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McArthy, Richard Leland

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Magnetic Susceptibility Studies Of Metal Ammine Complexes In Aprotic Media

Richard L. McArthy
Lt. U. S. N.

MAGNETIC SUSCEPTIBILITY STUDIES OF METAL AMMINE COMPLEXES IN APROTIC MEDIA

by
Richard Leland McArthy
Lt. USN

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1957

CERTIFICATE OF APPROVAL

This thesis is accepted and approved in partial fulfillment of the requirements for the degree of Master of Science.

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Richard McArthy

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I Introduction

The subject matter of this thesis was prompted by recent studies concerning the extent of complexing of metals by amines in aprotic media. Myers (40) used cryoscopic techniques to determine $\overline{n}$, the average number of bound ligands per metal atom and found that the maximum number of coordination positions available to the amine is four for cobalt and five for manganese. Some of this work was repeated by Hoechstetter (26) with the result that $\overline{n}$ approached three for both cobalt and manganese. Yao (68) used the spectrophotometric method of Job (30) or the method of continuous variations to study complexing in benzene solutions. He found that with cobaltous naphthenate and ethylene diamine four coordination positions were used for coordination in benzene. He also observed a time dependent change in $\overline{n}$.

Magnetic susceptibility studies were suggested (40) as a means of adding to the knowledge of these reactions. The work was planned with the following main objectives;

1) Development of a simple and accurate method for determination of the magnetic susceptibility of liquids.
2) Preparation and characterization of metal ammine complexes in aprotic media.
3) Study of the magnetic properties of these solutions under various conditions with the aim of possibly learning how such things as robustness or equilibrium, maximum coordination number and bond type in aprotic media differ from aqueous media.

II Background

The magnetic properties of substances (excluding ferromagnetics) can be thought of as arising from three sources; (a) orbital motion of electrons, (b) spin of individual electrons and (c) the precession of the electron orbit in the presence of an external field. The first two, (a), (b), are always present in an atom, ion or molecule and are the source of paramagnetism. The latter gives rise to diamagnetism because the direction of precession is in such a direction as to produce a field which is in opposition to the applied field in accordance with Lenz's law. In a system containing paired electrons, i.e., the electron spins are coupled, the spin and orbital magnetic moments are canceled out and the resulting system has zero permanent magnetic moment. This results in diamagnetism. On the other hand if a system has unpaired electrons it will have a resultant permanent moment and will exhibit paramagnetism as well as diamagnetism. Although systems exhibiting paramagnetism are also diamagnetic, the diamagnetic contribution is very small compared to the paramagnetism and is often neglected. An interesting analogy exists between electrical molar polarization and magnetic molar susceptibility (38). $P_m = \frac{4}{3}\pi N (\alpha_o + \frac{\mu'^2}{3kT})$ where P_m = molar polarization, α_o = induced polarization due to distortion, μ' = dipole moment; $\chi_m = N (\alpha_o + \frac{\mu^2}{3kT})$ where α_o is the induced magnetic moment (diamagnetism), and μ is the permanent magnetic moment (paramagnetism).

If a substance is placed in a magnetic field of strength H, magnetism of intensity I will be induced in it. The resultant magnetic induction, B, is the result of I plus the superimposed H. $B = 4\pi I + H$, the 4π resulting from Gauss' Law which states that the total normal magnetic induction over a closed surface is 4π times the total amount of pole within it. Mathematically,

$\int \mu' H \cdot \cos\theta \cdot ds = 4\pi \sum m$ where m = pole strength.

Gauss' Law also defines $\mu' H = B$, the magnetic induction. I is defined as magnetic moment per volume, or pole per unit area. μ' is the magnetic permeability and may be thought of as a measure of the degree, relative to a vacuum, to which magnetic lines of force pass through a substance. Dividing the equation $B = 4\pi I + H$ by H gives $B/H = 4\pi I/H + 1$ or $\mu' = 4\pi k + 1$ where k, (kappa), is defined as the volume magnetic susceptibility and is the proportionality factor between I and H. k/ρ, where ρ is the density is given the symbol χ (chi) and is defined as the mass magnetic susceptibility. χ times the molecular weight is called the molar susceptibility, χ_m. The quantities χ_A and χ_i are defined respectively as the atomic susceptibility and the ionic susceptibility.

Magnetic moments can be used to distinguish between types of bonding in metal complexes, particularly those of the first transition group. For example ferric tris (acetylacetone) has a moment of 5.9 B.M. (Bohr magnetons) indicating five unpaired electrons, whereas potassium ferricyanide has a moment of about 2.3 B.M. indicating one unpaired electron. Pauling (46) has suggested that the bonds in the first compound are ionic while the bonds in the latter are

covalent. The change in magnetic moment is accounted for by assuming that in the latter compound the two 3d orbitals needed for bond formation are made available by electron pairing leaving only one unpaired 3d electron. In the first case the five 3d electrons are unaffected by complex formation. The crystalline field theory advanced by Van Vleck (62) to explain the magnetic data is not in agreement with Pauling's theory. Van Vleck's theory is of a very complex nature and because of this is less well known. Orgel (44) has pointed out a qualitative similarity between the two theories and shown that both should lead to same conclusions concerning stereochemical configurations. Pauling's concept of essentially ionic or covalent bonds has been later modified by himself (47). He expresses the difference as being between "strong covalent bonds, using good hybrid bond orbitals and with the possibility of unsynchronized ionic-covalent bonds using poor bond orbitals, and the necessity for syncronization of the covalent phases of the bonds." Instead of simple "ionic" or "covalent", Burstall and Nyholm (12) suggest that bonding by "higher" and "lower" covalent orbitals is a better concept. Orgel (44) shows that the magnetic moment indicates roughly whether the covalent character of the bond has passed a certain limiting value. Pauling's original approach is still widely used in discussions of stereochemistry.

The terminology of Taube (59) is considered best by this author. When using the magnetic criterion for bond type it is believed best to use the term "outer orbital complex" when referring

to complexes which do not disturb the electrons in the d level as shown by no change in magnetic moment between complexed and uncomplexed metal ions. The term "inner orbital complex" refers to complexes in which the innermost 3d electrons have been redistributed (paired) as shown by magnetic data.

Practically all complexes of divalent manganese in aqueous solution or in the solid state are of the ionic or outer orbital type in which complexing does not disturb the five unpaired 3d electrons. The exception to this is the cyanide complex which has a moment corresponding to one unpaired electron. Thus for $Mn(o - phen)_2Cl_2$, $Mn(NH_3)_6Br_2$, $K_2Mn(C_2O_4)_2 \cdot 2H_2O$, and (21) $Mn(C_5H_5NH)_2Cl_2$ the magnetic moment of the manganese is the same as that for the uncomplexed ion. This is believed to be due to the stability of the favored $3d^5$ configuration. It was hoped that with aprotic solvents and in the absence of water that magnetic data would show the formation of an inner orbital manganese ammine.

In aqueous solutions it is well known that cobalt(II) complexes are very unstable with respect to oxidation to cobalt(III) complexes. The reason given for this is that for d^2sp^3 hybridization in Co(II) a lone electron is promoted to the 5s level where it is easily lost to give the corresponding cobalt(III) complex. Oxidation potentials show the difference between the complexed and uncomplexed species (37).

$$Co^{+2}\ (aq.) \rightleftharpoons Co^{+3}\ (aq.) + e^{-} \qquad E = -1.842 \text{ volts}$$

$$\left[Co(NH_3)_6\right]^{+2} \rightleftharpoons \left[Co(NH_3)_6\right]^{+3} + e^{-} \qquad E = -0.1 \text{ volt}$$

Cobalt (III) complexes such as $Co(NH_3)_6Cl_3$ have zero magnetic moment while cobalt (II) complexes such as $Co(NH_3)_6Cl_2$ have moments corresponding to three unpaired electrons plus a large orbital contribution.

Yao (68) has concluded that with cobalt naphthenate and di-n-propylamine in carbon tetrachloride solution complex formation is slow and several different species may be present depending upon the age of the solution.

III Experimental

The Quincke method was selected by the author mainly because of its ease of use and adaptability to liquids.

The equation which is applicable to the Quincke method is

$$(\rho - \rho_o)\, gh\, (1 + \frac{s}{S}) = \frac{1}{2}\, (k - k_o)\, H^2.$$ (See appendix II).

Apparatus

The magnet used was a large electromagnet which was made earlier in this laboratory. The parallel pole faces were cylindrical iron rods having a diameter of 48 mm. The distance between pole faces was 6 mm. The 115 volt ac laboratory power supply was regulated with a Variac autotransformer before being rectified by an Electromatic Products Co. electronic rectifier. The coils of the electromagnet were connected in parallel. A 0-15 amp. direct current ammeter was connected in series with the coils. (See figure 1).

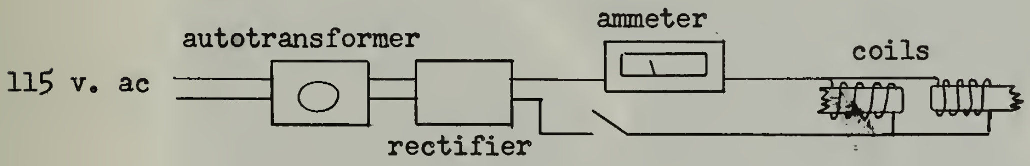

Figure 1

The current flowing in the coils was maintained at 4.00 amperes at all times in order to obtain a constant reproducible magnetic field. Comparison with data on a similar magnet used by Schuler (50) indicates that the field is essentially homogenous out to a distance of 1 cm from the center of the pole faces.

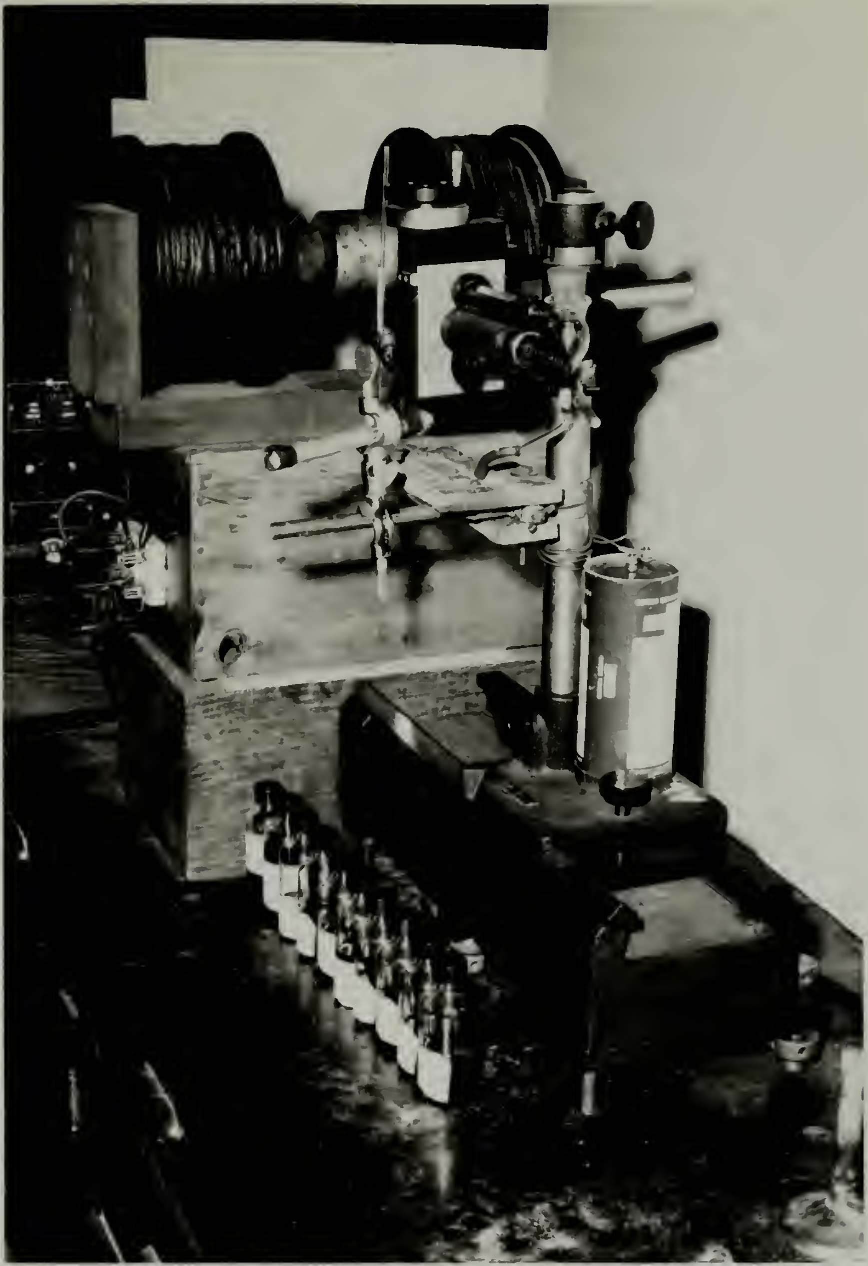

Figure 2

Apparatus

The sample tubes were prepared from 4 mm O.D., 2.5 mm I.D., Pyrex glass tubing bent into the shape of an L. The horizontal arm of the L was connected by means of a short section of rubber tubing to a thistle tube bulb of maximum diameter 30 mm. The open end of the L tube and the bulb were stoppered with finely slotted corks to reduce evaporation to a minimum and still permit pressure equalization.

A traveling microscope was used to measure the position of the liquid level. Displacement of the liquid level could be measured to within 0.0002 cm. The L tube and bulb were firmly mounted on the movable carriage of the traveling microscope. The microscope and tube assembly could thus be moved as a unit by sliding the microscope carriage on its tracks. The liquid level could then be placed between the poles or retracted away from the field without changing the position of the tube relative to the microscope. Since a small amount of residual magnetism remained in the pole pieces when no current was applied, the position of the meniscus at zero field was observed when the liquid was removed about 8 inches from the pole pieces. The meniscus was illuminated by a small penlight type of self-focusing bulb which was powered by a one and a half volt dry cell battery. The microscope was maintained at a constant level by a liquid bubble type leveler. The meniscus was positioned visually at the center of the pole faces and equidistant from each.

In order to insure that the temperature measured was that of the liquid in the tube rather than the surrounding air, a small bead thermistor was inserted through a hole in the vertical arm of

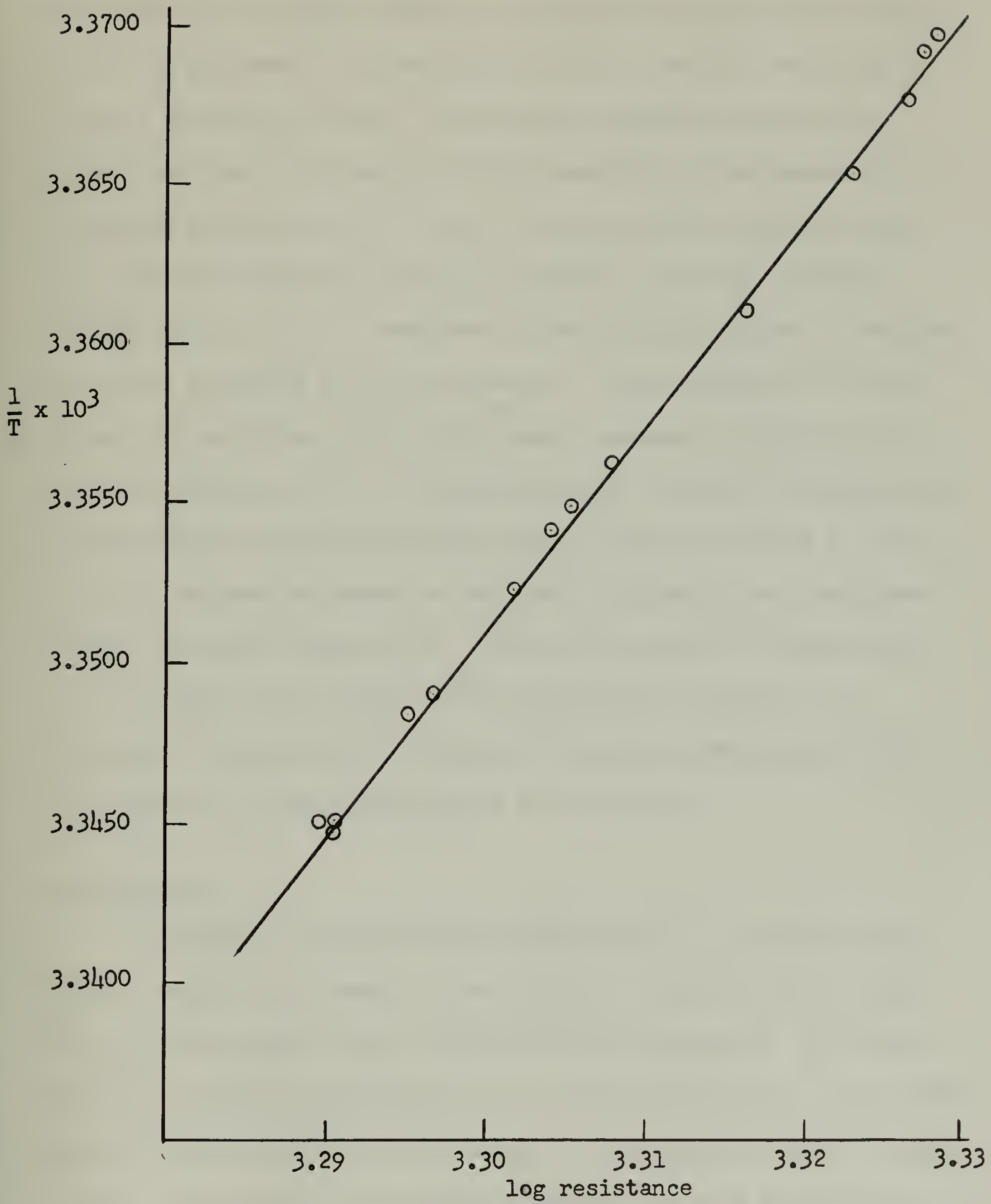

Figure 3

Thermistor Calibration

the L tube. The junction between the glass jacket surrounding the thermistor bead and the sample tube was sealed with sealing wax. The thermistor was thus immersed in the test liquid about 2 inches below the meniscus. The resistance of the thermistor was measured using a Wheatstone bridge. The variable resistance arm of the bridge included a 200 ohm calibrated precision potentiometer which permitted resistances to be read to 0.1 ohm. The thermistor used was a Western Electric type 14 B which had a nominal resistance of 2000 ohms at 25° C. Resistance rises 4.7% per degree of temperature drop according to the manufacturer. The thermistor was calibrated by comparison with a 0-50° range thermometer which could be read to within ± .05°. The thermometer was calibrated by using the sodium sulfate decahydrate triple point and the ice point of water. A linear calibration graph was obtained by plotting log resistance versus reciprocal temperature. Using this method the temperature of the liquid in the sample tube was measured to 0.05°. The thermistor thermometer was capable of measuring temperatures to a much higher accuracy than required in this work.

Calibration

In order to calculate the susceptiblity of a liquid by the Quincke method, the density of the liquid, change of liquid position and the magnetic field strength must be measured. By using a solution of known susceptibility the field strength may be calculated and this value may be used to calculate the susceptibility of unknown liquids. One of the most popular solutions for this calibration is

a concentrated solution of nickel chloride (11, 41, 29, 2). The gram susceptibility of nickel chloride solutions over a wide range of temperatures and concentrations is given by the formula (41)

$$\chi_x = \left[\frac{10300}{T} p - 0.720 (1 - p)\right] x 10^{-6}$$

where p is the weight percent of nickel chloride in the solution and -0.720×10^{-6} is the gram susceptibility of water. Two different aqueous solutions of Bakers analyzed reagent grade $NiCl_2 \cdot 4H_2O$ were prepared. These solutions were found to contain 23.7 and 26.6 percent $NiCl_2$ by weight. The standard dimethylglyoxime procedure (23, 51) for determining nickel was used. The nickel dimethylglyoxime precipitates were collected on sintered glass filtering crucibles and weighed on a standard analytical balance. Three different sets of data were taken with each of these two solutions. The density of the solutions was determined using a 10 ml pyncnometer. The height of rise of the liquid was of the order of 0.8 cm. The field strength of the electromagnet with 4.00 amp applied was calculated to be 15.0×10^3 oersteds with a standard deviation of 0.08×10^3 oersteds.

Evaluation and Criticism of Method and Apparatus

The combination of the Quincke method and $NiCl_2$ calibration solutions has been used by other investigators for measuring the strength of magnetic fields even when the fields were to be used for other reasons (53).

To obtain a check on the apparatus and method, measurements were made on Eastman specto-grade benzene, and the average change in the liquid level, h, was determined to be 0.0835 ± .0003 cm. The gram susceptibility of benzene was calculated to be $-0.702 \pm .003 \times 10^{-6}$ using the following values:

Volume susceptibility of air	0.0294×10^{-6} emu
Density of benzene	0.879 gm/cc
$^{s}/_{S}$	0.01
H	15.0×10^{3} oersteds
g	980 cm/sec^{2}
Density of air	neglected

The values of the gram susceptibility of benzene given in the literature are -0.7038×10^{-6} (52) and -0.7020×10^{-6} (17).

It was found that benzene and benzene solutions were much easier to work with than aqueous solutions because of their lower surface tension. In glass tubes cleaned with sulfuric acid-dichromate cleaning solution the water solutions still adhered unevenly to the surface in small, scattered droplets. In an attempt to overcome this difficulty the inside of the glass tubes were siliconized by treatment with Dow D-30 siliconizing suspension. The meniscus formed in tubes so treated was planar and no droplets of liquid tended to form on the walls. However, the aqueous solutions still tended to "creep" and approach its "own level" asymptotically. In addition to this "creep", the aqueous solutions in siliconized tubes appeared to rise or fall to a false level. A small puff of air would

displace the meniscus causing it to come to rest at a new level. By repeatedly "bouncing" the meniscus with air puffs and allowing sufficient time, reproducible data were obtained. No difficulty was encountered using benzene solutions in "clean" tubes. It was discovered later that the use of aqueous solutions could be facilitated by the addition of a small amount of a commercial wetting agent produced by American Cynamid Co. and designated "Aerosol OT". According to the degree of accuracy desired, the contribution to the susceptibility of the solution by the wettting agent could either be 1) neglected, 2) calculated by using Pascal's (7) constants, or 3) measured in a solvent of known susceptibility.

The average deviation from the mean for all readings taken was 0.0005 cm.

Materials

In preparing for the study of metal ammine complexes in aprotic media one of the first considerations was the choice of an aprotic solvent. Benzene naturally suggested itself because of its inherent stability, its lack of any tendency to interact with the solute, its excellent solvent powers and its availability in a highly purified form. Eastman spectrographic grade benzene from freshly opened uncontaminated bottles was used in all experiments.

Buam (normal butyl amine) was selected as the ligand for the following reasons; a) a large bottle of reportedly high grade n-butyl amine supplied by the Sharples Chemical Co. was available, b) it was very soluble in benzene, c) it should form complexes similar

to ammonia complexes, d) the four-carbon chain should not cause any complications due to steric effects as a more bulky amine might do, e) it could be readily handled quantitatively in the liquid state.

The choice of a source of metal was a little more difficult. Myers (40) in his cryoscopic studies of Mn and Co complexes in benzene used anhydrous cobaltous acetate and anhydrous manganous chloride but had to resort to high concentrations of amine to get complete solution. It was considered desirable that a metal compound completely soluble in benzene be used in order that low concentrations of amine could be studied. Some samples of commercial paint drying catalysts containing Co and Mn were available and were used as the source of Co and Mn. The metal was present either as the naphthenate or the octoate in a paint solvent and certified to contain 6.0% metal. Naphthenic acids (36) are isomeric mixtures of acids derived from petroleum and are generally considered to be alkyl cyclopentyl carboxylic acids. The main constituent is reported to be methyl-cyclopentane carboxylic acid. The empirical formula $Mn(C_7H_{13}O_2)_2$ was assumed for manganese naphthenate.

No further purification of the benzene was attempted. The buam was purified by the addition of large quantities of sodium wire. After evolution of hydrogen ceased, the amine was distilled in a four foot fractionating column packed were glass helices and samples collected at a 5:1 reflux ratio. Boiling point ranges of 77.30 - 77.35°C and 77.20 - 77.30°C were obtained. Near the end

of the distillation the pot contained a white solid which was presumed to be the sodium amide of buam formed by the reaction of sodium with the amine (37). This reaction liberates hydrogen and is catalyzed by traces of iron or Fe_2O_3 which could have come from the sodium wire extrusion press. The amount of water in the amine could not be judged by the evolution of hydrogen. The handbook value for the boiling point is 77.8°C.

About 10 grams of the manganese naphthenate solution was checked for the presence of water by refluxing with benzene in a Stirling-Bidwell condenser. The benzene in the trap became only slightly cloudy. The naphthenate and octoate solutions were considered essentially free of water.

Experimental Results

A solution of manganese naphthenate in benzene which was 0.105 molar in manganese was prepared. The h for this solution was determined to be 0.0807 - .0006 cm. The magnetic moment, μ , of manganese was calculated to be 5.86 Bohr magnetons by using the equation on page 7 and the equation $\chi m = N\beta^2\mu^2/3kT$ (38). The assumption was made that the manganese naphthenate solvent had the same susceptibility as benzene. The Weidemann additivity law, which states that the susceptibility of a mixture is equal to $\sum pi\chi i$ was also assumed to hold. The theoretical magnetic moment for manganese in the plus two oxidation state is 5.92 B.M. corresponding to five unpaired electrons. Observed values (42) of μ in the literature range from 5.85 to 5.95 B.M. Similar measurements and calculations were made

Manganese naphthenate - C_6H_6 - buam Magnetic Data

Solution	[Mn]	[A]	A/M	h(mm)	ρh	Age ~~(days)~~ hours when measured	
1	0.021	0		-0.504	-0.440		
2	0.0416	0		-0.189	-0.166		
3	0.070	0		0.265	0.232		
4	0.105	0		0.807	0.712		
5	0.0991	0.574	5.78	0.296	0.258	2	
6	0.066	0.574	8.7	-0.092	-0.08	1	
7	0.0392	0.574	14.6	-0.425	-0.37	2	Days
8	0.0198	0.574	29.0	-0.654	-0.57	1-2	
9	0.104	0.1003	0.965	0.580	0.51	1-2	
10	0.102	0.295	2.89	0.453	0.397	1-2	
11	0.0939	1.085	11.55	0.430	0.372	24	
11'	0.0939	1.085	11.55	ca. 0.01	ca. 0.01	28	
12	0.0955	0.920	9.63	ca. 0.005	ca. 0.005	20	
5'	0.0991	0.574	5.78	0.023	0.020	168	
9'	0.104	0.1003	0.965	0.44	0.388	48	
10'	0.102	0.295	2.89	0.275	0.251	48	
13	0.101	0.389	3.86	0.160	0.14	20	
14	0.102	0.199	1.95	0.315	0.277	23	
10"	0.102	0.295	2.89	0.247	0.216	96	
6'	0.066	0.574	8.7	-0.258	-0.222	168	
7'	0.0392	0.574	14.6	-0.521	-0.448	240	

Table 1

with a 0.0834 molar solution of cobalt octoate in benzene. The value $\mu = 4.45$ B.M. was obtained. The theoretical "spin only" value is 3.87 B.M. for three unpaired electrons but cobalt exhibits an unusually high orbital contribution to the magnetic moment and values of 4.3 to 5.3 B.M. have been reported for divalent cobalt (42). These results are considered to be good evidence that the manganese and cobalt used were in the plus two oxidation state.

To study the complexing of manganese with buam, the solutions described in Table I were prepared and observed in the Quincke apparatus. At constant field the quantity ρh is directly proportional to the volume susceptibility. These data are plotted in figures four and five. In figure four the number along side the plotted point is the solution number. Primed solution numbers differ from corresponding unprimed numbers only in the age of the solution. In figure five the first number alongside a plotted point is the solution number and the second number is the approximate age of the solution in hours. Points marked with an x are solutions having the same concentration of manganese within ± 5.0%. The amber colored solutions of manganese naphthenate in benzene darkened immediately upon addition of amine. Upon standing, further darkening appeared to occur until after a period of weeks the solutions were very dark brown and opaque. A dark brown sludge-like precipitate was observed in the opaque solutions after about a week. The solutions with high $^A/M$ values contained the most sludge. Since in strongly basic aqueous solution Mn(II) is oxidized to Mn(III) even by

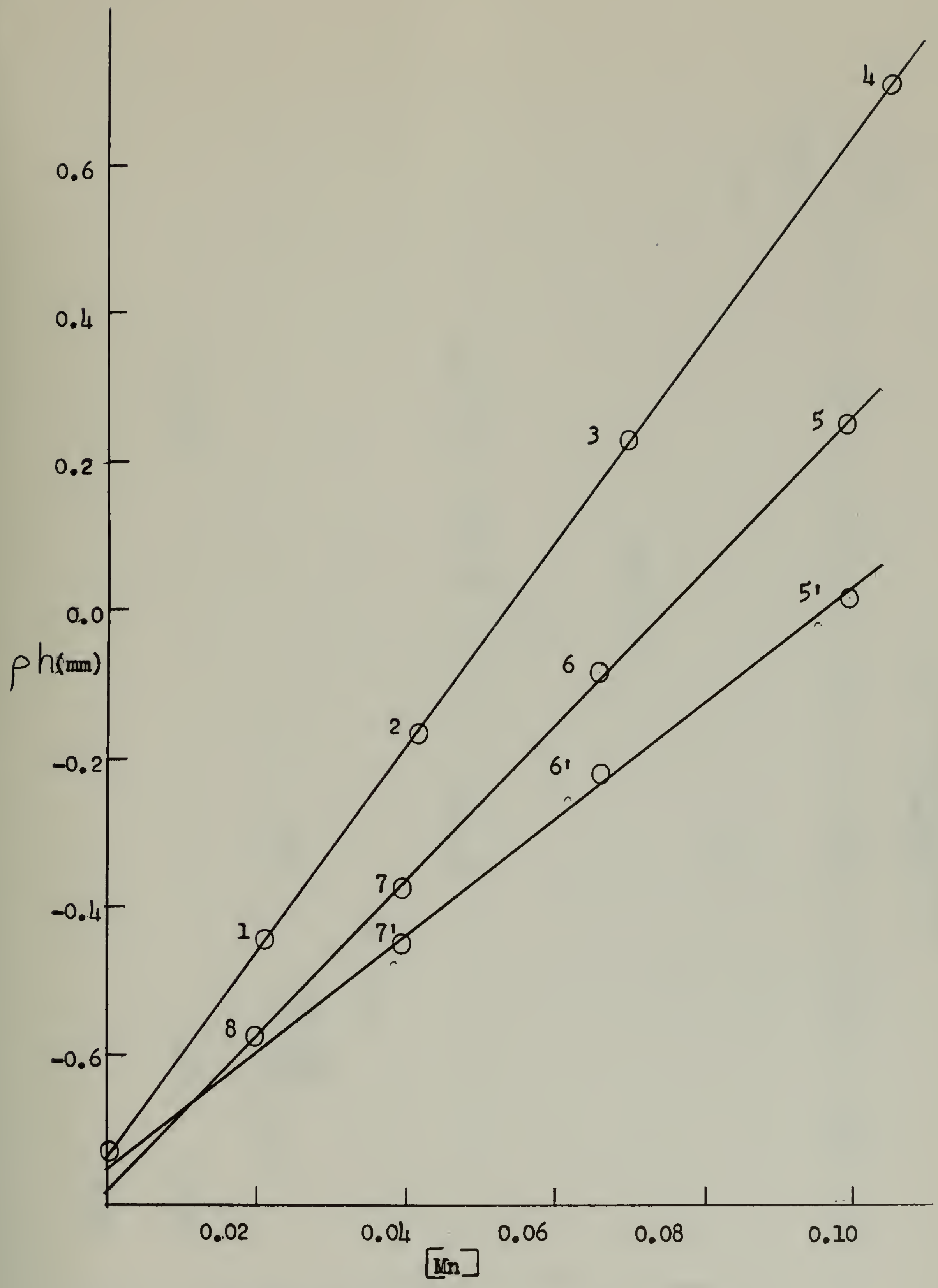

Figure 4
Manganese Magnetic Data

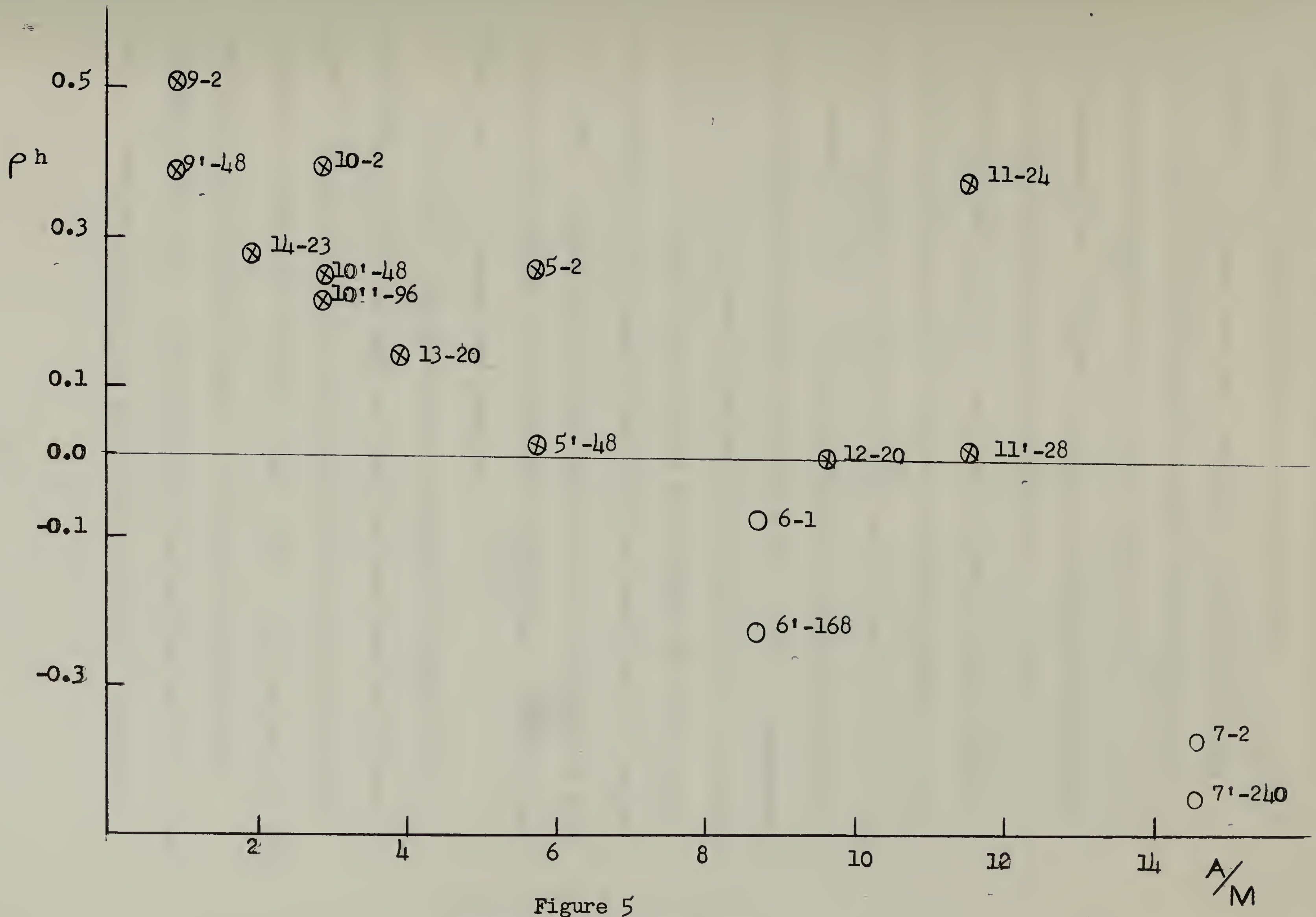

Figure 5
Magnetic Manganese Data

atmospheric oxygen (37), the effect of the atmosphere was investigated. It was found that solutions prepared in nitrogen atmosphere darkened less and produced no observable sludge. Small samples of the solutions in Table I were diluted with benzene and examined for the Tyndall effect. Solutions with $^A/M$ greater than six showed evidence of being colloidal while the others appeared to be true solutions. This sludge-like precipitate was separated from the solution by centrifuging, washed in water and acetone and air dried from acetone. It was insoluble in water, acetone, benzene and n-bu-am but was soluble in concentrated HCl. The acid solution was heated in the presence of KIO_4 and the characteristic purple color of permanganate resulted. The infra-red spectrum of the precipitate was obtained in the 2 to 15 micron region using the pressed KBr disc method. The benzidine test, commonly used for the detection of nitrogen in organic qualitative analysis, applied to the precipitate gave positive indications of the presence of nitrogen. The Prussian blue test for nitrogen was negative.

The light brown precipitate obtained by adding buam to an aqueous solution of $MnCl_2$ was also examined with the infrared spectrophotometer. This precipitate after being air dried was probably a mixture of $Mn(OH)_3$ or $MnO \cdot MnO_2 \cdot nH_2O$ and $Mn(OH)_2$.(33). The infrared absorption spectra of the two precipitates were decidedly different. The precipitate from aqueous solution showed only a broad absorption band from 2900 to 3600 cm^{-1} centered on

Cobalt Octoate - C_6H_6 - buam Magnetic Data

Solution	[Co]	A/M	h	Date Prepared	Date Measured
15	0.170	0	1.20	4/22	4/22
16	0.0834	0	0.158	4/1	4/1
17	0.0336	6	-0.78	3/30	4/8
18	0.0448	6	-0.73	3/30	4/3
19	0.0538	6	-0.76	3/30	4/4
20	0.0671	6	-0.73	3/30	4/5
21	0.0807	6	-0.73	3/30	4/4
22	0.1008	6	-0.76	3/30	4/5
23	0.1075	6	-0.73	3/30	4/8
24	0.1343	6	-0.78	3/28	4/8
25	0.156	5.73	0.69	4/22	4/23
25'	0.156	5.73	0.29	4/22	4/26
25"	0.156	5.73	-0.61	4/22	5/6

Table 2

3400 cm^{-1} characteristic of the hydroxide group. The precipitate from benzene solution exhibited absorption peaks at 2850, 1530, 1450, 1400 and 980 cm^{-1} which could be due partially to organic groupings. Hill and Alexander (23) have examined the infrared absorption spectra of complex cobalt compounds of the type $Co(NH_3)_6X_2$ and found four absorption bands at approximately 3000, 1600, 1350 and 850 cm^{-1}. They have attributed these four bands to the ammonia ligand and in particular have attributed the 850 cm^{-1} band to the rocking frequency of the metal-nitrogen bond.

Because of the precipitate formed and the lowering of the susceptibility with time, the data in table one are difficult to interpret.

The solutions described in table two were prepared using cobalt octoate, C_6H_6 and n-bu-am. No insoluble material was observed in any of the cobalt solutions. The uncomplexed solutions were blue-violet in color and changed to a ruby-red when complexed. Solutions 17-23 were prepared by diluting aliquots of solution 24 with benzene. Solutions 16-24 were prepared in an air atmosphere. Solutions 15 and 25 were prepared completely in a dry box which had been thoroughly flushed with dry nitrogen. Solution 25 was exposed to the atmosphere only during the short time required to fill the sample tube, make the measurement, and drain it back into the bottle. The data from table two are plotted in figure sixr. The manganese line is included for comparison. Figure sixrindicates that no paramagnetism was left in the solutions after the addition of amine. The data indicate the possibility that air

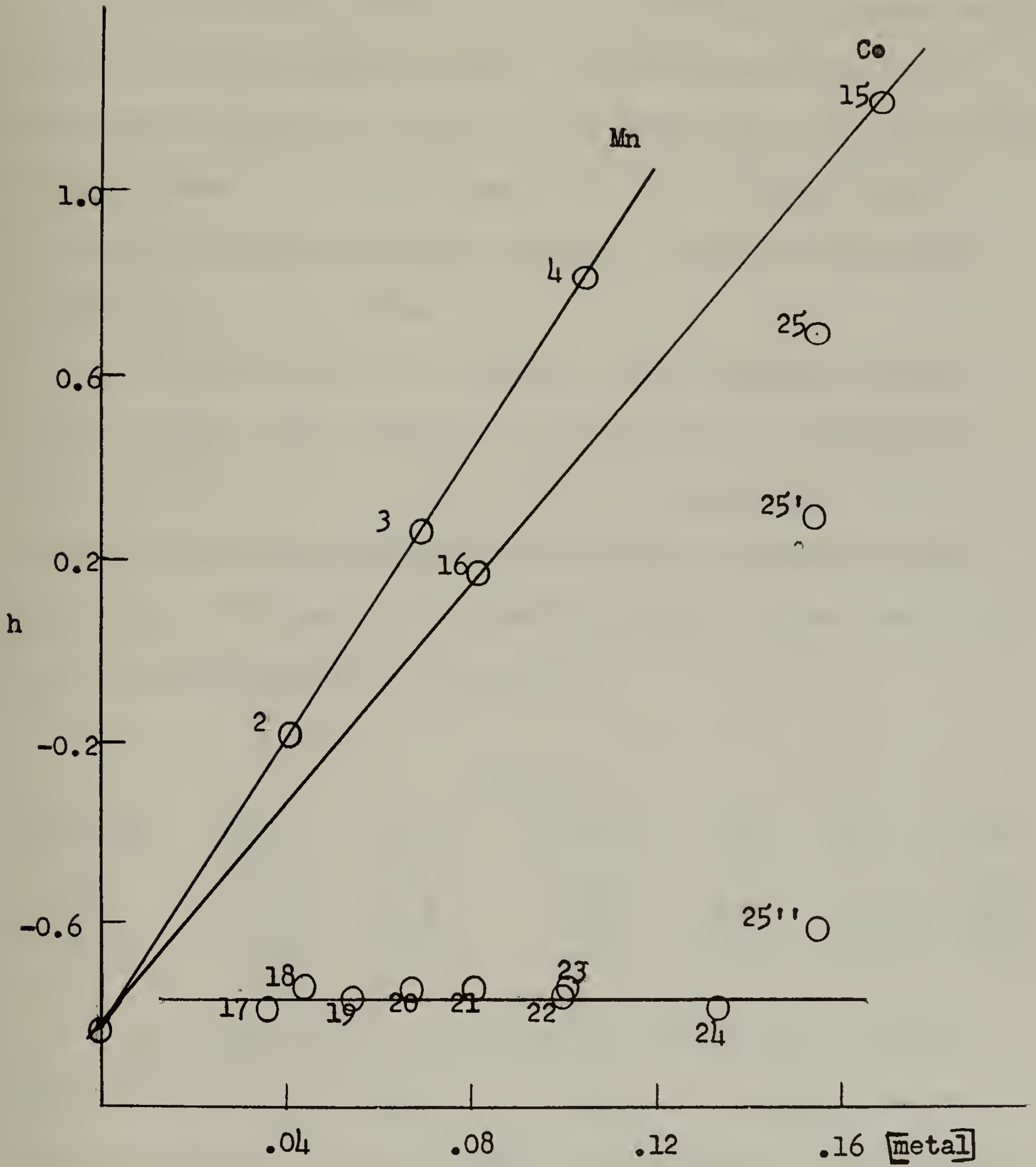

Figure 6

Cobalt Magnetic Data

oxidation, while preparing the solutions, produced the Co(III) complex from the Co(II) complex. The drop in the susceptibility of solution 25 after each measurement indicates the extreme ease with which this oxidation occurs. It is believed that in all solutions a Co(II) outer orbital type complex was originally formed with no change in magnetic moment but that oxidation quickly forms the diamagnetic Co(III) complex. This is in accord with behavior in aqueous media.

These solutions were prepared with a constant $^A/_M$ and variable [A]. Visual range spectrophotometry was planned with these solutions with the hope that if an equilibrium exists it could be detected by correlating the shift of absorption peaks with [A]. Unfortunately the spectrophotometer became inoperative and these measurements were not made.

Table 3

Solution	[Mn]	h(mm)	$K(x10^6)$	$^A/_M$	[A]	Date
26	0.122	1.05	0.772	0	0	3/12
27	0.110	0.834	0.640	8.2	0.90	3/12
28	0.110	0.770	0.592	8.2	0.90	3/13

The solutions in table three were prepared in a dry-box which had been flushed with dry nitrogen. The sample tube was flushed with CO_2 before filling and an atmosphere of CO_2 was maintained over the surface of the liquid while magnetic measurements were being made. Solution 26 was not actually measured but h was determined graphically from figure four which applies to an air

atmosphere above the sample. To obtain a comparison between the three solutions the volume susceptibility was calculated since in this case h is not directly proportional to k. The data indicate that even if precautions are taken against oxidation the addition of amine lowers the susceptibility of Mn. However, it is still possible that oxygen could have been introduced during the very short period when the solution was being poured into the sample tube from the bottle.

One further attempt was made to eliminate oxygen from the $Mn(Np)_2 - C_6H_6$ - buam solutions. A "closed" sample tube was formed from glass tubing roughly in the shape of a square. The two open ends, used for filling, faced each other at the top of the square and were spaced about four cm. apart. After the tube was half filled with solution the open ends were joined by a short length of Tygon tubing. All operations were carried out in a nitrogen atmosphere in the dry box. The data taken with this tube were considered invalid due to contamination from the Tygon and/or evaporation of benzene from the solutions during and after filling of the tube.

IV Summary and Conclusions

The use of a simplified version of the Quincke method for studying the magnetic properties of liquids has been very satisfactory. It has been shown to be capable of measuring magnetic susceptibilities and magnetic moments to three significant figures with errors less than 1.0%.

The studies of manganese and cobalt complexes in benzene were complicated and prolonged by effects of atmospheric oxygen. The extreme sensitivity of Co(II) complexes to oxidation to Co(III) complexes has been demonstrated in aprotic media.

The manganese data were complicated by sludge formation and indicate either that the solutions are very sensitive to oxidation or a slow complex reaction occurs which produces several different species, perhaps polynuclear, in time. It is conceivable that magnetic changes in the solutions were masked by particles of near colloidal size which slowly precipitated. This type of study warrants further investigation.

V Suggestions for Future Work

If this work could be continued it is believed that very valuable information concerning the nature of inorganic complexes in aprotic media could be obtained. Magnetic data are most valuable if the compound being measured can be definitely characterized as far as its composition is concerned.

Infrared spectroscopy should be applied to the solutions to attempt to characterize the complex formed. If benzene should be too absorbent perhaps carbon tetrachloride would be suitable.

Visual spectrophotometry should be utilized on those solutions adaptable to it.

An attempt should be made to prepare salts of the transition metals of definite composition in a very pure form which would be soluble in aprotic solvents.

The sludge formed in the manganese solutions should be more thoroughly investigated perhaps by quantitative analysis.

Magnetic data should be obtained using the method of Job or the method of continuous variations.

A glass sample tube which can be permanently sealed should be used to hold the solutions. In this way solutions could be studied to determine any equilibrium effects without disturbances from the outside air.

The sample tube should be fitted with a thermal jacket to study temperature coefficients of susceptibility.

The magnet should be calibrated at several field strengths so that the effect or presence of any ferromagnetic impurities could be detected. This would be done by plotting k vs H and extrapolating to zero field. Since for ferromagnetics k is a function of H and for paramagnetics k is independent of H the contribution due to ferromagnetics could be detected.

The studies should be extended to many other types of ligands, metals and solvents.

APPENDIX I

Definitions of Symbols and Abbreviations Used

$[A]$	Total concentration of amine in moles per liter.
$^{A}/_{M}$	Mole ratio of amine to metal.
B	Magnetic Induction.
β	Fundamental unit of magnetic moment, $^{eh}/_{4\pi mc}$, 0.917×10^{-20} erg/oersted.
B.M.	Bohr magneton, same as β.
buam	Normal butyl amine.
χ	Specific magnetic susceptibility, susceptibility per gram.
χ_m	Magnetic susceptibility per mole.
χ_i	Specific susceptibility of "i th" component of a mixture or solution.
g	980 cm/sec^2
H	Magnetic field strength.
I	Intensity of magnetization; magnetic moment per volume.
h	Change in liquid level due to H.
k	Magnetic susceptibility per unit volume of liquid. $(^{I}/_{H})$
k_o	Magnetic susceptibility per unit volume of gas above meniscus.
Np	Naphthenate.
$\bar{n}$	Average number of bound ligands per metal atom.
N	Avogadro's number.
Ω	Magnetic Potential.

o-phen	Ortho-phenanthroline.
P	Weight fraction of $NiCl_2$ in aqueous solution.
P_i	Weight fraction of "i th" component of a mixture or solution.
ρ	Density of liquid.
ρ_o	Density of gas above meniscus.
s	Cross section of sample tube between poles of magnet.
S	Cross section of sample tube outside the magnetic field.
T	Absolute temperature.
μ	Magnetic moment.
μ'	Magnetic permeability. $({}^{B}/_{H})$

APPENDIX II

Derivation of Quincke Method Equation

The equations given on page 35 are the source of the equation $(\rho - \rho_o)\, gh\, (1 + s/S) = \frac{1}{2}(k - k_o)\, H^2$ which is used in the Quincke method. These equations may be derived in several ways.

One way is to borrow the equation (28)

$$F_x = -\rho \frac{\partial V}{\partial x} - \frac{E^2}{8\pi} \frac{\partial \epsilon}{\partial x} + \frac{\partial}{\partial x}\left(\frac{E^2}{8\pi}\, \tau \frac{\partial \epsilon}{\partial \tau}\right)$$

from electrostatic theory where F_x is the force in the x direction on a dielectric body in an electrostatic field. ρ is the density of electric charge, V is the potential, E is the electric field intensity, ϵ is the dielectric constant and τ is the density of the body. It has been shown that the electromagnetic analog of this equation can be obtained by replacing electrostatic quantities by corresponding electromagnetic quantities, thus

$$F_x = -\rho \frac{\partial \Omega}{\partial x} - \frac{H^2}{8\pi} \frac{\partial \mu'}{\partial x} + \frac{\partial}{\partial x}\left(\frac{H^2}{8\pi}\, \tau \frac{\partial \mu'}{\partial \tau}\right)$$

F_x is the force per unit volume on a body in an electromagnetic field, ρ is the density of magnetic poles, Ω is the magnetic potential, H is the magnetic field strength, μ' is the magnetic permeability and τ is mass density of the body. In a liquid which is isotropic and has no permanent magnetism the quantities $\rho \frac{\partial \Omega}{\partial x}$ and $\frac{\partial \mu'}{\partial x}$ are equal to zero. The permeability is proportional to the density therefore we can write $\mu' - 1 = C\tau$ where C is a constant. Making this substitution and performing the indicated differentiations

the following results;

$F_x = \frac{C\uparrow}{8\pi} \frac{\partial H^2}{\partial x} = \frac{\mu' - 1}{8\pi} \frac{\partial H^2}{\partial x}$. Since $\mu' = 1 + 4\pi k$ one obtains

$F_x = \frac{k}{2} \frac{\partial H^2}{\partial x}$ or $F_x = kH \frac{\partial H}{\partial x}$ per unit volume.

Another approach to these equations is to consider the potential energy of an inductively magnetized body in a magnetic field (57). This potential energy, W, equals

$$- \int \left\{ \int_0^H \mathbf{I} \cdot d\mathbf{H} \right\} dv$$

but the quantity k is defined as $^I/_H$ and therefore

$$W = - \int \left\{ \int_0^H k\mathbf{H} \cdot d\mathbf{H} \right\} dv.$$

The force may be calculated from the energy since

$$F = -\nabla W = \tfrac{1}{2}k \int \nabla H^2 \, dv.$$

For small specimens this may be replaced by $F = \frac{1}{2}kv\nabla \mathbf{H}^2$

When the field gradient is in the x direction

$$F_x = \tfrac{1}{2}kv \frac{\partial H^2}{\partial x} = kvH \frac{\partial H}{\partial x} \quad \text{or}$$

$$F_x = \frac{k}{2} \int \frac{\partial H^2}{\partial x} dv = \frac{k}{2} \int A \frac{\partial H^2}{\partial x} dx = \tfrac{1}{2}kAH^2$$

where v and A are volume and area respectively. If k is replaced by $k - k_o$ and F_x replaced by $(ghA\rho)$ the equation in section III results.

APPENDIX III

Units and Dimensions of Magnetic Quantities

Some confusion exists in the literature (54) concerning the units and dimensions of k, the volume susceptibility. This confusion arises from a consideration of whether or not I and H are quantities of the same kind. The magnetic field strength or intensity, H, is numerically equal to the force exerted on a unit magnetic pole and as such is measured in dynes per unit pole. H is often expressed as, and is also numerically equal to, the number of lines of force passing through unit area normal to the field. Because of this its units are usually oersteds. The unit gauss was formerly used prior to the Electrotechnical Commission convention in 1930 (15). Gauss is now reserved for B, the magnetic induction, but much of the literature does not conform to this convention. Dimensionally H is $\left[\mu'^{-\frac{1}{2}} m^{\frac{1}{2}} l^{-\frac{1}{2}} t^{-1}\right]$ in the electromagnetic system (18). I, the intensity of magnetization, is a measure of magnetic moment per unit volume or magnetic poles per unit area. I is also numerically equal to lines per unit area and dimensionally is $\left[\mu'^{\frac{1}{2}} m^{\frac{1}{2}} l^{-\frac{1}{2}} t^{-1}\right]$. Since k is the ratio of I to H it has the dimensions of μ', the magnetic permeability, which is the fourth dimension added to a mass, length, and time physical system of dimensions in order to extend it to electromagnetic quantities (18).

Any unit of k therefore must be a derived unit. In the MKS system it is sometimes assigned the units of weber/amp-turn meter (56). In most handbooks where values of k or χ are tabulated they

are given the units of emu per volume or gram. The unit, magnetic moment per unit volume per unit field, is considered to be the most useful derived unit for k.

APPENDIX IV

Literature Review

I Methods for Determining Magnetic Susceptibility

Many methods for determining susceptibilities have been devised. Generally they may be grouped into two classes; (a) non-uniform field methods and (b) uniform field methods. These methods depend upon one of two equations (28); (a) $F_x = (k - k_o)vH_y \frac{\partial H_y}{\partial x}$, (b) $F_x = \frac{1}{2}(k - k_o)\ AH^2$ where F_x is the force per unit volume in the x direction acting on the specimen, k is the susceptibility of specimen, k_o is the susceptibility of surrounding medium, A is the cross sectional area of cylindrical specimen, and v is the volume of specimen. These equations are derived in appendix II.

The Faraday (14, 19) method for determining susceptibilities makes use of the force in a non-homogeneous field. The non-homogeneous field is obtained by using pole faces inclined at a certain angle or by using specially shaped pole faces. (See figure 7). A small sample is placed in the position where $H_y \frac{\partial H_y}{\partial x}$ will be a maximum. Upon application of the field the sample moves to the position where $H_y \frac{\partial H_y}{\partial x}$ is equal to zero. The force required to return the sample to its original position is measured with a torsion head. H_y and $\frac{\partial H_y}{\partial x}$ must also be measured for absolute determinations. Difficulties arise in measuring $\frac{\partial H_y}{\partial x}$ and placing the sample in the region where $H_y \frac{\partial H_y}{\partial x}$ is a maximum.

A modification of the above method known as the Curie-Cheneveau (13) method eliminates difficulties in placing the sample in the region

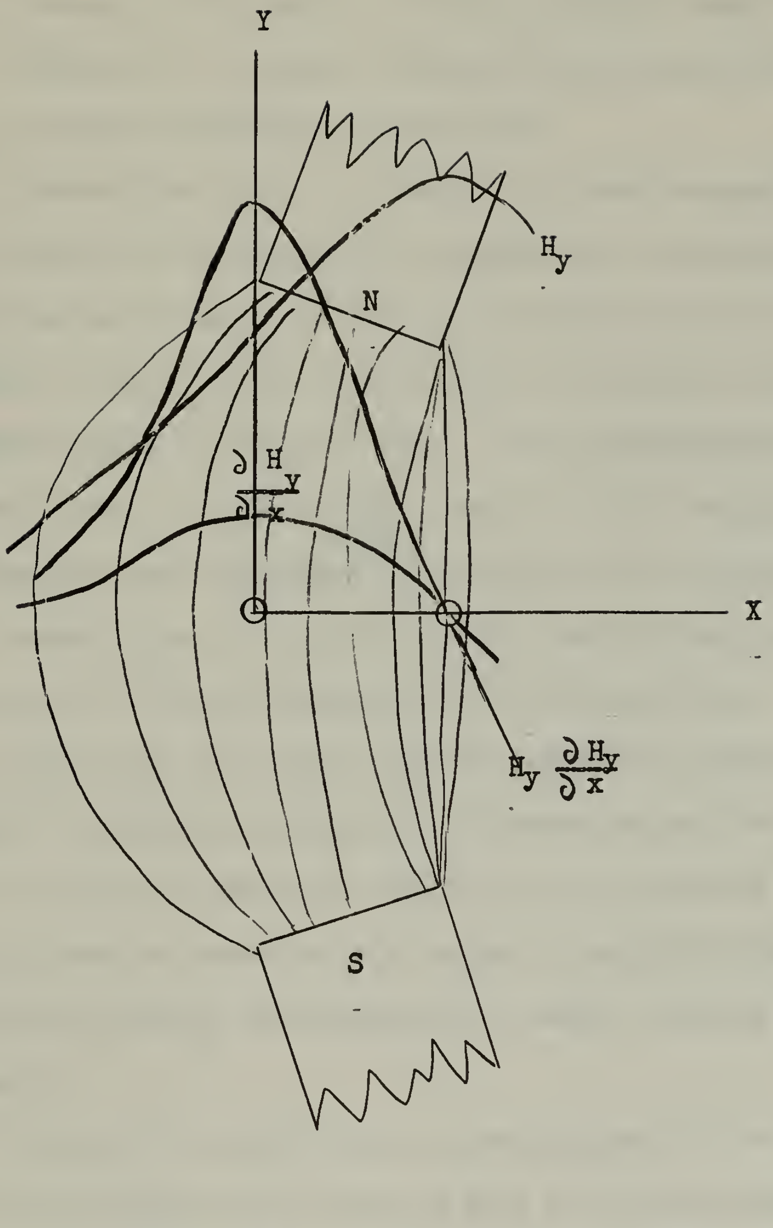

Figure 7

Faraday Method

of maximum force. One end of a torsion arm supports the sample which is free to move between the poles of a small permanent magnet. The magnet may be moved forward or backward with respect to the sample and, because of its magnetic susceptibility, the sample is either repelled or attracted. The sample automatically places itself in the region of maximum attraction or repulsion.

Most methods make use of a substance of known susceptibility such as water for calibrating the apparatus. For example in the Curie-Cheneveau balance, observations are made with the empty sample holder, the sample holder filled with the unknown substance, and the sample holder filled with water. The susceptibility is is calculated from $k = k_1 \frac{m_1}{m} \cdot \frac{\theta \pm \theta''}{\theta' \pm \theta''}$ where k is the susceptibility of the substance under examination, m the mass of the substance, m_1 the mass of water, θ and θ' deflections for the substance and water respectively, and θ'' is the deflection for the empty tube.

One of the most well known methods is the Gouy (22) method. In this method a cylindrical sample is suspended between the poles of a magnet so that one end of the sample is in a region of large field strength and the other is in a region of negligible field. The force is usually measured by suspending the sample from one pan of a microbalance.

The Quincke (48) method is one especially useful for liquids. The underlying principle is the same as that of the Gouy method. Instead of determining the force by direct weighing, the force due to the rise of the liquid in a capillary tube can be calculated from

a knowledge of the heigth to which the liquid rises, the density of the solution and the gravity constant. The liquid is placed in a U-tube one arm of which is placed between the poles of a magnet. Upon application of the field, the liquid will rise or fall depending upon whether it is paramagnetic or diamagnetic. This method has also been adapted for measuring susceptibilities of gases (9).

Numerous modifications of the above basic methods have been devised. Most of these are aimed at improving accuracy and precision, temperature control, ease of use, versatility, cost and ease of construction. A few of these modifications will be mentioned. Various methods of measuring the force in the Faraday and Gouy methods have been devised. Bhatnagor and Mathur (8) have devised an interference balance which is useful when investigating the susceptibilities of substances whose values are very close together. The principle of this magnetic balance is that if two converging beams of light are producing interference fringes and a moving glass plate be placed in the path of one, the shifting of the fringes will depend upon movements of the plate and can be a measure of it. Very small movements of the plate will produce considerable shifting of the fringes.

Sucksmith (58) describes a method in which the sample is suspended from a phosphor bronze ring which is fixed at its upper side. Two small mirrors are fixed to the ring at the optimum position so that on a scale at one meter distance the image of a lamp filament may be observed. Movement of the filament image is at least 150 times the movement of the sample.

A modification of the Faraday method by Foex (20) uses electrical compensating coils to measure the horizontal force on the sample.

In the method used by Hugo Theorell (60) the sample is suspended horizontally in a tube between the poles and the displacement observed with a microscope.

A ballistic susceptibility balance has been designed by Bhatnagor and Mathur (35). In this method the force due to the field acts only during a short interval of time and thus imparts a momentum to the suspended sample. This momentum is a measure of the susceptibility of the sample.

A method for gases has been devised by Vaidyanathan (61) in which a glass bulb is suspended in a field from a torsion balance. The gas surrounding the bulb can be changed and by measuring the deflections in different gases the susceptibility of one may be determined from the other.

The Quincke method has been adapted for use with gases by Wills and Hector (67) by using a manometric balance. The underlying principle is to balance the gas magnetically against a solution of known susceptibility. At the balance point no movement of the meniscus is observed and the gas and the liquid have the same susceptibility. The balance point is reached by changing the concentration of the solution, changing the temperature or by changing the pressure of the gas. The manometric method has been modified by Bitter (9) in such a way as to enable the relative susceptibilities of two gases to be easily determined.

An ingenious non-homogeneous field method for the comparison of liquid susceptibilities has been successfully used by Abonnenc (1). In this method drops fall from a tube, the orifice of which is in the non-homogeneous field region between the poles of a magnet. The magnetic susceptibility of the liquid, k, will be proportional to $\frac{m_o - m}{m}$ where m_o is the mass of the drops with no field and m is the mass with the field. If $\Delta m = m_o - m$ then for two liquids $k_1 : k_2 = \frac{\Delta m_1}{m_1} : \frac{\Delta m_2}{m_2}$. This method reportedly gives good results if the drops are formed regularly and if the liquids to be compared are similar in physical properties. Although the method is hardly suitable for measurements of high precision it is recommended for rough comparative measurements because of its simplicity.

Recently a microvibration method useful for very small amounts of material has been described (69). In this method, the force due to the periodic displacement of an elastic strip attached to the sample in a modulated magnetic field is measured dynamically in terms of a compensating electrostatic force. An electronic null indicator is used to indicate the equivalent point.

A dynamical method (57) depends on the fact that an elongated specimen suspended in a field will align itself in a position parallel or normal to the field depending upon whether it is paramagnetic or diamagnetic. If displaced from this position, oscillations will occur, and these, if the amplitude is small, will be simple harmonic, and of period independent of the precise form of the specimen, depending only on its susceptibility and on the magnetic field. This

method is of interest, but does not compare in accuracy and sensitivity with the other methods mentioned.

Salceanu (55) has developed a method of "magnetically neutral" solutions. If a paramagnetic substance is dissolved in a diamagnetic solvent such as water, there must be a certain concentration, at a definite temperature, at which the susceptibility is zero. Salceanu determines this condition by the rotation of a glass float placed in the liquid under investigation, between the poles of a magnet. The susceptibility of the solute may be calculated from a knowledge of the concentration at which the susceptibility of the solution is zero. This method has limited applicability.

An inductive method has been described (45, 16) which depends upon the change in the inductance of a coil of wire when a magnetic substance is placed in it. The small changes in inductance are measured by observing the change in beat frequency of an inductance-capacitance circuit. This method appears to be very good for routine measurements and should make measurements as simple as measuring pH or refractive index. The apparatus is commercially available in France.

A magnet balance described by Rankine (49) is a novel arrangement which has a permanent magnet as its moving system. In this method a small rod-shaped permanent magnet is suspended vertically from a torsion balance. A large plane-faced slab of the substance being examined is placed along side the magnet. The resultant force on the magnet is related to the susceptibility of the specimen. The method has been successfully used to determine the susceptibility of HDO and D_2O (27).

A method which is not as accurate as others mentioned but is unique in that no external magnetic field is required is the ortho-para hydrogen method (65, 31). The spin isomerization of hydrogen is catalyzed by inhomogeneous magnetic fields such as exist near paramagnetic ions or molecules. The rate of conversion is a function of the magnetic moment of the paramagnetic ion or molecule, and hence may be used as a rough measure of the susceptibility. This method has been successfully applied to the study of organic free radicals (39).

An elaborate modification of the Quincke method has been used by Auer (3) to determine the susceptibility of water. Auer used relatively wide tubes 10 mm in internal diameter in order to work quickly and to avoid "creeping" errors, i.e. errors brought about by an asymptotic approach to the proper surface level. He found the diamagnetic susceptibility of water at 16.3°C to be $0.72145 \pm 0.00048 \times 10^{-6}$ emu per gram.

II Magnetism and Magnetochemistry

Several excellent source books are available which deal with magnetism and magnetochemistry. The books by Selwood (54) and Bhatnagar (7) are concerned mostly with the chemical aspects of magnetism, while Stoner (57) and Bates (6) treat the subject mainly from the physicist's point of view. A thorough theoretical and advanced mathematical treatment is given by VanVleck (62). Jeans (28) covers the mathematical theory in detail.

A review by Nyholm (42) concerned with inorganic chemistry and magnetism was very helpful. The section in Weissberger's (64) books concerning magnetic susceptibility is a good general coverage of the subject.

III Complexes

Books by Bailar (4) and Martell and Calvin (34) are excellent sources for information on the general subject of complexes. An article by Goldenberg (21) describes the magnetic properties of manganese complexes in the solid state. Many literature references to cobalt complexes in the solid state or in aqueous solutions are given in Selwood (54).

A few references were found concerning the magnetic properties of transition metal complexes in non-aqueous media but nothing was found in which complexes had been formed and studied magnetically in aprotic media such as benzene. Certain planar diamagnetic complexes of nickel have been found to exhibit paramagnetism when dissolved in solvent such as chloroform, ethyl alcohol, pyridine, dioxane and benzene (15, 66, 43, 32). Bis (salicylaldoxime) Ni(II) is diamagnetic both in the solid state and in benzene solution, but has a moment indicating two unpaired electrons in pyridine solution. This has been ascribed to octahedral coordination in pyridine solution. On the other hand, bis (N-methyl-salicylaldimine) Ni(II) is diamagnetic in the solid state but paramagnetic in benzene. The tetrahedral structure is assumed in benzene (43, 32). Basolo and Matoush (5) reported that no direct correlation exists between the magnetic susceptibility of solutions

of bis (formylcamphor) ethylenediamine Ni(II) in methyl benzenes and the base strength of the solvents. If the paramagnetism were due to formation of octahedral complexes by expansion of the coordination shell of nickel, one might expect such a correlation. The data lead to the conclusion that tetrahedral Ni(II) complexes are formed in the solvent (5).

Data on cryoscopic studies of complexes prepared in benzene are found in Myers (40), Yao (68) and Hoechstetter (26). Data on the consecutive complexity constants for metal ammine formation in aqueous solutions is found in the classical work by Bjerrum (10).

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VITA

Richard Leland McArthy was born on June 10, 1928 in Wabash Indiana of William Leland McArthy and Martha Potterf McArthy. His elementary and secondary education were obtained in the Logansport Indiana public schools. In 1946 he entered Purdue University and was sworn into the U.S. Naval Reserve Officers Training Corps as a Midshipman USNR. While at Purdue he was a member of Pi Kappa Phi fraternity and The Quarterdeck Society. In 1950 he received a B.S. degree in Chemistry and a B.N.S. and T. degree (Bachelor of Naval Science and Tactics) from Purdue and entered the U.S. Navy on active duty as an Ensign. From 1950 until 1952 he served aboard the U.S.S. Chevalier (DDR-805). In 1952 he successfully completed the six month course of instruction at the Navy's School of Explosive Ordnance Disposal. In 1953 he served aboard the U.S.S. Goldcrest (AMCU-24). In 1954 he entered the U.S. Naval Postgraduate School at Monterey California where he received a B.S. degree in Ordnance Engineering (Explosives) in 2 years. In 1956 he entered Lehigh University to study for a masters degree. While at Lehigh he became an associate member of the Society of the Sigma Xi.

He is married to the former Miss Anna Mae Brown of Washington D. C. and is the father of a two year old girl, Linda.

Thesis 35897
M14 McArthy
Magnetic susceptibility studies of metal ammine complexes in aprotic media

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