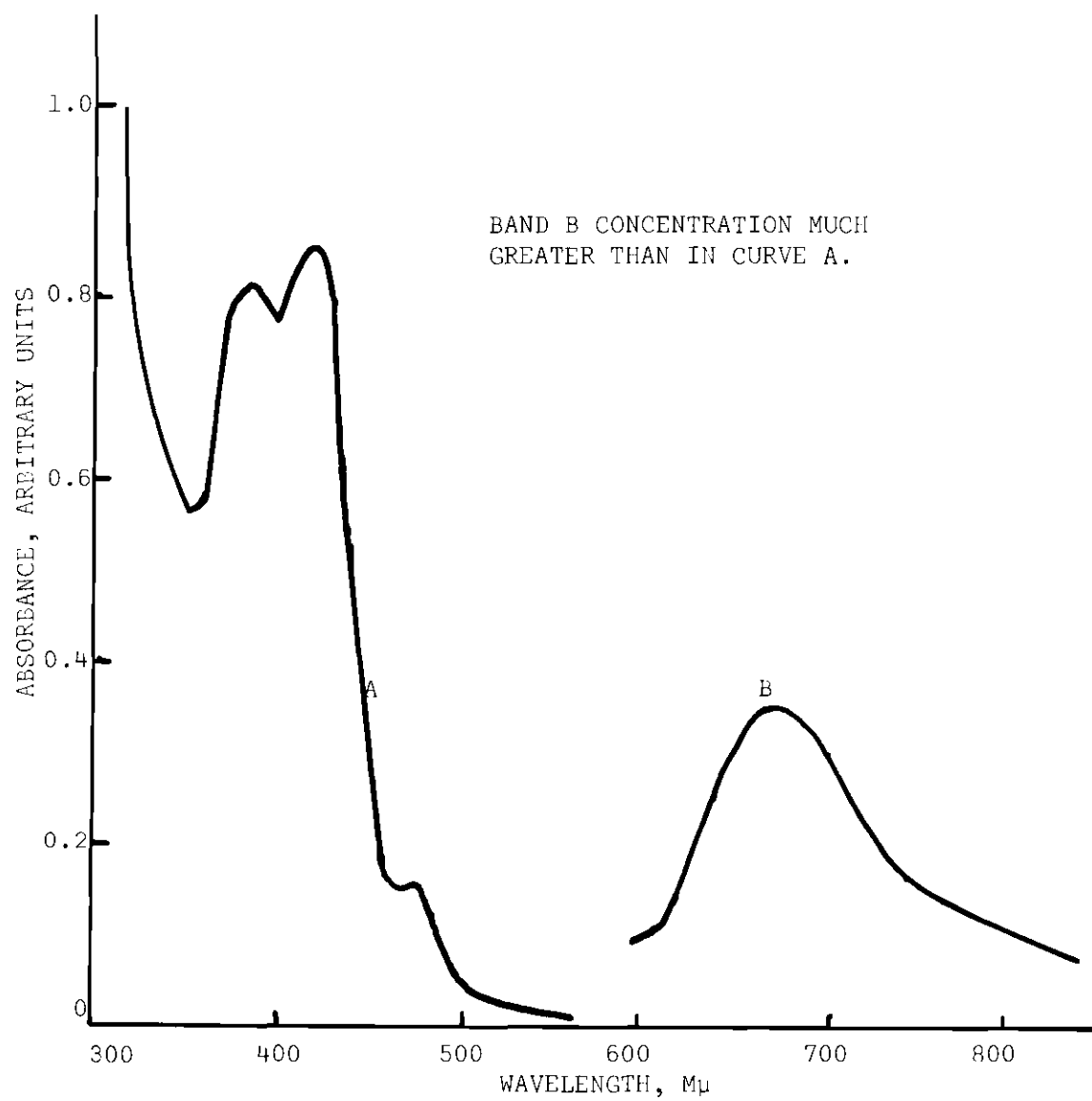
Figure 7. Absorption Spectrum of $(C_9H_8N)_2MoOBr_5$ in KBr Disc.

absorption maxima occur near 14,290 cm^{-1}(700mμ); 21,280 cm^{-1}(470mμ);
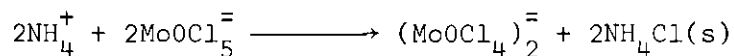
24,100 cm^{-1}(415mμ); 26,530 cm^{-1}(377mμ) (12).

C. Solutions in Acetone and Ethanol

It was observed that solid $(NH_4)_2MoOCl_5$ dissolved in absolute

ethanol to deposit a tan precipitate and to yield a brown solution. Over

a period of 10 to 14 days the brown solution turned green. When the

brown solution was evaporated, it also turned green as it became more

concentrated. Solid $(NH_4)_2MoOCl_5$ also reacted to yield the same solid

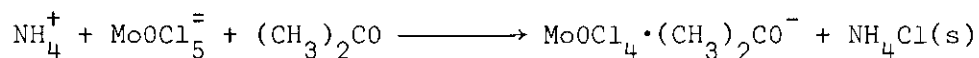and a green solution immediately in acetone.

The acetone and brown ethanol solutions obey the Beer-Lambert

Law while the green ethanol solutions exhibit negative deviations

(Table 12). Consistent with these observations is the existence of an

equilibrium between monomers and dimers in the green ethanol solutions,

and no such equilibria in the other solutions.

Magnetic measurements indicate that the molybdenum in the alcohol

and acetone solutions is paramagnetic (Table 13).

A careful determination of the weight of solid remaining after

$(NH_4)_2MoOCl_5$ was dissolved in acetone indicated that the reaction,

$$2NH_4^+ + 2MoOCl_5^= \longrightarrow (MoOCl_4)_2^= + 2NH_4Cl(s)$$

or possibly,

$$NH_4^+ + MoOCl_5^= + (CH_3)_2CO \longrightarrow MoOCl_4 \cdot (CH_3)_2CO^- + NH_4Cl(s)$$

has occurred. The solid dissolved readily in water and exhibited the usual qualitative tests for ammonium and chloride ions. The discoloration was attributed to the occlusion of traces of molybdenum. A chloride determination on the acetone solution confirmed the expected 4:1 chloride to molybdenum ratio.

Because NH_4Cl is insoluble in acetone any reaction, such as,

$$2NH_4^+ + MoOCl_5^= \longrightarrow MoOCl_3 + 2NH_4Cl,$$
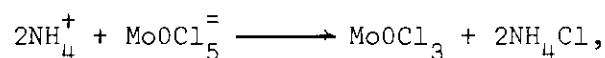
may be excluded. Because of the solubility of NH_4Cl in ethanol a similar unambiguous interpretation is not possible for such solutions. However, it seems unlikely that $MoOCl_3$ would exist in the presence of Cl^- in ethanol (which coordinates less well than acetone) when it does not exist in acetone in the absence of Cl^-.

The apparent extinction coefficients, A/C_o, of the green ethanol solutions decrease with increasing molybdenum concentration (Table 12), indicating a value of greater than 31 for the monomer and less than 8 for the dimer. Assuming that the single species in the brown ethanol solution is one of the two in the green ethanol solution, one is led to the conclusion that it is the monomer. The resemblance of the acetone solution and the green ethanol solution thus suggests the existence of a dimer in these solutions.

Spectral data for solutions of $(NH_4)_2MoOCl_5$ in acetone and 11.86F HCl are presented in Table 14. The spectra are very similar. Absorption by the acetone prevented observation of bands in the ultraviolet.

It was not possible to study $(NH_4)_2MoOBr_5$ in ethanol due to the

Table 12. Absorbance Data for Molybdenum (V) in
Ethanol and Acetone Solutions[a]

$(NH_4)_2MoOCl_5$ in Ethanol

Brown Ethanol Solution			Green Ethanol Solution		
C_o	A_{520}	A/C_o	C_o	A_{520}	A/C_o
0.02	1.18	59	0.05	0.410	8.2
0.01	0.613	61	0.02	0.329	16.4
0.006	0.376	63	0.01	0.241	24.1
0.005	0.304	61	0.006	0.180	30.0
			0.005	0.154	31.0

$(NH_4)_2MoOCl_5$ in Acetone			$(NH_4)_2MoOBr_5$ in Acetone		
C_o	A_{450}	A/C_o	C_o	A_{700}	A/C_o
0.04066	0.582	14.3	0.07878	1.571	19.9
0.03050	0.429	14.1	0.04727	0.935	19.8
0.02542	0.359	14.1	0.03939	0.797	20.2
0.02033	0.292	14.4	0.03151	0.640	20.3
0.01017	0.145	14.3	0.01576	0.326	20.7
			0.007878	0.170	21.6

[a]Light path is one centimeter.

Table 13. Magnetic Data for Molybdenum (V), C_o = 0.05F
In Non-Aqueous Solvents

Compound	Solvent	$-f_{Solution}$ (mg)	$-f_{Solvent}$ (mg)	f_{Mo} [a,b,c]
$(NH_4)_2MoOCl_5$	Acetone	41.19	43.82	2.63
$(NH_4)_2MoOCl_5$	Ethanol, Green Solution	46.83	49.01	2.18
$(NH_4)_2MoOCl_5$	Ethanol, Brown Solution	46.83	49.00	2.17
$(NH_4)_2MoOBr_5$	Dimethyl Sulfoxide	51.24	50.98	-0.26
$(NH_4)_2MoOBr_5$	Acetone	41.12	43.78	2.66

[a] Obtained by subtracting fourth column from third column.

[b] Values of f_{Mo} are approximate in that no allowance has been made for there being less solvent in the solution than in the pure liquid.

[c] Positive sign denotes a paramagnetic solute; negative sign, diamagnetic solute

rather rapid formation of molybdenum blue. The behavior of $(NH_4)_2MoOBr_5$ in acetone is analogous to that of $(NH_4)_2MoOCl_5$. The solutions obey the Beer-Lambert Law (Table 12) and they contain a paramagnetic species, data in Table 13. The bromide ion concentration in the solutions was found to be four times that of the molybdenum concentration. It is then reasoned that the species, $(MoOBr_4)_2^=$, exists in these solutions, although the possibility of it being $MoOBr_4 \cdot (CH_3)_2CO^-$ cannot be entirely discounted.

A yellow brown solution, very similar in appearance to solutions in concentrated HBr, was formed when $(C_9H_8N)_2MoOBr_5$ was dissolved in acetone. No deposit formed when the material was dissolved. Since C_9H_8NBr is soluble in acetone, the existence of the $MoOBr_5^=$ ion in acetone solution is possible. The spectral features of the acetone solutions of $(NH_4)_2$ $MoOBr_5$ and $(C_9H_8N)_2MoOBr_5$ are presented in Table 15. For comparison, data taken from (12) for Mo(V) in concentrated HBr is presented. Relative to the HBr solution, the absorption bands of the acetone solutions undergo red shifts, and the band near 470 mμ has apparently undergone some sort of solvolysis reaction resulting in a loss of intensity in both acetone solutions. The important thing to notice, however, is the intensity of the various other bands. The intensities of the bands of the acetone solution of $(C_9H_8N)_2MoOBr_5$ are very similar to those of the corresponding bands of Mo(V) in HBr, whereas those of the solutions obtained by dissolving $(NH_4)_2MoOBr_5$ in acetone are not. From these data and the spectrum of solid $(C_9H_8N)_2MoOBr_5$ it is deduced that the spectrum of Mo(V) in concentrated HBr is that of the $MoOBr_5^=$ ion.

Solutions of $(NH_4)_2MoOBr_5$ in dimethyl sulfoxide showed the same spectra as those reported by J. F. Allen and Neumann (21), but a measure-

ment of the magnetic force on such solutions indicated that the molyb-
denum species were diamagnetic (Table 13). Thus, solutions in dimethyl
sulfoxide could not possibly contain the $MoOBr_5^=$ ion.

Table 14. Visible Spectral Features of Molybdenum (V)
in Acetone and HCl[a].

$(NH_4)_2MoOCl_5$ in Acetone			$MoOCl_5^=$ in 11.86F HCl		
λ Max (mμ)	cm^{-1}	A/C_o	λ max (mμ)	cm^{-1}	A/C_o
737	13,600	18.5	710	14,100	16.6
450	22,250	13.9	448	22,300	14.0

[a]Pathlength is one centimeter.

Table 15. Visible and Ultraviolet Spectral Features
of Molybdenum (V) in Acetone and HBr[a]

$(C_9H_8N)_2MoOBr_5$ in Acetone			$(NH_4)_2MoOBr_5$ in Acetone			$Mo(V)$[b] in 8.6F HBr		
λ Max (mμ)	cm^{-1}	A/C_o	λ Max (mμ)	cm^{-1}	A/C_o	λ Max (mμ)	cm^{-1}	A/C_o
735	13,600	18.0	735	13,600	19.4	700	14,290	17
489	20,450	180	490	20,400	295	470	21,280	560
420	23,800	3020	422	23,700	4580	415	24,100	3200
384	26,040	2580	384	26,040	3700	377	26,530	2500

[a]Light path is one centimeter.

[b]Data of E. A. Allen, *et al.* (12).

CHAPTER V

CONCLUSIONS

A. $(NH_4)_2MoOCl_5$ in HCl

The results summarized in Table 7 point to the existence of at least three dimers in 7 to 4F HCl solutions. The first dimer appearing at 7F HCl, is paramagnetic and has a small absorption at 520 mμ.

The second dimer, which predominates in 5-6F HCl, is the one identified by Haight (17). From spectrophotometric studies in the 5-6F HCl region he postulated the existence of only one dimer in equilibrium with $MoOCl_5^=$

$$2 \ MoOCl_5^= + H_2O \ \Longleftrightarrow \ (MoOCl_4)_2O^{-4} + 2 \ H^+ + 2 \ Cl^-$$
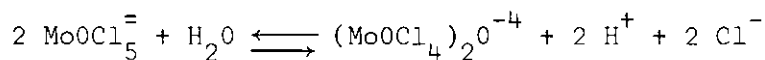
He reported equilibrium constants of 56 in 5F HCl and 3.9 in 6F HCl. His data for the 6F HCl solution has a large scatter, and the extrapolation technique he used is not really feasible in this case. It appears that he assumed the same intercept as for the 5F HCl solutions and did the extrapolation accordingly, thus obtaining the conclusion that there was only one dimer present. Studying the hydrogen and chloride ion dependences led to the proposed species, $(MoOCl_4)_2O^{-4}$. There is no reason to question his formulation of this dimer. It can now be concluded that this dimer is diamagnetic.

The paramagnetic dimer must have a formula consistent with its

appearance between $MoOCl_5^=$ and $(MoOCl_4)_2O^{-4}$ as the HCl concentration is lowered. It is postulated to be $(MoOCl_4)_2^=$.

It is possible to obtain estimates of the two equilibrium constants corresponding to the dimerizations

$$2\ MoOCl_5^= \rightleftharpoons (MoOCl_4)_2^= + 2\ Cl^-$$

$$2\ MoOCl_5^= + H_2O \rightleftharpoons (MoOCl_4)_2O^{-4} + 2H^+ + 2\ Cl^-$$
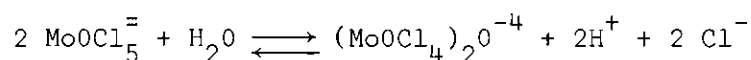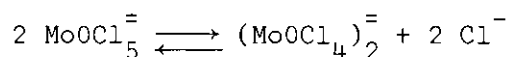
A measure of the concentration of the paramagnetic dimer is obtained from the difference in the fraction of the total paramagnetism and the concentration of monomer at a given acid concentration.

At a given acid concentration, the two equilibrium constants are formulated now as

$$K_c^{(1)} = [D_1]/[M]^2 \quad and \quad K_c^{(2)} = [D_2]/[M]^2$$

in which M is $MoOCl_5^=$, D_1 is $(MoOCl_4)_2^=$, and D_2 is $(MoOCl_4)_2O^{-4}$.

The equilibria are now formulated as thermodynamic constants:

$$K_a^{(1)} = \frac{[D_1][a_{Cl^-}]^2}{[M]^2} = K_c^{(1)}[a_{Cl^-}]^2$$

$$K_a^{(2)} = \frac{[D_2][a_{H^+}]^2[a_{Cl^-}]^2}{[M]^2[a_{H_2O}]} = K_c^{(2)}\frac{[a_{H^+}]^2[a_{Cl^-}]^2}{[a_{H_2O}]}\ .$$

Once one knows $K_c^{(1)}$ and $K_c^{(2)}$ for any solution, then the K_a's

may be computed, and then the K_c's can be calculated for any other solution. In computing the K_c's, [M] is calculable from Equation (4) in Chapter III and the data in Table 5. $[D_1]$ can be computed from the relation,

$$[D_1] = \frac{fC_o - [M]}{2} \quad ,$$

the new symbol, f, is the fraction of total paramagnetism and is the ratio of the apparent atomic susceptibility to the atomic susceptibility of the monomer at any acid concentration. $[D_2]$ is obtainable by subtracting the concentrations of the other species from C_o. It is assumed that the activities of the monomer and dimers are equal to their concentrations and that the activities of the hydrogen ions and chloride ions can be approximated by the mean activities. The activity data was taken from Akerlof and Teare (33). The data for the 4.98F HCl solutions seemed most amenable to treatment, although there is a third dimer whose concentration is being neglected at this HCl concentration. The values of the K_a computed are: $K_a^{(1)} = 2.85(\pm 0.60) \times 10^3$; $K_a^{(2)} = 2.70(\pm 0.50) \times 10^6$. The values of the activities used in 4.98F HCl were: HCl, 15.4; water, 0.717 (33). The values of the K_c's obtained by inserting the appropriate values of the activities in the thermodynamic constants are shown in Table 16. The sum, $K_c^{(1)} + K_c^{(2)}$, should be comparable to the values for K reported in Table 7. The computed values are higher, due primarily to the neglect of the third dimer in the 4.98F HCl solution.

Table 16. Estimates of Equilibrium Constants for
Dimerizations in HCl, (T = 25°C)

[HCl], FW/L	$K_c^{(1)}$	$K_c^{(2)}$	K_T, $K_c^{(1)} + K_c^{(2)}$	$a_\pm^a$	$a_{H_2O}^a$
5	12	33	45	15.6	0.715
6	3.5	2.6	6.1	28.4	0.627
6.5	2.4	1.2	3.6	34.1	0.581
7	1.1	0.21	1.3	51.1	0.536
8	0.35	0.02	0.37	89.6	0.448
9	0.12	0.00	0.12	154	0.367

[a]Akerlof and Teare (33).

Table 17. Calculated Equilibrium Constants
for Dimerizations in HBr
(T = 25°C)

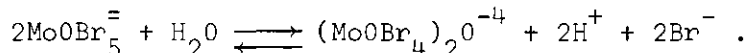| [HBr], FW/L	$K_c^{(1)}$	$K_c^{(2)}$	K_T
6.99	3.9	3.3	7.2
6.50	10	32	42
6.11	20	215	235

B. $(NH_4)_2MoOBr_5$ in HBr

There seems little doubt that the molybdenum species present in concentrated HBr is the $MoOBr_5^=$ ion. The same equilibria are involved as occur with molybdenum in HCl. The existence of $MoOBr_5^=$ over a much smaller range of acid concentration than the $MoOCl_5^=$ ion is the main difference between the two systems.

The conclusion reached by J. F. Allen and Neumann (21) that the spectrum of Mo(V) in concentrated HBr was due to the $(MoOBr_4)_2^=$ ion appears now to be untenable. The critical point in their work was the observation that the spectra of concentrated HBr solutions of Mo(V) were dissimilar to the spectrum of solid $(NH_4)_2MoOBr_5$. Their absorbance data for the Mo(VI)—Mo(V) equilibrium cannot, by itself, offer a decisive choice between the species being monomeric or dimeric in HBr. Due to the hygroscopic nature of $(NH_4)_2MoOBr_5$, this compound hydrolyzes even while dispersed in the KBr medium, and the spectrum they report as that of the $MoOBr_5^=$ ion is probably that of the hydrolyzed material.

The equilibria involved in 8.7 to 6F HBr are, therefore,

$$2MoOBr_5^= \rightleftharpoons (MoOBr_4)_2^= + 2\ Br^-\ .$$

$$(MoOBr_4)_2^= + H_2O \rightleftharpoons (MoOBr_4)_2O^{-4} + 2H^+\ ,$$
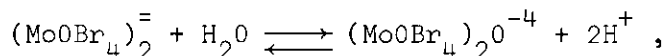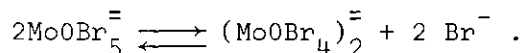
with the second dimerization being the sum of the two,

$$2MoOBr_5^= + H_2O \rightleftharpoons (MoOBr_4)_2O^{-4} + 2H^+ + 2Br^-\ .$$

In 6F HBr there is another dimer present and still others probably at lower HBr concentrations. In analogy to the chloride case, $MoOBr_5^=$ and $(MoOBr_4)_2^=$ are the only paramagnetic species, all others being diamagnetic.

The individual dimerization constants, $K_c^{(1)}$ and $K_c^{(2)}$, were also estimated; however, since activity data for solutions of HBr were not available at the concentrations used, the K_c were calculated at each HBr concentration in the manner described for the 4.98F HCl solution. The data in Tables 2, 3, and 9 were used. The results are presented in Table 17 and representative data for the computation in the 6.11F HBr solution is shown in Table 18 in Appendix I.

The results in Tables 16 and 17 indicate that the concentration of $(MoOX_4)_2O^{-4}$ builds up very rapidly in the solutions as the concentrations of HBr and HCl are lowered. Small amounts of $(MoOCl_4)_2^=$ exist, even in 9F HCl, while it is likely that there is some $(MoOBr_4)_2^=$, though in small amount, in HBr of concentration greater than 8F.

It should be noted at this point that Equation (13) of Chapter III would hold for a dimer-tetramer equilibrium as well as for a monomer-dimer equilibrium. However, for all of the foregoing results to be interpreted in terms of dimer-tetramer equilibria, it would be required that there be no monomer present, if Equation (13) is to hold.

C. Structure Speculations

A proposed structure for the dimer, $(MoOX_4)_2^=$, is
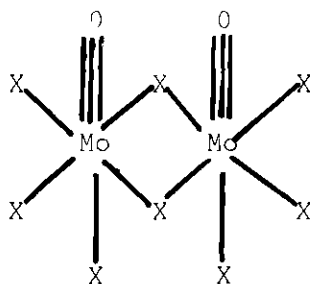
Bridging through the halogens allows retention of paramagnetism, as in the case of the $(MoCl_5)_2$ molecule (24). Furthermore, the local environment of each molybdenum atom is the same as the monomer,
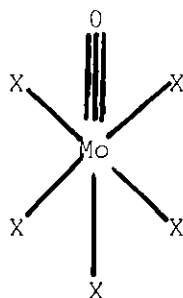

leading one to expect an absorption spectrum very similar to the monomer.

In view of the proposed structure of the paramagnetic dimer, $(MoOX_4)_2^=$, the question arises as to the molecular nature of the solids formulated as $RMoOX_4$. If coordination number six is to be preserved these compounds should be formulated as $R_2(MoOX_4)_2$, thus having the same structure as that proposed for the dimer in solution. All of these compounds show magnetic moments expected for d_1 systems (10, 11, 12, 15), although the magnetic moment cannot offer a choice between the

two possibilities. This question can only be decided by X-ray studies of the compounds.

The second dimer would have the formula proposed by Haight (17), and would have a structure like that of the xanthate complex (25)
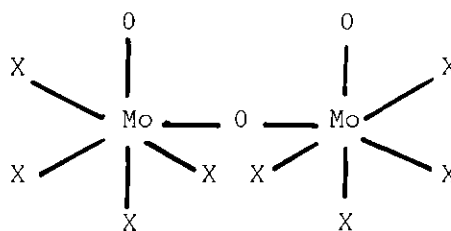
The diamagnetism of this dimer could arise from a super exchange interaction involving the two molybdenum atoms and the bridging oxygen (34).

APPENDICES

APPENDIX I

Table 18. Data for Computation of K_1 and K_2 for
Molybdenum (V) in 6.11F HBr

C_o	$X_{Mo}(10^6)$	f^a	$[M]^b$	fC_o	$[D_1]^c$	$[M]^2(\times 10^6)$	K_1
0.0304	396	0.291	0.00704	0.00885	0.000905	0.496	18.3
0.0665	325	0.239	0.01084	0.0159	0.00253	1.18	21.6
0.0736	303	0.224	0.01150	0.01650	0.00249	1.32	18.9

[a] $f = \dfrac{X_{Mo}}{1360(\times 10^6)}$.

[b] Obtained from $C_o = [M] + 2[M]^2 235$.

[c] $[D_1] = \dfrac{fC_o - [M]}{2}$.

APPENDIX II

DERIVATION OF THE FORMULA: $f = \dfrac{\chi_v}{2} A(H^2 - H_o^2)$

The potential energy stored in a magnetized medium is
$\dfrac{-\mu_2 H^2 v}{8\pi}$ where μ_2 is the permeability of the medium, H is the magnetic field strength and v is the volume of the medium.

If we now imagine a small body, constructed of the material of permeability, μ_2, placed in a magnetic field, and the region around the body evacuated, the potential energy of the body is

$$V = \frac{-(\mu_2 - 1)H^2 v}{8\pi}, \qquad (1)$$

since the permeability of free space is 1.

If the body is transferred to a medium of permeability μ_1, it displaces a volume of the medium whose potential energy was $-(\mu_1 - 1)H^2 v/8\pi$. The change in potential energy resulting from this process is

$$dV = \frac{-(\mu_2 - \mu_1)H^2 v}{8\pi} . \qquad (2)$$

There exists a force, f_x, which tends to move the body along a given direction, which will be denoted the x direction for the time being:

$$f_x = - \frac{\partial V}{\partial x} \tag{3}$$

$$= - \frac{\partial}{\partial x} \left(\frac{-\mu_2 + \mu_1}{8\pi} \right) H^2 v$$

$$= \frac{(\mu_2 - \mu_1)}{8\pi} \frac{\partial (H^2) v}{\partial x} \quad .$$

Using the relation between permeability and the susceptibility per unit volume, χ_v,

$$\mu_1 = 1 + 4\pi \chi_v^{(1)} \tag{4}$$

$$\mu_2 = 1 + 4\pi \chi_v^{(2)} \quad ,$$

we obtain

$$f_x = \frac{(\chi_v^{(2)} - \chi_v^{(1)})}{2} \frac{\partial (H^2) v}{\partial x} \tag{5}$$

$$= \frac{(\chi_v^{(2)} - \chi_v^{(1)})}{2} \left(\frac{\partial H_x^2}{\partial x} + \frac{\partial H_y^2}{\partial x} + \frac{\partial H_z^2}{\partial x} \right) v \quad ,$$

since $H^2 = H_x^2 + H_y^2 + H_z^2$. Equation (5) is correct only when we assume that the field is not appreciably disturbed by the introduction of the body. Since the quantity, $(\chi_v^{(2)} - \chi_v^{(1)})$, is very small, this assumption is reasonable.

Now, if we imagine the body to be in the form of a rod of uniform cross section and that the rod is suspended in the field, H, between

two poles, the magnetic force will act on a small element of length, dx, and volume, dv, of the sample as follows:

$$f = \frac{(\chi_v^{(2)} - \chi_v^{(1)})}{2} \left(\frac{\partial H_x^2}{\partial x} + \frac{\partial H_y^2}{\partial x} + \frac{\partial H_z^2}{\partial x} \right) dv \ . \tag{6}$$

The relevant coordinate system may be pictured as:

One end of the sample is in the field, H, between the magnet poles. The field would be directed along the positive y axis. The field at the other extremity of the sample is denoted as H_o. We may say that H_x, H_z, $\frac{\partial H_x^2}{\partial x}$, and $\frac{\partial H_z^2}{\partial x}$ are very small. Thus the force on the sample may now be written as

$$f = \frac{(\chi_v^{(2)} - \chi_v^{(1)})}{2} \frac{dH_y^2}{dx} dv \tag{8}$$

$$f = \frac{(\chi_v^{(2)} - \chi_v^{(1)})}{2} \frac{dH_y^2}{dx} A \ dx$$

where A is the cross-sectional area. Integrating,

$$f = \frac{(\chi_v^{(2)} - \chi_v^{(1)})}{2} A \int_{H_y = H_o}^{H_y = H} \frac{dH_y^2}{dx} dx \ , \tag{9}$$

we obtain the well-known result,

$$f = \frac{(\chi_v^{(2)} - \chi_v^{(1)})}{2} \, A(H^2 - H_o^2) \ . \tag{10}$$

If the susceptibility of the medium is negligible, then the equation reduces to

$$f = \frac{\chi_v^{(2)}}{2} A(H^2 - H_o^2) \ . \tag{11}$$

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