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ABSTRACT

STRUCTURE AND BONDING IN METAL-AMINE SOLUTIONS AS DETERMINED BY ELECTRON PARAMAGNETIC RESONANCE AND OPTICAL SPECTRA

by Larry Raymond Dalton

An extensive study has been made of the magnetic and optical properties of solutions of the alkali metals dissolved in a number of amine, diamine, and amino-ether solvents.

The results of these studies emphasize the differences as well as the similarities between metal-amine and metal ammonia solutions. At least two additional species not present in metal-ammonia solutions appear to be required to explain the physical properties of metal-amine solutions.

The various models for metal-amine solutions have been examined in the light of the experimental evidence. Correlation of the optical and EPR results precludes the assignment of the visible absorption to the monomeric species responsible for hyperfine splitting.

A detailed analysis of hyperfine splittings, g values, spin concentrations, and relaxation processes has permitted the development of semi-quantitative models for the monomeric species. Although both stationary single-state and dynamic multi-state models are considered, the dependence of the magnetic parameters upon temperature and upon

metal and solvent composition indicates that a multi-state equilibrium among monomeric species of different electronic configurations is operative in the solutions.

The nature of the singlet observed at $g = 2.0019 \pm 0.0002$ in the EPR spectra is considered. Evidence is presented supporting the assignment of this singlet to the solvated electron, $e^-(\text{solv.})$.

Measurements of the viscosities of methylemine and ethylemine permit further analysis of nuclear spin-dependent relaxation processes in metal-emine solutions. In particular, the dependence of the linewidth upon the nuclear spin quantum number n_I is evaluated in the light of a two-state equilibrium and a multi-state distribution. These two expressions are shown to result in the same functional dependence upon n_I .

STRUCTURE AND BONDING IN METAL-AMINE
SOLUTIONS AS DETERMINED BY ELECTRON
PARAMAGNETIC RESONANCE AND
OPTICAL SPECTRA

by

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To my wife Lauraine

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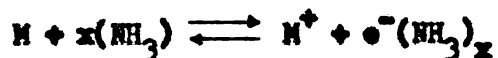
INTRODUCTION

There are two reasons for studying solutions of the alkali metals dissolved in ammonia and the amines. From a theoretical standpoint these solutions are of interest in that they represent systems of solvated fundamental particles. That is, the solutions are considered to be characterized by equilibria involving solvated electrons, metal monomers and dimers, metal molecule ions, and metal anions and cations. In the gas phase these fundamental particles and their interactions and reactions have been the subject of detailed quantum mechanical, thermodynamical, and statistical thermodynamical analyses. The study of these particles in solution provides considerable insight into the nature of the dissolution process and the nature of the liquid state. Insight is also provided into the methods of applied mathematics and the limitations of these methods.

From a practical standpoint these solutions are of interest because they represent a convenient source of electrons to be used in chemical reactions. The solutions are of particular value in the study of the kinetics of electron-attachment reactions.

The physical properties of alkali and alkaline earth metals in ammonia have been the subject of experimental and theoretical interest for over one hundred years. Since the early work of Weyl (1) many chemists and physicists have studied these systems because of their unusual physical and chemical properties. When metals dissolve in ammonia, metastable blue solutions are formed which become copper-bronze in color as the solutions become more concentrated.

Much of the early work on metal-ammonia solutions was carried out by C. A. Kraus. Kraus (2) hypothesized that the dissolved metal ionized according to the mass action expression



where M is the metal atom, M^+ is the positive metal ion, and e^- is the solvated electron. It was also hypothesized that the equilibrium shifted to the right as the concentration decreased giving only metal ions and solvated electrons at infinite dilution.

The solutions should be paramagnetic if they contain unpaired electrons. This was verified by Freed and Sagarman (3) and by Hexter (4,5). These workers measured the static susceptibility of sodium, potassium, cesium, calcium, and barium in ammonia as a function of temperature and concentration. At high dilution the static susceptibility approaches the value expected for free spins. Dilute barium solutions have susceptibilities greater than expected for one electron per barium atom indicating that both valence electrons are ionized. Quantitative electron paramagnetic resonance experiments have shown the paramagnetic susceptibility of sodium and potassium in ammonia (6) and potassium in deuterio-ammonia (7) increases but the molar susceptibility decreases with increasing concentrations. These results are in agreement with the static measurements and show that a concentration-dependent equilibrium exists between the paramagnetic and diamagnetic species.

Transference number measurements (8,9,10) have shown the primary current carrier to be anionic. The negative species carries about seven times more current at low concentrations than does the positive carrier. The percentage of the current carried by the negative species increases with increasing concentration until it is greater than 99% at high concentrations.

Nuclear magnetic resonance experiments on metal-ammonia solutions (11,12,13,14) have shown a chemical shift for the nitrogen and metal nuclei (Knight shift) but no detectable chemical shift for the protons. These results indicate considerable electron density at the nitrogen and metal nuclei but very little electron density at the proton nucleus.

In contrast to solutions of inorganic salts in ammonia, which increase in density and viscosity with increasing concentration, solutions of metals in ammonia show a decrease in both density and viscosity with increasing concentration (15,16).

The optical spectra of metal-ammonia solutions have been investigated extensively (17,18,19,20). All solutions are characterized by a single broad peak in the near infrared which is asymmetrically broadened on the high energy side. The spectra are independent of the nature of the cation, and there is no marked change in the form of the spectra when temperature and concentration are varied.

The preceding paragraphs indicate the intensity of experimental investigation directed toward metal-ammonia solutions. Theoretical efforts have been no less exhaustive. Several theories have been proposed, two of which gained early prominence (21,22). Both models involve the ionization of the metal in dilute solution to give a metal cation and a solvated electron, as first postulated by Kraus. The main difference between the theories relates to the position of the electron in the intermediate concentration range (0.005 to 0.1 molar). The "cavity" model (21) considers the electron to be completely removed from the metal and located in a "cavity" within the solvent. The Becker, Lindquist, Alder (BLA) model (22) considers the electron to be in an orbit about the metal ion but outside of its solvation sheath. Both models also consider the dimerization of the species just described.

Arnold and Patterson (23) have shown that correlation of the magnetic and conductance data necessitates the existence of a diamagnetic, negatively-charged species. This observation has generated extended interest in models for metal-amine solutions (24,25). Unfortunately no model capable of explaining the full range of physical properties has yet been forthcoming.

Alkali metals have also been observed to dissolve in a number of amines, diamines, and ethers forming strongly reducing blue solutions. The visual and chemical similarity of these solutions to metal-ammonia solutions has prompted the idea that these solutions are stoichiometrically equivalent to metal-ammonia solutions. Unfortunately the metal-organic solvent systems have until recently received only cursory attention.

The purpose of this project was to investigate extensively metal-amine solutions by optical and magnetic resonance techniques. It was hoped that the relationship of these solutions to metal-ammonia solutions could be deduced and that a detailed model for metal-amine solutions could be developed.

HISTORICAL

A. Models for Metal-Amine Solutions

In spite of the complexity of the optical spectra of metal-amine solutions including the appearance of several bands not found for metal-ammonia solutions, there existed an initial tendency to describe metal-amine solutions by extension or modification of the existing theories of metal-ammonia solutions (21,22).

Blades and Hodgins (26), after studying solutions of certain of the alkali metals in methylamine, ethylamine, and amine-ammonia mixtures, attributed the three characteristic optical absorptions of metal-amine solutions to solvated electrons existing in different types of solvent traps. In metal-ammonia solutions the positive end of the ammonia molecule is made up of three hydrogen atoms and is symmetrical so that the array of molecules at the edge of any hole will be identical. This will make the configurational co-ordinates and consequently the transition levels for each hole identical, with the result that a single maximum is observed for all the solutions in liquid ammonia. It was further argued that since the methylamine and ethylamine molecules are not symmetrical about the nitrogen it was possible that two different aspects of the molecule might be presented at the boundary of a trap. These two orientations may or may not be mixed depending on how readily they fit around the hole, the size of the hole, and on what other forces are at work in the rest of the liquid. On the basis of this model the methylamine

spectra were broken into two groups, called by Blades and Hodgins, amine bands and aliphatic bands. The former represented the condition where the methylamine molecules are oriented so that an ammonia-like trap is produced. This trap was viewed as giving rise to the infrared band (1250 to 1400 μ m). Aliphatic bands, accounting for the absorption at 650 to 725 μ m (visible band), arose from traps in which the methyl group participated in the formation of the trap boundary. The red band (840 to 1000 μ m) observed for dilute solutions of potassium in methylamine was considered to arise from a mixture of the two possible orientations.

Symons (27) viewed metal-amine solutions as being characterized by two absorptions, the visible band and the infrared band. On the basis of existing experimental evidence and by analogy with F centers in alkali halide crystals and P centers in crystalline silicon, Symons assigned the visible absorption to a diamagnetic species such as the dimer of the model of Becker, Lindqvist and Alder (BLA). Continuing, he assigned the infrared absorption to the solvated or cavity electron. From analogy with the results of addition of large concentrations of sodium salt to dilute solutions of sodium in ammonia (28), Symons attributed the red band to a monomer of the BLA type.

Cafasso and Sandheim (29) presented results for solutions of the alkali metals in others which seemed to fit the general description given by Symons (27,30). On the basis of studies of the alkali metals in ethylenediamine, Windsor and Sandheim (31) postulated that the visible (650 to 725 μ m) absorption is due to a species which shows no electron paramagnetic resonance (EPR) absorption and that the intermediate absorptions (800 to 900 μ m) for K and Rb solutions might be associated with a dimer.

Dainton, Wiles, and Wright (32) have presented strong evidence that the visible absorption peak for potassium in dimethoxyethane and tetrahydrofuran arises from the heterogeneous nature of the solutions. They were able repeatedly to decrease the absorbance significantly by centrifugation of the solutions. This suggested that the solutions are actually colloidal in nature. It has been pointed out that these results might be due to the presence of undissolved metal or precipitated decomposition products.

The first detailed model for metal-amine solutions was developed by Dye and Dewald (33). This model was unique in that it viewed the visible and red bands as arising from species not characteristic of metal-ammonia solutions. Covalent dimers, similar to those existing in the gas phase for the alkali metals, were considered responsible for the red band. This assignment was based upon correlation of this band with the intense $1L_g^+ \leftarrow 1L_u^+$ transition for the gaseous dimers of K and Cs (34) and upon the fact that, consistent with the assignment to a dimeric species, the red band is favored at high metal concentrations. The visible band was attributed to a combination of a solvated molecule-ion, M_2^+ , with an electron trapped in the field of this ion. The dissociation of M_2^+ would involve the breaking of a covalent metal-metal bond, accounting for the slow rate of interconversion of optical species. The slow interconversion rate also explained the lack of reproducibility of results by different investigators (31,35,36). Since the resultant electron density would be largely outside of the primary solvation layer, the nature of the cation in the M_2^+ species would be expected to have little effect upon the electronic energy levels, which explains the independence of peak position and shape upon the particular metal used. Comparison of optical

spectra and conductance measurements for alkali metals in ethylenediamine with the corresponding measurements for metal-ammonia solutions led these investigators to attribute the infrared absorption in amine systems to the solvated electron in the species: (e^-) , $(M^+ \cdot e^-)$, $(e^- \cdot M^+ \cdot e^-)$, $(M^+ \cdot e^- \cdot M^+)$, and $(M^+ \cdot e^-)_2$. These species were collectively referred to as "solvated electrons".

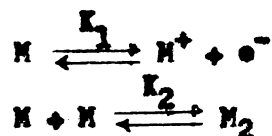
A new era of metal-amine research was introduced when Vos and Dye (37) at Michigan State University and Bar-Eli and Tuttle (38) independently at Brandeis University observed hyperfine splitting from a single metal nucleus in the EPR spectra of solutions of rubidium and cesium in methyldiamine and of potassium in ethyldiamine. These observations established unequivocally the existence of a species of stoichiometry M in metal-amine solutions. It also suggested the possibility that by comparison of the EPR and optical spectra of a given solution one could establish or disprove the assignment of the visible absorption to the monomer.

Ottolenghi, Bar-Eli, Linschitz, and Tuttle (39) examined the decay kinetics of solutions of potassium and rubidium in ethyldiamine. Comparison of the rate of change of absorbance with that of the EPR signal during decomposition of a potassium-ethyldiamine solution, and comparison of the rates of disappearance of the absorbances at 675 and at 915 m μ for solutions of potassium and rubidium in ethyldiamine led them to assign the visible absorption to a monomer of the EIA type. These authors were in agreement with Dye and Dowd (33) with regard to the assignment of the red and infrared bands.

More recently, Ottolenghi, Bar-Eli, and Linschitz (40) have studied solutions of the alkali metals in ethyldiamine by flash photolysis. Relying

upon the assignments made in Ref. 39 these authors evaluate their data in terms of a model involving BLA species and excited BLA species.

Thus despite the dissimilarities in the EPR and optical spectra of metal-amine and metal-ammonia solutions, it appeared that the properties of both systems could be explained by the same model. To investigate further the relationship between solutions of the alkali metals in the amines and in ammonia, workers in this laboratory (41,42) undertook the study of solutions of the alkali metals in amine-ammonia mixtures. This investigation conclusively showed the assignment by Ottolenghi *et al.* (39) of the visible band to the monomer to be in error. The reasons may be summarized as follows: (a) Measurement of spin concentrations for solutions of potassium in amine-ammonia mixtures (42) in solutions of low ammonia content show the concentration of the hyperfine species to be approximately 10^{-6} M. Even if the molar absorptivity of this species were as high as $5 \times 10^4 \text{ cm}^{-1} \cdot \text{mole}^{-1} \cdot \text{liter}$, the absorbance in a 1-cm cell would have a value of only 0.005. However, the absorbance of the visible peak observed in these solutions was unity or higher, more than 200 times that possible if the same species were responsible for both phenomena. (b) The absorbance of the optical species and the spin concentration of the hyperfine species change in opposite directions with changing temperature (41,42). (c) The dependence of spin concentration of the hyperfine species and the absorbance of the optical band (corrected to unit path length) upon ammonia concentration also show that different species are responsible for these two effects (41,42). (d) Bar-Kli and Tuttle(43) contend that the contributions to the EPR and optical spectra are determined by the equilibria:



Since no electron peak is observed in the EPR spectra of potassium in ethylamine, they assume that $K_1 \ll 10^{-4}$. They then reason that the concentration of M_2 will increase when the concentration of M decreases. Dalton et al. (41,42) found the opposite to be true. (c) Although the kinetics of decomposition observed by Ottolenghi et al. (39) would indicate that the visible and red band species are in a 2:1 stoichiometric relationship, decomposition studies in this laboratory (42) do not yield this result but rather are in a 1:1 relationship.

Since the presence of an EPR absorption attributable to the solvated electron accounted for only a fraction of the total infrared absorption, the work performed in this laboratory (41,42) showed electron-pairing reactions to be important in metal-amine solutions. It also showed that the red band should be assigned to the ${}^1\Pi_g^+ \leftarrow {}^1\Sigma_g^+$ transition of the alkali metal dimers rather than the ${}^1\Sigma_u^+ \leftarrow {}^1\Sigma_g^+$ transition as was originally proposed by Dye and Dowald (33).

The model of Dye and Dowald (33) was further challenged by the pulsed radiolysis studies of Anbar and Hart (44). These workers reported that pulsing solutions of anhydrous ethylenediamine resulted in an absorption maximum at 920 nm in direct disagreement with the assignment by Dye and Dowald of the infrared absorption at 1280 nm observed for solutions of the alkali metals in ethylenediamine to the solvated electron. This disagreement was particularly surprising in light of the excellent agreement between the assignment of the solvated electron in metal-ammonia solutions and the electron absorption found in the pulse radiolysis studies of anhydrous ammonia by Compton and co-workers (45).

Subsequent pulse radiolysis studies of anhydrous amines and diamines by Dalton, Dye, Fielden and Hart (46) showed the results of Anbar and Hart to be in error. Moreover, this study tended to confirm the assignment by Dye and Dewald (33) of the infrared band to the solvated electron.

Although the recent studies in this laboratory (40,41,45) have provided support for the assignments of Dye and Dewald (33) of the red band to covalent metal dimers and the infrared band to solvated electrons and aggregates and have shown the assignment of Ottolenghi *et al.* (39) of the visible band to alkali metal monomers to be in error, these investigations have not elucidated the nature of the species responsible for the visible band.

Most recently J. D. Rynbrandt (47) has attempted to explain the properties of metal-amine solutions by assignment of the visible band to species of stoichiometry M^- . This model, although capable of explaining many of the experimental data and in particular the flash photolysis results of Ottolenghi, Bar-Eli, and Linachitz (40), possesses several faults common to other models. The model will be discussed in greater detail later in this dissertation.

B. Models for the Monomer

The observation of hyperfine splitting by a single metal nucleus (37,38) showed conclusively that monomeric metal species exist in metal-amine solutions. The magnitude and marked dependence of this hyperfine interaction upon temperature and solvent rules out the assignment solely to a species whose electronic configuration is identical with that of a gaseous alkali metal atom.

The first detailed description of the monomeric species was attempted by Bar-Eli and Tuttle (43). They assumed that the monomeric species in

metal-amine solutions was essentially a monomer of the BIA type. They also assumed that the spherically symmetrical "shape" of the wavefunction does not change with temperature but that an expansion occurs as the temperature is decreased. This expansion presumably results from an increase in the size of the monomer as additional solvation spheres are added. The unpaired electron density is assumed to be distributed over the solvation layers according to the ratio of the solvent binding energy to kT . Over the temperature range which they studied, Bar-Eli and Tuttle (43) found the scaling factor for the wavefunction to be linear in $1/T$. Workers in this laboratory (42) found, however, that extending the temperature range yields a scaling factor that is not a linear function of $1/T$. Furthermore, calculations using this model require the average radius of the electron distribution to increase by a factor of two over a 100 degree temperature range.

O'Reilly (48,49), also using a monomer model, proposed a different explanation of the temperature dependence of the hyperfine splitting in metal-amine solutions. The alkali-metal ion was assumed to be octahedrally surrounded by solvent molecules at a distance $r = a$, while the remainder of the solvent ($r > b$) was treated as a continuous dielectric medium. The potential function used was that of the free gaseous atom plus an inverted square well of radius a to account for dipolar, quadrupolar, and polarisability effects of the solvent. An approximate calculation, ignoring the quadrupolar term, indicated that the temperature variation of the hyperfine splitting could be accounted for on the basis of an expansion of the cation-solvent distance of about 0.2% per degree. In attempting to apply O'Reilly's model to their results, Dalton *et al.* (42) found that the high and low temperature regions require different coefficients of expansion.

Using an iterative procedure to calculate Δ as a function of temperature (50) gives $(1/\Delta) (d\Delta/dt) = 5.84 \times 10^{-4}$ below 40°C and 4.73×10^{-3} above this temperature.

Both of these models require rather large changes in monomer dimensions with temperature. Moreover none of the models predicts the sharp change in the temperature dependence of the hyperfine interaction observed in this laboratory (41,42). Neither do these models explain the strong dependence of the hyperfine splitting upon ammonia concentration observed for amine-ammonia mixtures (41,42).

Dalton, Rynbrandt, Hansen, and Dye (42) have developed a model which meets these objections and which gives excellent quantitative agreement with experimental results. In this model they consider an equilibrium among two or more monomeric species with distinct magnetic properties. The relaxation time for the interconversion of these species must be faster than the reciprocal of the hyperfine interaction frequency but slower than molecular rotation. Because of the extrapolation of the hyperfine splitting (hfs) to the free-atom value at high temperatures, one of the species (A) is considered to be the solvated atom, with a splitting the same as that for gaseous atoms. The ammonia dependence of the hfs requires, in addition to atoms, two solvated monomeric species $\text{M}(\text{EtNH}_2)_x$ and $\text{M}(\text{EtNH}_2)_{x-1}(\text{NH}_3)$ represented by B and C, respectively. According to this scheme the following equilibria are involved:



in which x is the mole fraction of ammonia. The measured hyperfine splitting Δ_p is related to the concentration of these species and their respective splittings by

$$A_F = (n_A A_A^\circ + n_B A_B^\circ + n_C A_C^\circ)/n \text{ with, of course, } n = n_A + n_B + n_C. \quad (2)$$

For the case of saturated solutions, it would be expected that the concentration of atoms would vary according to

$$\ln [A] = (\Delta H^\circ/RT) + (\Delta S^\circ/R) \quad (3)$$

in which ΔH° and ΔS° are the molar enthalpy and entropy of solution of the metal to give atoms. The strong dependence of A_F upon temperature above 40°C indicates that the temperature dependence of atom concentration is much greater than that of the other two species. This permitted an approximate separation of the splitting due to atoms from that due to the species B and C by extrapolation of the low-temperature behavior. This separation was accomplished using the approximation

$$n_A = n(A_F^\circ - A_H^\circ)/(A_A^\circ - A_H^\circ) \quad (4)$$

in which A_H° was first obtained from a linear continuation of the low-temperature splitting. The atom concentration was used with Eq. 3 to evaluate ΔH° and ΔS° . Then calculated atom concentrations were combined with the experimental splittings to yield new A_H° values. The correct value of A_H° represented the splitting which would be observed in the absence of atoms. It is given by

$$A_H^\circ = (n_B A_B^\circ + n_C A_C^\circ)/(n_B + n_C) \quad (5)$$

These were fitted to a linear equation in temperature using a least-squares technique. Iteration gave the results in Table I. Calculated and experimental splittings are shown in Fig. 1 for a 2.7 mole % ammonia solution.

It is seen from Table I that the value of ΔG° is reasonably independent of ammonia concentration as are ΔH° and ΔS° at the lower concentrations. This provided support for the treatment used, especially in the light of the large variation of A_F and n with ammonia concentration.

TABLE I. Least-Squares Values from Analysis of Atom-Monomer Equilibria^a

<u>Mole percent</u> <u>ammonia</u>	ΔH° (kcal)	ΔS° (cal/degree)	ΔG° (25°C) (kcal)
1.2	8.3	-9.8	11.2
2.7	9.8	-5.5	11.4
5.8	9.1	-7.2	11.9
9.6	12.9	5.6	11.3
11.8	14.6	12.8	10.8
14.2	15.1	15.4	10.5

^aStandard states are one mole per liter for both gaseous and solvated atoms.

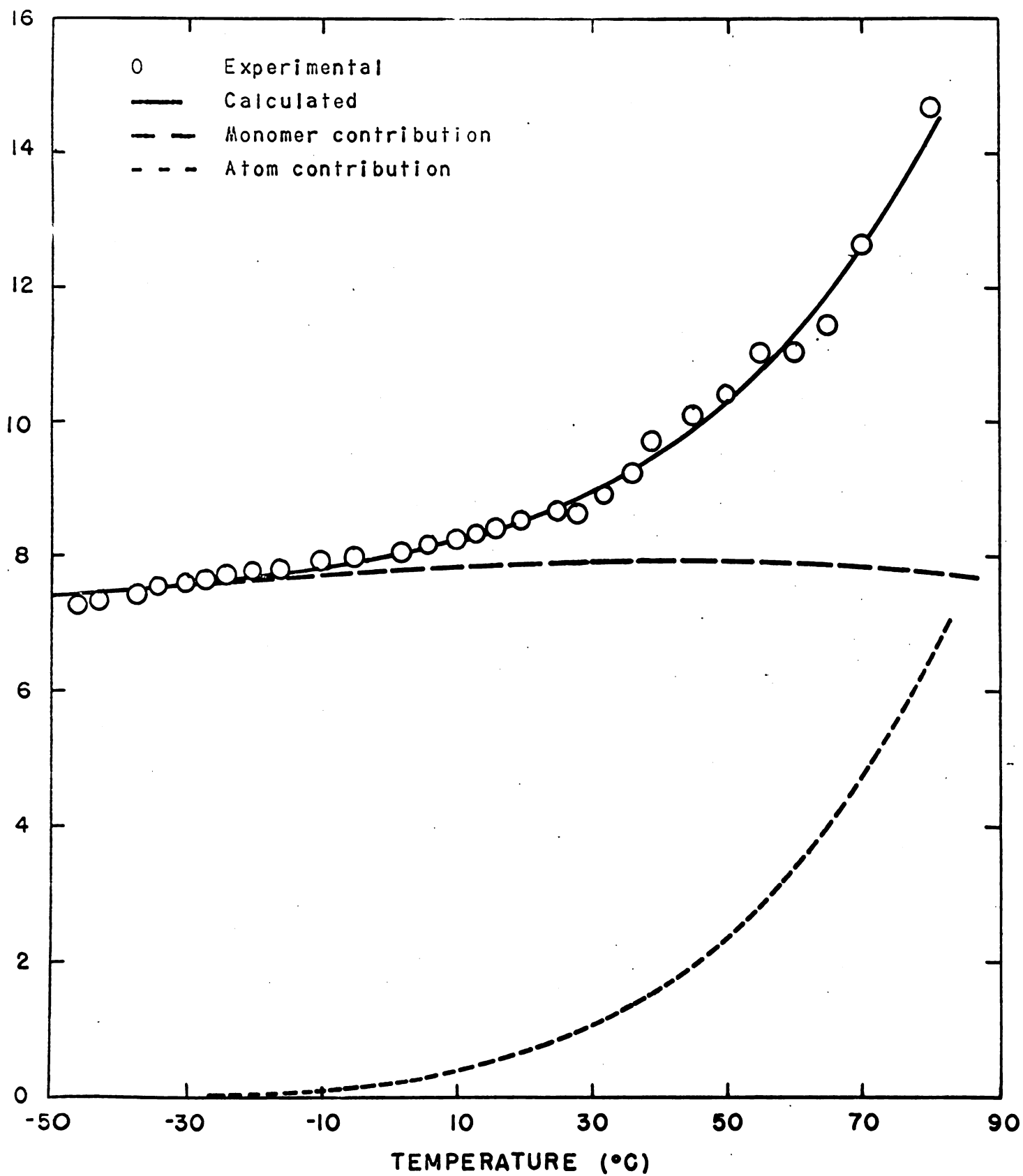


Figure 1. Separation of hyperfine splitting into atomic and monomeric contributions

The average value of ΔG° , combined with the free energy of formation of the gaseous atoms yields $\Delta G^\circ = -5.2 \text{ kcal mole}^{-1}$ for the solvation process



using standard states of 1 mole/liter for both the gas phase and the solution. Results for the three lowest ammonia concentrations yield $\Delta H^\circ = -12.4 \text{ kcal mole}^{-1}$ and $\Delta S^\circ = -24.2 \text{ cal mole}^{-1} \text{ deg}^{-1}$ for this process. Because of the limited studies at higher ammonia concentration and possible unsaturation of the solutions, the values of ΔH° and ΔS° especially in the high ammonia region, are subject to considerable uncertainty.

However, Dalton et al., (42) point out that even if the solutions were unsaturated above room temperature, the atom-monomer model could be used to explain the variation of the hyperfine splitting with temperature. Using the equilibria given in Eq. 1, and the expressions for hyperfine splitting one obtains

$$K_a \left\{ 1 + K_1^{(\circ)} \left[I/(1-I) \right] \right\} = (A_A^\circ - A_F) / (A_F - A_H^\circ), \quad (7)$$

which is valid whether or not the solutions are saturated. Because of its sensitivity to the small value of $(A_F - A_H^\circ)$ at low temperatures, this equation was used only to evaluate K_a by extrapolation to $I = 0$. Use was made in this extrapolation of the $K_1^{(\circ)}$ values obtained as described below.

Variation of K_a with temperature gave $\Delta H_a^\circ = -6.6 \text{ kcal mole}^{-1}$, $\Delta S_a^\circ = -14.7 \text{ cal deg}^{-1} \text{ mole}^{-1}$ and $\Delta G_a^\circ = -2.2 \text{ kcal mole}^{-1}$ at 25°C . These values agree with those obtained from the previous experiment.

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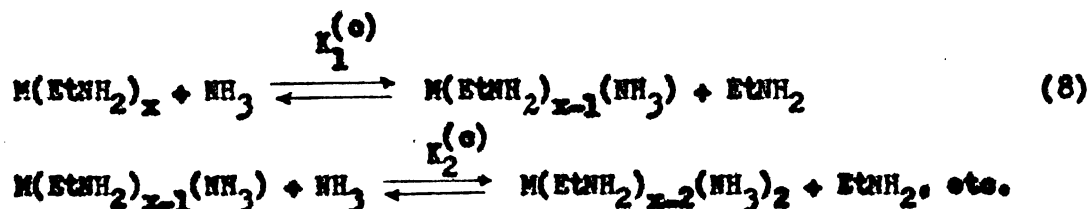
$$K_A \left\{ 1 + K_1^{(c)} \left[I/(1-X) \right] \right\} = (\Lambda_A^\circ - \Lambda_F^\circ)/(\Lambda_F^\circ - \Lambda_H^\circ), \quad (7)$$

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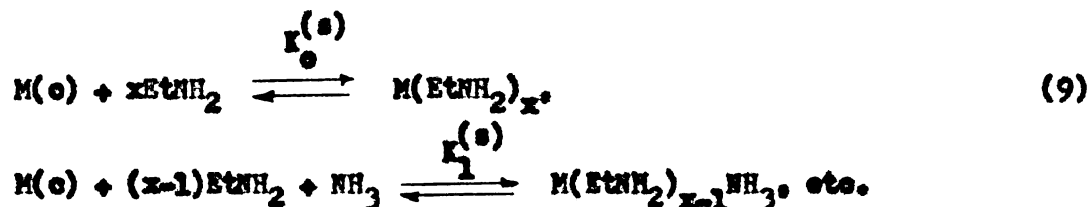
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While inclusion of atoms in the equilibrium model successfully accounts for the high-temperature behavior of the hfs including the

sharp break just above room temperature, the residual variation with ammonia concentration requires further consideration. Dalton et al. point out that this suggests an equilibrium involving substitution of ammonia for ethylamine in the vicinity of the metal nucleus. Such a substitution might involve simple replacement of ethylamine by ammonia in the first co-ordination sphere of a monomer unit, or else a significant alteration of the monomer structure by ammonia. The possible substitution reactions are represented by



Since saturated solutions are involved, the following solubility equilibria are also involved:



Where, of course,

$$\begin{aligned} K_1^{(s)} &= K_o^{(s)} K_1^{(o)}, \\ K_2^{(s)} &= K_1^{(s)} K_2^{(o)} = K_o^{(s)} K_1^{(o)} K_2^{(o)}, \text{ etc.} \end{aligned}$$

To determine the extent of ammonia substitution at a given temperature one can independently examine the variation of spin concentration and of $h\nu$ with ammonia concentration. Consideration of the equilibria (assuming mole fractions equal to activities for ammonia and ethylamine) yields

$$\begin{aligned}
 n - n_A &= [M(EtNH_2)_x] + [M(EtNH_2)_{x-1}NH_3] + \dots \\
 &= K_0^{(s)} + K_0^{(s)} K_1^{(o)} [NH_3] + K_0^{(s)} K_2^{(o)} [NH_3]^2 + \dots \\
 &= K_0^{(s)} [1 + K_1^{(o)} x + K_1^{(o)} K_2^{(o)} x^2 + \dots]
 \end{aligned} \tag{10}$$

for small mole fractions of ammonia and

$$\begin{aligned}
 n - n_A &= K_0^{(s)} (1-x)^x \left[1 + \frac{K_1^{(o)} x}{(1-x)} + \frac{K_1^{(o)} K_2^{(o)} x^2}{(1-x)^2} + \dots \right. \\
 &\quad \left. + \frac{K_1^{(o)} K_2^{(o)} \dots K_x^{(o)} x^x}{(1-x)^x} \right]
 \end{aligned}$$

for larger mole fractions of ammonia. Within experimental error, graphs of $[n - n_A]$ versus x_{NH_3} at various temperatures are linear up to about 10 mole % ammonia (top line, Fig. 2), showing that the addition of only one molecule of ammonia is important over this range. Values of $K_0^{(s)}$ and $K_1^{(o)}$ obtained from spin measurements are given in Table II.

An independent check on $K_1^{(o)}$ can be made using the hf's data and the assumption that species B and C have different splittings which are independent of temperature. The residual splitting Λ_H° obtained by eliminating the contribution from atoms is related to the concentrations and splittings of B and C by

$$\Lambda_H^\circ = (n_B \Lambda_B + n_C \Lambda_C) / (n_B + n_C). \tag{11}$$

(It is to be noted that the contribution from atoms is negligible below about 10°C. Above this temperature, Λ_H° must be calculated from the total splitting and presumed atom concentration.)

From the equilibrium (1) with x = mole fraction of ammonia, one obtains

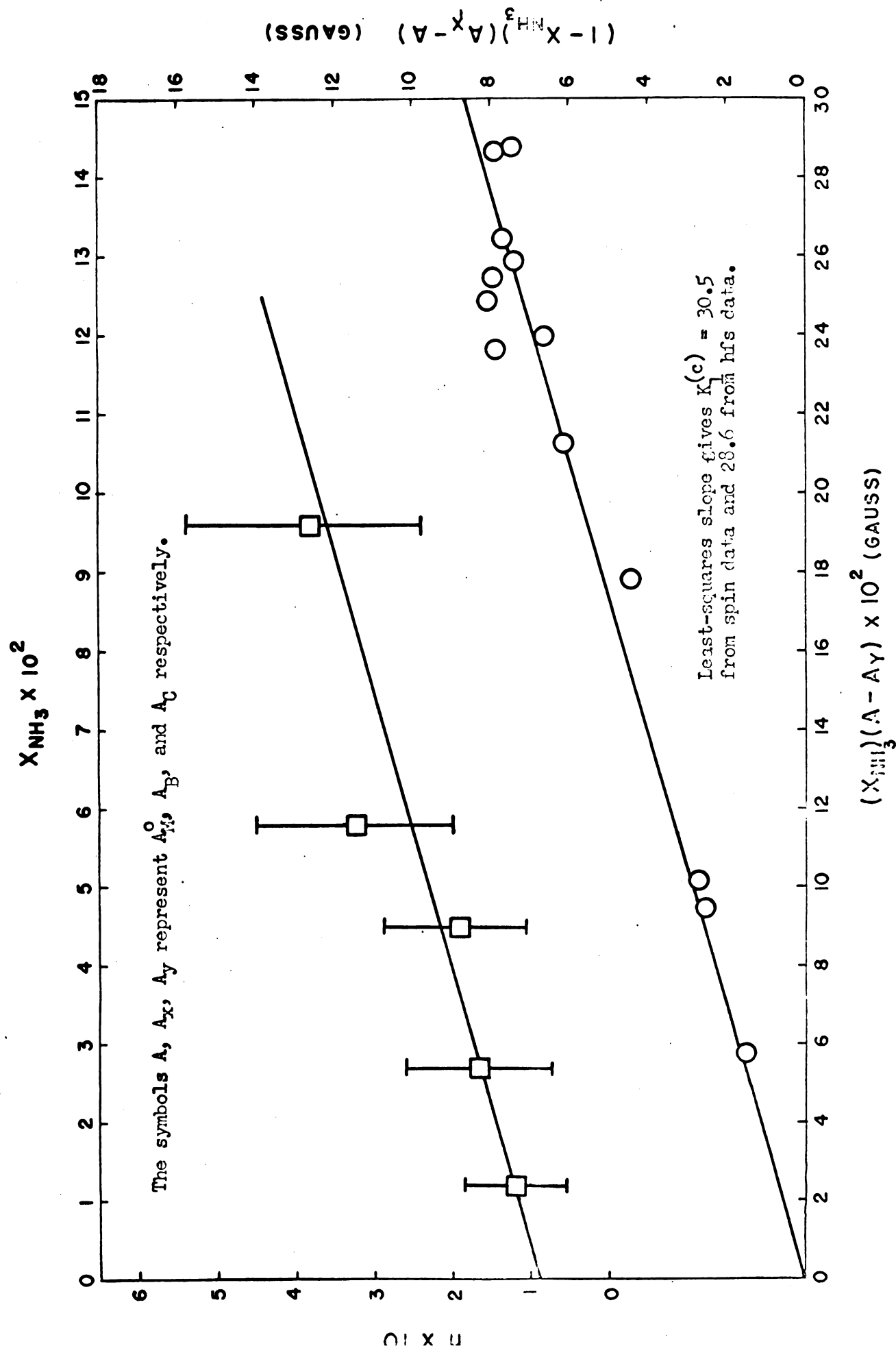


Figure 2. Calculation of complexation constants from spin concentration data (squares) and independently from hfs data (circles).

TABLE II. Equilibrium Constants for the Solvation and Complexation Equilibria as Calculated from Spin Concentration and Hfs Measurements.

Temp °C	$K_0^{(s)} \times 10^7$ (from spin concentrations)	$K_1^{(s)}$	$K_1^{(s)}$ (from hfs values)
75 ^a			18.9
40 ^a			22.4
25 ^a	2.3	24.2	23.9
0	2.1	22.9	22.5
-25	1.7	27.7	27.7
-40	1.5	30.5	28.6
-60	1.3	35.4	37.6

^aAbove 25°C the effects of the stem-monomer equilibria were taken into account. Molar concentrations were used for potassium; mole fractions for ammonia and ethylamine.

$$K_1^{(0)} = (n_C/n_B)[(1-X)/X],$$

which yields

$$K_1^{(0)} = [(A_B - A_H^0)/(A_H^0 - A_C)] [(1-X)/X]. \quad (12)$$

Extrapolation of A_H^0 versus X to $X = 0$ gives an intercept of A_B , while extrapolation of A_H^0 versus $(1-X)/X$ to $X = 1$ gives an intercept of A_C . Using these values, $K_1^{(0)}$ was calculated by a least-squares fit of Eq. 12 as shown in Fig. 2. The results are given in Table II. Since little deviation of A_B and A_C with temperature was noted, constant values were used. In addition, $K_1^{(0)}$ is nearly independent of temperature. The agreement of $K_1^{(0)}$ obtained from hyperfine splittings and from the completely independent spin concentration measurements is gratifying.

In summary, the equilibrium model not only describes such qualitative features as the unusual dependence upon temperature and ammonia concentration, but also is in quantitative agreement with the experimental results. Although three species were required to fit the data, the nature of the effects observed makes it very difficult to describe them with a simpler model.

It is possible to describe the variation of hf's with ammonia concentration at a single temperature using Eq. 19 of Bar-Eli and Tuttle (20):

$$A = \frac{a_1 x_1 \exp(\Delta E/kT) + a_2 x_2}{x_1 \exp(\Delta E/kT) + x_2}$$

and a suitable value of E . For example, at -40°C , using $a_1 = 12.0 \text{ G}$, $a_2 = 0$, and $E = -1.48 \text{ kcal mole}^{-1}$, an excellent fit of the hf's data

is obtained. Using the same value of ΔE at 25°C, however, gives a very poor fit even when the values of a_1 and a_2 are adjusted.

The large change of h_f 's upon substitution of a single ammonia molecule for ethylamine is rather surprising. However, within the framework of the equilibrium model, one is forced to the conclusion that only one ammonia molecule is involved. In view of this, the substitution of ammonia for ethylamine must result in considerable distortion of the electron distribution in the monomer. This could result from the introduction of considerable p character in the ground-state wavefunction, or, in the extreme case, by stabilization of an ion pair between the cation and a solvated electron.

Catterall *et al.* (51,52) have employed an equilibrium formalism very similar to that developed in this laboratory to describe hyperfine interactions in potassium-amine solutions. The major contributor to the observed hyperfine splitting is considered to be the solvated atom.

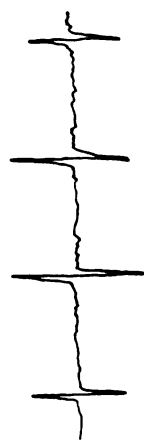
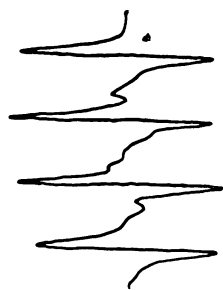
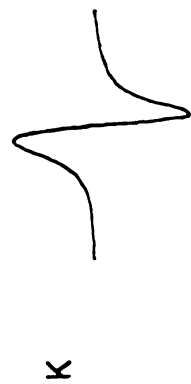
C. Paramagnetic Relaxation in Metal-Amine Solutions

One of the most puzzling features of the EPR spectra of metal-amine solutions is the dependence of the linewidth upon hyperfine component (see Fig. 3) observed for solutions of rubidium and cesium in methylamine and for solutions of potassium, rubidium, and cesium in ethylamine and propylamine (53). The usual explanation for such behavior is in terms of a strong anisotropy of the electric field at the splitting nucleus, modulated by tumbling of the paramagnetic species. This "McConnell mechanism" (54) requires the linewidths to be dependent upon both viscosity and frequency and has successfully

METHYLAMINE

ETHYLAMINE

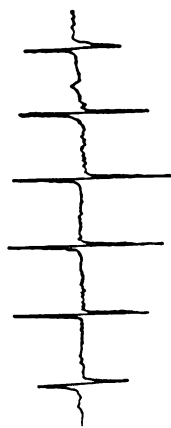
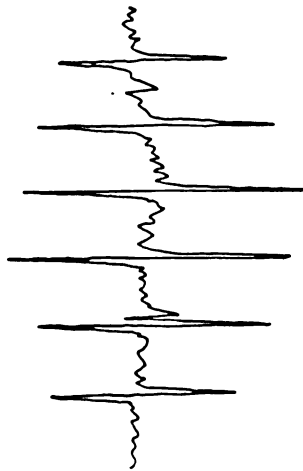
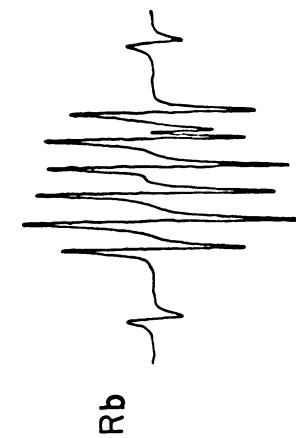
PROPYLAMINE



23°C, $g = 2.00170$

50°C, $g = 2.00149$, $a = 13.00G$.

23°C, $g = 2.00150$, $a = 14.00G$.

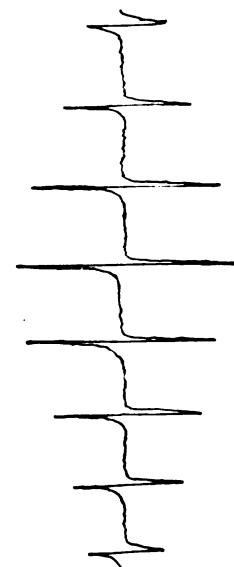
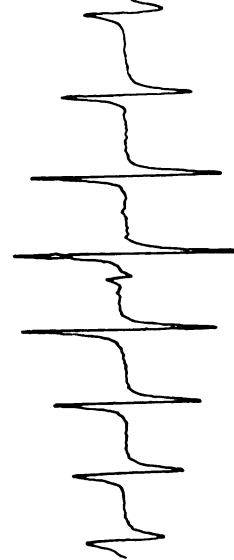
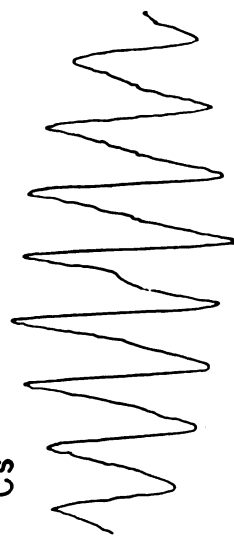


23°C, $g = 1.99986$, $a = 25.60G$.

23°C, $g = 1.99982$, $a = 64.06G$.

23°C, $g = 1.99979$, $a = 33.91G$.

Cs



23°C, $g = 1.99481$, $a = 55.39G$.

23°C, $g = 1.99434$, $a = 127.6G$.

23°C, $g = 1.99479$, $a = 171.5G$.

Figure 3. EPR spectra of alkali metals in some amines; data given for ^{39}K , ^{85}Rb , and ^{131}Cs .

explained the EPR spectra of several first and second row transition metal ions and complexes (54,55,56,57,58,59). In all these cases, a marked asymmetry of the field can logically arise from the geometry of the ion in the presence of its ligands.

Several refinements of the original treatment of McConnell have been made (56,60). Recently, Wilson and Kivelson (57) have modified the treatment for the case of large hyperfine interactions by including second-order effects and have given expressions for the dependence of linewidth upon m_I through third-order.

It is difficult to rationalize interactions between alkali metal ions and amine solvent molecules which are strong enough to result in a marked asymmetry of the electric field. However, the introduction of such a field anisotropy is required to explain the experimental linewidths by the McConnell mechanism.

Dalton et al. (42) have proposed an alternate mechanism which could also result in a dependence of linewidth upon m_I . This mechanism involves the rapid interconversion of two monomeric species, A and B, having different hyperfine contact densities. For exchange slower than the exchange-narrowed limit, this leads to an expression for linewidths (42)

$$\tau_2^{-1} = p_A/T_{2A} + p_B/T_{2B} + p_A^2 p_B^2 (a_A - a_B)^2 (\tau_A + \tau_B) m_I^2 \quad (13)$$

in which a_A and a_B are the time-independent hyperfine splitting frequencies of the two species undergoing exchange, p_A and p_B are the respective fractions of these species, T_{2A} and T_{2B} are the relaxation times of A and B in the absence of exchange, and τ_A and τ_B are the mean lifetimes of the two species. Although Eq. 13 shows dependence

only upon m_I^2 , the high-field approximation was used, and it was assumed that A and B have the same g-values.

Dye and Dalton (53) have recently modified the exchange mechanism to include the case of intermediate splittings (15 to 150 gauss) and the case for which $g_A \neq g_B$. Using third order corrections obtained from perturbation theory they wrote for the frequency of the transition involving hyperfine component m_I in species A in the absence of exchange,

$$\omega_A^{\circ}(m_I) = \omega_A^{\circ} - a_A m_I - a_A^2 [I(I+1) - m_I^2] / 2 \omega_A^{\circ}(m_I) + a_A^3 / 4 \omega_A^{\circ}(m_I)^2 \quad (14)$$

in which $\omega_A^{\circ}(m_I)$ is the transition frequency of a particular line,

ω_A is the transition frequency in the absence of hyperfine interaction, and a_A is the hyperfine splitting frequency. A similar expression describes the transition frequencies of species B.

If A and B are rapidly interconverted, the inverse relaxation time of the exchange-narrowed line may be approximated by

$$[T_2(m_I)]^{-1} = P_A/T_{2A} + P_B/T_{2B} + P_A^2 P_B^2 (\gamma_A + \gamma_B) [\omega_A^{\circ}(m_I) - \omega_B^{\circ}(m_I)]^2 \quad (15)$$

Eq. 15 assumes exchange narrowing to a single Lorentzian line for each hyperfine component. Substitution of the frequencies given by Eq. 14 into Eq. 15 leads to an expression of the form

$$[T_2(m_I)]^{-1} = P_A/T_{2A} + P_B/T_{2B} + P_A^2 P_B^2 \gamma_A \gamma_B [\alpha + \beta m_I + \gamma m_I^2 + \delta m_I^3 + \epsilon m_I^4] \quad (16)$$

Expressions for the coefficients of various powers of m_I are given in Table III.

Instead of describing the variation of magnetic parameters with temperature in terms of two or more interconverting species,

TABLE III. Coefficients of m_I in the Linewidth Expression using the Two-State Model.

$$\Gamma_2(m_I)^{-1} = \frac{P_A}{\Gamma_{2A}} + \frac{P_B}{\Gamma_{2B}} + P_A^2 P_B^2 (\gamma_A + \gamma_B) [\alpha + \beta m_I + \gamma m_I^2 + \delta m_I^3 + \varepsilon m_I^4]$$

$$\alpha = \{F_1 + F_3 I(I+1)\}^2$$

$$\beta = 2\{F_1 + F_3 I(I+1)\} \{F_2 + \frac{1}{2}F_4 - I(I+1)F_4\}$$

$$\gamma = [\{F_2 + \frac{1}{2}F_4 - I(I+1)F_4\}^2 - 2F_3\{F_1 + F_3 I(I+1)\}]$$

$$\delta = [2F_4\{F_1 + F_3 I(I+1)\} - 2F_3\{F_2 + \frac{1}{2}F_4 - I(I+1)F_4\}]$$

$$\varepsilon = [2F_4\{F_2 + \frac{1}{2}F_4 - I(I+1)F_4 + F_3^2\}]$$

where

$$F_1 = (\omega_A^0 - \omega_B^0)$$

$$F_2 = (a_A - a_B)$$

$$F_3 = \frac{a_A^2}{2\omega_A} - \frac{a_B^2}{2\omega_B}$$

$$F_4 = \frac{a_A^3}{2\omega_A^2} - \frac{a_B^3}{2\omega_B^2}$$

The above coefficients of Eq. 16 are obtained when Eq. 14 is replaced by the expansion of the Breit-Rabi equation given by Fessenden and Schuler.^{8b}

$$\omega_A(m_I) = \omega_A^0 + a_A m_I + \frac{a_A^2}{2\omega_A} [I(I+1) - m_I^2] + \frac{a_A^3}{2\omega_A^2} \{m_I[m_I^2 + \frac{1}{2} - I(I+1)]\}$$

^{8b}R. W. Fessenden and R. H. Schuler, J. Chem. Phys., 43, 2704 (1965).

Dye and Dalton (53) point out that one can consider stationary-state models in which the wavefunction for the unpaired electron is strongly dependent upon solvent configuration about the M unit. Two models based upon this assumption have been used to explain hyperfine interactions in metal-amine solutions (43,49).

These models require a distribution of electron environments in the solution with a broad range of hyperfine contact densities. Such a distribution is necessary since a change in temperature brings about a change in the observed hyperfine splitting. Presumably this distribution arises from variations in solvent structure about the monomer. If the correlation time associated with fluctuations of the solvent environment is long enough to contribute significantly to line-broadening, then the linewidths of the individual hyperfine components will be different, with broader lines resulting for the higher m_I values. If a significant portion of the distribution of solvent structures arises from molecules outside of the primary solvation layer, one would expect abrupt changes in hyperfine splitting and linewidth at the freezing point. A quantitative treatment of this model would require knowledge of the distribution of hyperfine splittings and g -values, and has not yet been carried out. It should be possible, using the observed variation of these two parameters with temperature and the assumption of a Gaussian distribution, to describe the linewidth behavior with a temperature-dependent correlation time.

Dye and Dalton (53) have attempted to determine which of these mechanisms is operative for metal-amine solutions by intensively investigating the spectra of cesium in ethylamine. The analysis of the m_I -dependent relaxation observed in metal-amine solutions was carried

out by evaluating the coefficients of $1/T_2$ to various powers of n_1 . To eliminate the effect of intermolecular relaxation processes (e.g. spin exchange and chemical exchange) only solutions estimated to be less than 5×10^{-4} molar in metal were used in this analysis. The experimentally observed coefficients for several cesium-ethylamine solutions are shown in Fig. 4 as functions of temperature. Analysis of the results showed that only terms through the third power in n_1 are significant. Of particular interest is the opposite temperature dependence exhibited by the coefficients of the linear and quadratic terms.

The predominant term is quadratic in n_1 . Since the sign of the coefficient of the cubic term is opposite to that of the first-power term, both of these coefficients are very sensitive to experimental error and show considerable scatter. The dependence upon n_1 is significant. Of particular interest is the opposite temperature dependence exhibited by the coefficients of the linear and quadratic terms.

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When considered in detail, none of the treatments described above was able to explain all aspects of the observed n_1 -dependent relaxation.

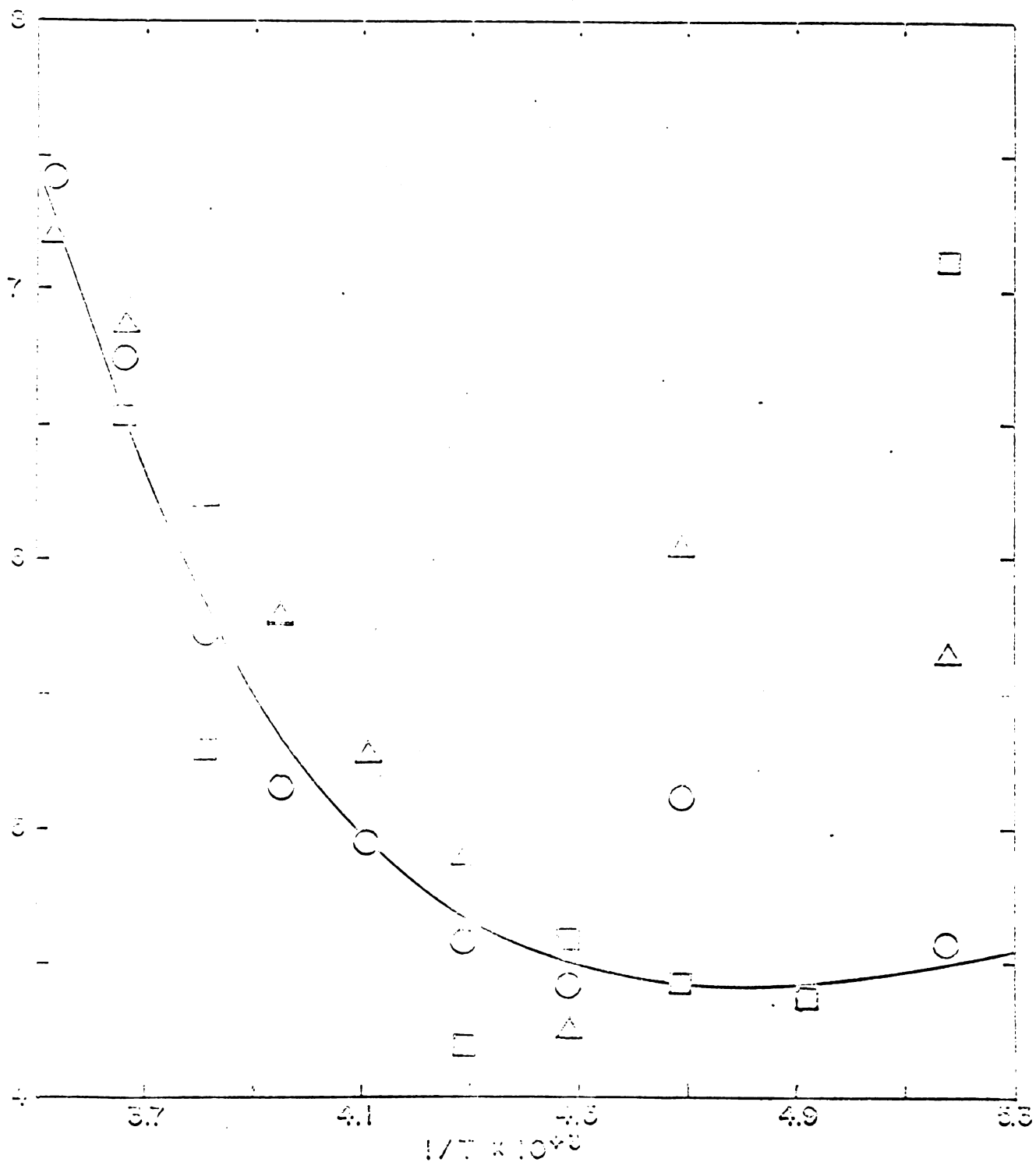


Figure 4a. Variation of the residual linewidth (Co) with $1/T$: Cs in ethylamine. Results are shown for three different sample preparations.

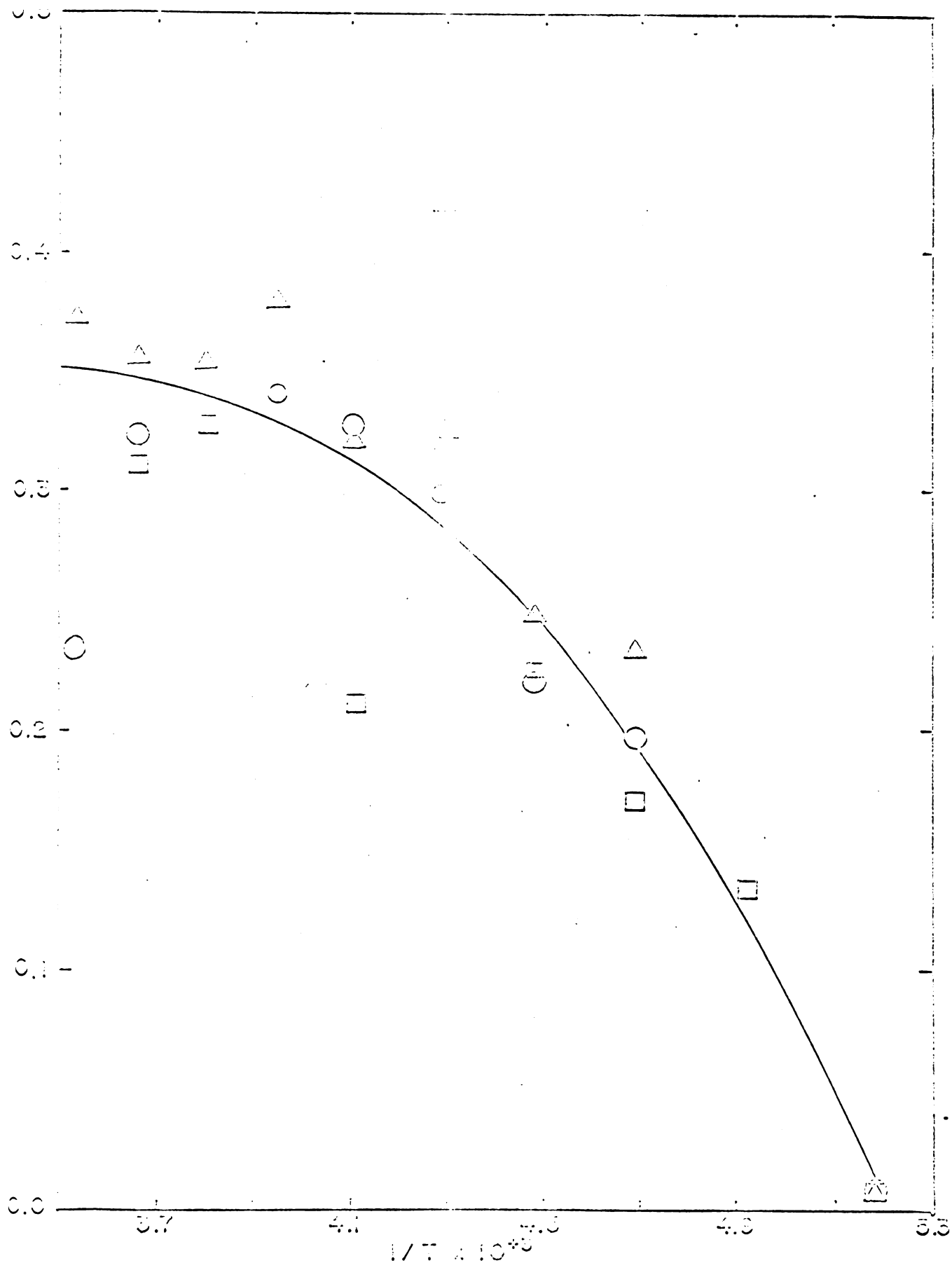


Figure 4b. Variation of the coefficient of m_- (C_1) with $1/T$: Cs in ethylamine. Results are shown for three different sample preparations.

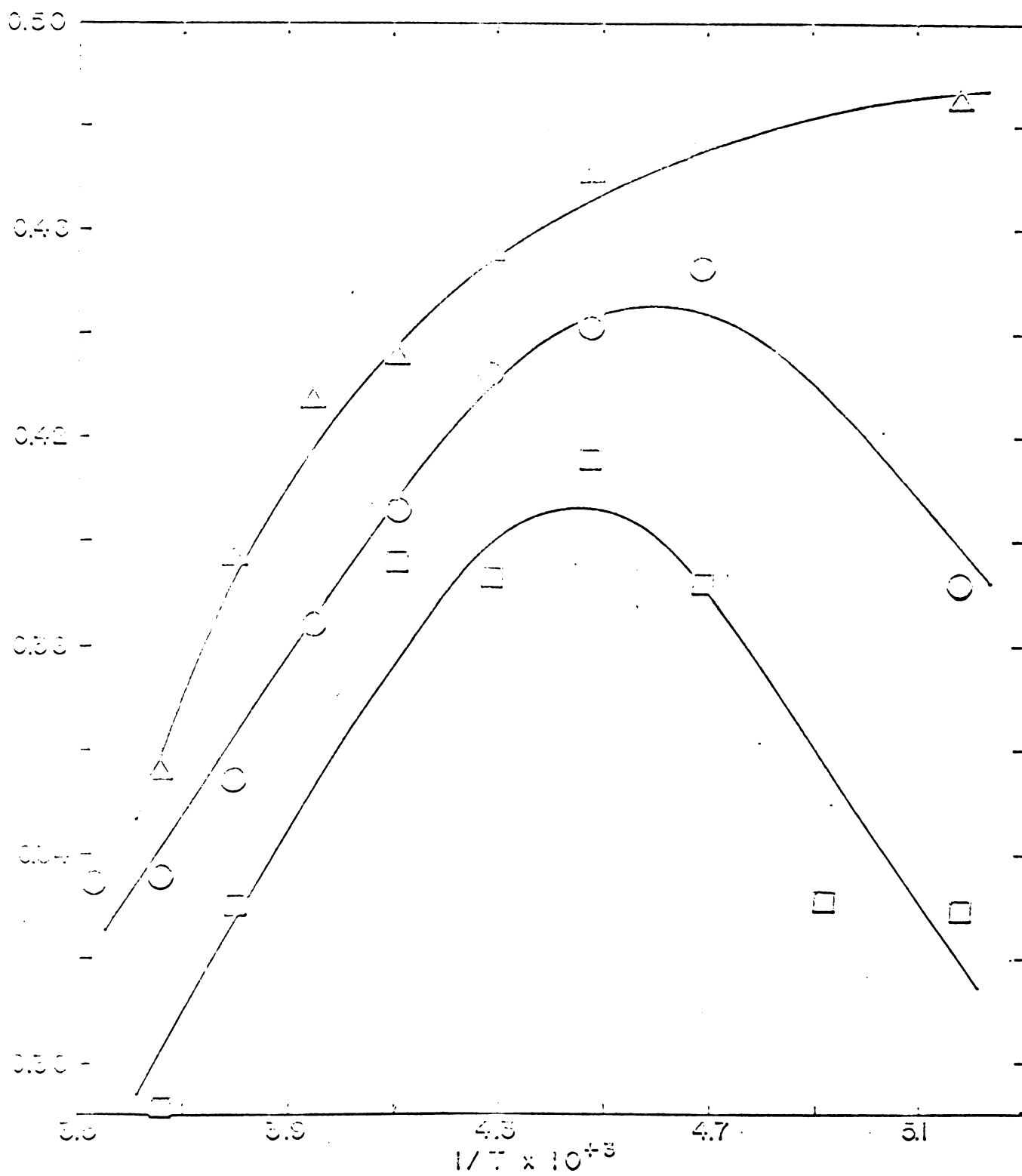


Figure 4c. Variation of the coefficient of m_1^2 (C_2) with $1/T$: Cs in ethylamine. Results are shown for three different sample preparations.

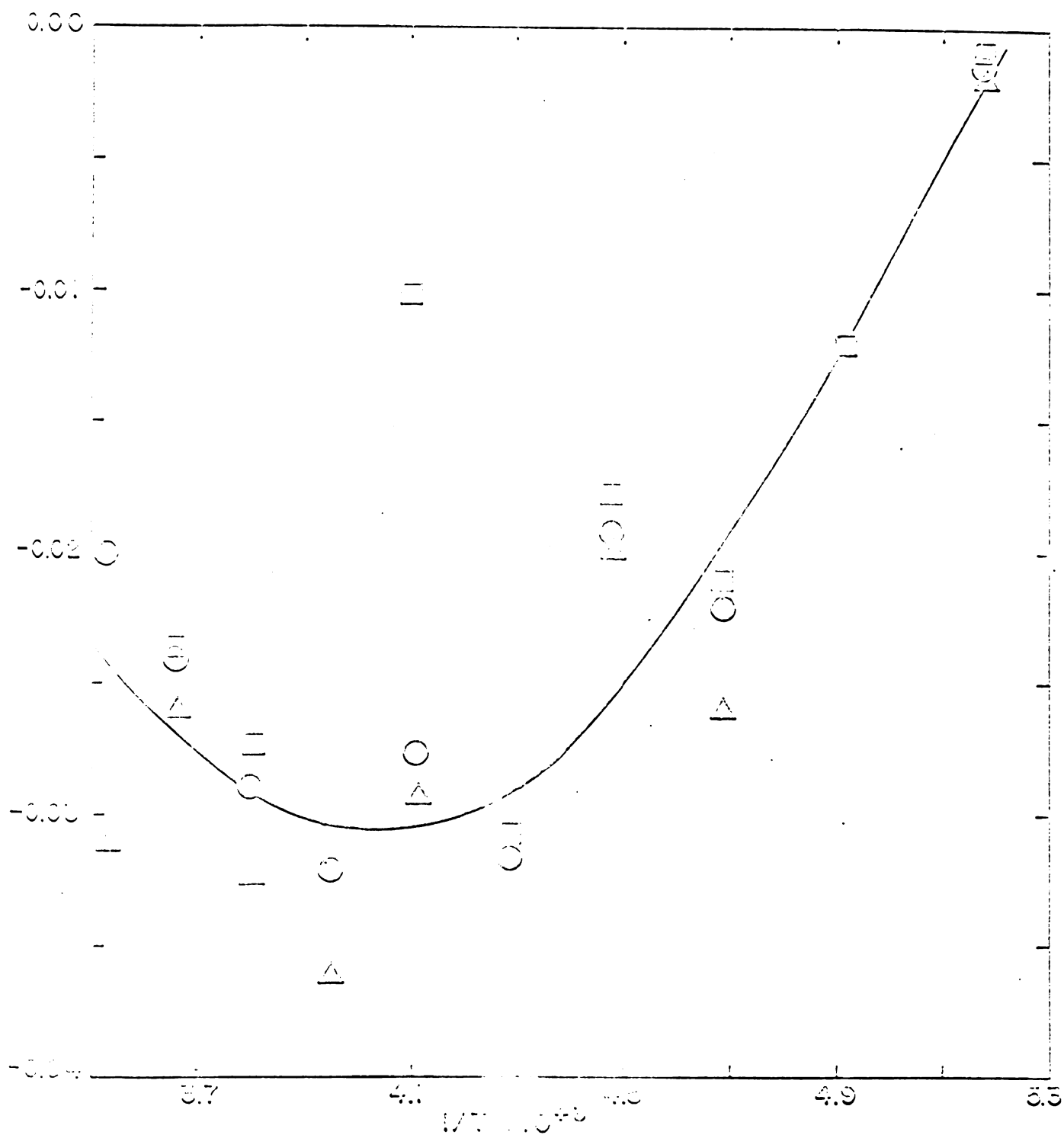


Figure 4d. Variation of the coefficient of $m_I^3(C_3)$ with $1/T$: Cs in ethylamine. Results are shown for three different sample preparations.

In addition to examining n_T -dependent relaxation mechanisms, Dalton *et al.* (42) have considered the problem of accounting for the residual linewidth. There exist several mechanisms which must be considered as possible contributors to n_T -independent transverse relaxation in dilute metal-amine and metal-amine-ammonia solutions. These are as follows: (a) spin-orbit coupling to solvent molecules and metal ions, (b) nuclear hyperfine coupling, (c) anisotropy of the g factor, (d) nuclear dipolar interactions, (e) nuclear quadrupolar interactions, (f) exchange effects, and (g) effects of fluctuating magnetic environment.

These authors point out that the increase in linewidth with metal concentration indicates the importance of interactions with other metal nuclei. This interaction may be in the form of hyperfine interaction, quadrupolar interactions, spin exchange, or net chemical reactions, with the correlation time of the respective processes determining the relative contributions to linewidths.

The qualitative nature of the spectra indicates that spin exchange and chemical equilibria would be expected to be important in determining the observed linewidths. Unfortunately, the large number of species prohibits detailed analysis of the spin-exchange processes. Even in ammonia which shows only a single optical absorption, ions and loose aggregates such as M^+ ; e^- ; $M^+ \cdot e^-$, (M); $e^- \cdot M^+ \cdot e^-$, (M^+); and $(M^+ \cdot e^-)_2$, (M_2) seem to be required to explain the properties of the solutions. In ammonia-ethylamine mixtures, the infrared absorption had an intensity much larger than could be accounted for by the extra EPR line. This indicates that electron-ion aggregation is even more predominant in these systems than in ammonia. The appearance of the

visible and red optical absorptions requires two additional species and the nature of the hyperfine interaction appears to require three neutral monomeric species.

The earlier treatment of metal-amine solutions by Bar-Kli and Tuttle (43) was based upon a model restricted to four species. The existence of other species forces one to consider many other chemical and spin exchange processes. To assess the importance of a given process requires estimation of the rate constants and concentrations involved. The spin concentrations and optical spectra measured in this laboratory permit estimation of the contribution to linewidth of spin exchange processes involving $M + M$ and $M + e^-$ and such reactions as $M \rightleftharpoons M^+ + e^-$ and $2M \rightleftharpoons M_2$. Assuming diffusion-controlled, second-order processes (which gives the maximum contribution to linewidth), it was concluded that none of these processes can contribute more than 0.1 G to the linewidth. Spin exchange with species as M^+ and M_2^+ would also be without effect at concentrations of these species below $10^{-4}M$, but could contribute as much as 0.2 G to the linewidth at $10^{-3}M$. The observed linewidth (0.5 to 2.5 G) of the hyperfine pattern for potassium in ethylamine-ammonia mixtures appears, therefore, to arise from other processes or reactions.

D. Paramagnetic Relaxation in Alkali Metals

In metals it is the spin-lattice relaxation time T_1 which determines the line width. Several mechanisms for spin-lattice relaxation have been proposed. Overhauser (61) has discussed several interactions of which the one giving rise to the shortest relaxation time is the interaction between the magnetic moment of one electron and the

field caused by the translational motion of a second electron. Elliott (62) has discussed a process whereby the small amount of orbital angular momentum associated with the spin state causes the spin to flip. He obtains the following expression for the spin-lattice relaxation time:

$$\tau_1 = \alpha \tau_R / (\Delta g)^2 \propto 1/[(\Delta g)^2 \rho] \quad (17)$$

Therefore,

$$\Delta H \propto (\Delta g)^2 \rho$$

The spin-orbit coupling enters through the g-shift g , which is proportional to λ/Δ , where λ is the spin-orbit coupling constant and Δ is the energy level separation. The g-shift has been calculated for conduction electrons in several metals by Yafet (63) and Brooks (64). τ_R is the mean time between collisions for electrons as determined by resistivity measurements; ρ is the resistivity in ohm-centimeters. α is a constant, of the order of 0.03 for phonon collisions. Yafet has examined Elliott's assumptions, and he finds that the factor α is a function of temperature such that the relaxation has a $1/T$ dependence at low temperatures instead of $1/T^3$ as predicted by Elliott.

The experiments of Fehér and Kip (65) provided the following information about spin-lattice relaxation times in metals:

1. Sodium—The relaxation time is approximately proportional to conductivity from 4°K to 300°K.
2. Lithium—The relaxation time is independent of temperature between 4°K and 300°K but is longer the more highly purified the samples.

The results in sodium appear to confirm the Elliott-Yafet mechanism of relaxation inasmuch as the linewidth follows the same law as does the resistivity. The data for lithium are a bit confusing since the highest purities obtained have yielded intrinsic relaxation times.

Extension of the measurements to higher temperatures would provide a better check on the theory especially if the melting points of the metals could be exceeded, since there the resistivities have discontinuities. Levy (66,67) has carried out measurements on all the alkali metals to temperatures above their melting points. Resonance was observed only in sodium and lithium as expected from theory, since the spin-orbit interactions are too large in the other alkalis to produce observably narrow lines.

EXPERIMENTAL

A. Glassware Cleaning and Reagent Purification

The cleaning of glassware and purification of reagents has been described previously (42,46,68,69,70). For a more detailed account of the techniques employed than given here the reader is referred to the above references.

1. Glassware cleaning. The items were first rinsed briefly with a hydrofluoric acid-detergent cleaning solution (5% hydrofluoric acid, 33% concentrated reagent grade nitric acid, 2% acid-soluble detergent, and 60% distilled water, by volume), then ten times or more with distilled water. Next, the glassware was filled with fresh aqua regia and heated to boiling, followed by ten more rinses and/or soakings in double-distilled conductance water. After each use and a preliminary cleaning, the glassware was heated in an annealing oven at 550°C before being cleaned as described above.

2. Reagent purification. The reagents used in this work and their commercial sources are given in Tables IV and V.

(a) Metal purification. Sodium and potassium were cleaned, cut, and then degassed under high vacuum. Repeated vacuum distillations were used to obtain small metal samples in sealed ampoules which were used to make up metal solutions.

The rubidium and cesium used in this work came in sealed ampoules. The ampoules were cooled in liquid air, broken, and immedi-

TABLE IV. Alkali Metals and Solvents Employed and their Commercial Sources

<u>Reagent</u>	<u>Commercial Sources</u>
Lithium	Lithium Corporation of America
Sodium	J. T. Baker
Potassium	Mallinckrodt
Rubidium	Fairmount Chemical Company
Cesium	Dow Chemical Company
Ammonia	Matheson, Coleman, and Bell
Methylamine (MeNH_2)	Matheson, Coleman, and Bell
Ethylamine (EtNH_2)	Eastman White Label
n-Propylamine (n-PrNH_2)	Matheson, Coleman, and Bell
iso-Propylamine (i-PrNH_2)	Matheson, Coleman, and Bell
n-Butylamine (n-BuNH_2)	Matheson, Coleman, and Bell
3-Methoxy-n-propylamine (3-MPA)	Eastman
Ethylenediamine (EDA)	Matheson, Coleman, and Bell
1,2-Propanediamine (1,2-PDA)	Matheson, Coleman, and Bell
1,3-Propanediamine (1,3-PDA)	Matheson, Coleman, and Bell
Hexamethylphosphoric triamide	Eastman

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1,3-Propanediamine (1,3-PDA)	Matheson, Coleman, and Bell
Hexamethylphosphoric triamide	Eastman

TABLE V. Reference standards used for determination of spin concentrations.

Reference Standard	Source	<u>g value</u>	(K)	
			<u>Lorentzian</u>	<u>Gaussian</u>
P doped Si in polyethylene	E. A. Gere, Bell Telephone Laboratories	1.99875 $\pm$ 0.00010	1.0	0.29
Pitch in KCL (powder)	Varian Associates Palo Alto, California	2.00280 $\pm$ 0.00005	0.66	0.19
DPPH in benzene	Eastman Organic Chemicals	2.00354 $\pm$ 0.00003	1.6	0.47
DPPH in chloroform	Eastman Organic Chemicals		1.6	0.5
DPPH (powder)	Eastman Organic Chemicals	2.0036 $\pm$ 0.0002	1.0	0.29
NO(SO ₃) ₂ = (titrated aqueous NaCO ₃ solution, pH = 10)	Alfa Inorganics, Inc.	2.00550 $\pm$ 0.00005	1.0	0.29
CuSO ₄ .5H ₂ O (crystal)	Matheson Coleman and Bell (recrystallized from H ₂ O)		1.0	0.29
K ₃ [Cr(CN) ₅ NO] (aqueous)	H. Kuska, Michigan State University	1.99454 $\pm$ 0.00005	3.5	1.0
VO ₂ SO ₄ (aqueous)	Fisher Scientific Company	1.962 $\pm$ 0.002	1.0	0.29
Mn ⁺⁺ in MgO	Baker and Adamson	2.00774 $\pm$ 0.00050	3.5	1.0

immediately transferred to the metal make-up vessel. It was necessary to cool the samples to avoid excessive oxidation of the metal during transfer. The metal make-up then proceeded as described for sodium and potassium.

The lithium used in the initial phase of this project was cleaned mechanically in a Caenec Model 39 dry-box filled with high purity helium (99.7%) which had been passed through an activated silica gel column at liquid nitrogen temperature.

(b) Solvent purification. The solvents used were purified by one of two methods. The first method involved reaction with alkali metals or appropriate drying agents (e.g. a mixture of potassium hydrazide and barium oxide), followed by freezing and pumping, several distillations in vacuo, and further reaction with alkali metals. This procedure was followed by a distillation in a nitrogen stream similar to the method described by Donald (71); a final distillation was made in vacuo into a storage flask containing a film of potassium metal. Before use in sample preparation the solvent was then frozen and degassed. Methylamine, ethylamine, propylamine, iso-propylamine, n-butylamine, t-butylamine, and 3-methoxy-n-propylamine were purified by this method.

A second method involved placing the solvent in a large separatory funnel, slowly freezing it and then melting and discarding the core (69,70). Pre-purified nitrogen was used as a covering gas throughout this procedure. The freeze-melt procedure was repeated at least five times. Following freeze purification the solvent was further purified by the procedure of method 1. Ethylenediamine, 1,2-propanediamine, and hexamethylphosphoric triamide were purified by this method.

(c) Nitrogen purification. As has been previously mentioned, nitrogen was used in distillations and as a covering gas. It was purified by passing it over copper turnings in a tube furnace, through an Ascarite column, a dry-ice trap, and finally a silica gel column at 77°K in which some condensation occurred. This nitrogen was then stored in two-liter bulbs on the vacuum line.

(d) Purification of EPR reference samples. VOSO_4 and $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ were purified by recrystallisation from water. Baker $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ was first scavenged with Mg metal and then precipitated with ammonium hydroxide. The precipitate was washed with distilled water and dried in a controlled-temperature furnace. The other reference standards were used without further purification.

B. Solution Preparation

As can be seen from Table IV a wide range of metal-amine and mixed solvent solutions were studied. Moreover, it was desired to investigate these solutions under a variety of experimental conditions. These factors necessitated the construction and employment of a number of unique solution preparation vessels. These vessels will be discussed in relation to their use.

Prior to actual sample preparation, the following technique was employed to maximize sample stability. After evacuation and flaring, the sample tube was allowed to fill several times with the vapor of the amine under consideration. The amine vapor was then removed to a liquid-nitrogen-cooled trap and the sample tube was evacuated to 10^{-5} torr or better.

1. Preparation of metal-amine solutions for EPR measurement.

Solutions of sodium, potassium, rubidium, and cesium in the amines listed in Table IV and in mixtures of these amines were prepared using the apparatus shown in Fig. 5. This apparatus was attached to a high vacuum system to which the appropriate solvent storage flasks had previously been attached. The sealed ampoule containing the alkali metal was frozen with liquid air, broken, and dropped into the distillation arm attached to the manifold shown in Fig. 5. The distillation arm was then capped and the solution preparation apparatus evacuated to at least 5×10^{-6} torr. The metal was subsequently distilled into the EPR sample tubes. After a film of metal had been obtained on the walls of each of the sample tubes, the appropriate amine was distilled into the tube, the solution frozen with liquid nitrogen and degassed, and the sample tube sealed off. In order that spin concentration measurements could be extrapolated to samples of infinitesimal size, the diameter of the lower section of the EPR tubes was varied from tube to tube as shown in Fig. 5.

When lithium solutions were desired, the apparatus shown in Fig. 6 was placed in the dry-box along with a stick of Apieson W wax, a heating coil, a knife, and some lithium bars. The dry-box was first evacuated and then filled with high purity helium. The lithium metal was cleaned mechanically, placed in the solution preparation apparatus, and the apparatus was capped using the W wax and the heating coil. Once sealed the apparatus was removed from the dry-box and attached to the vacuum line containing the storage flasks of the appropriate amine solvents. The solution preparation apparatus was then evacuated and an appropriate amount of solvent was subsequently distilled over the

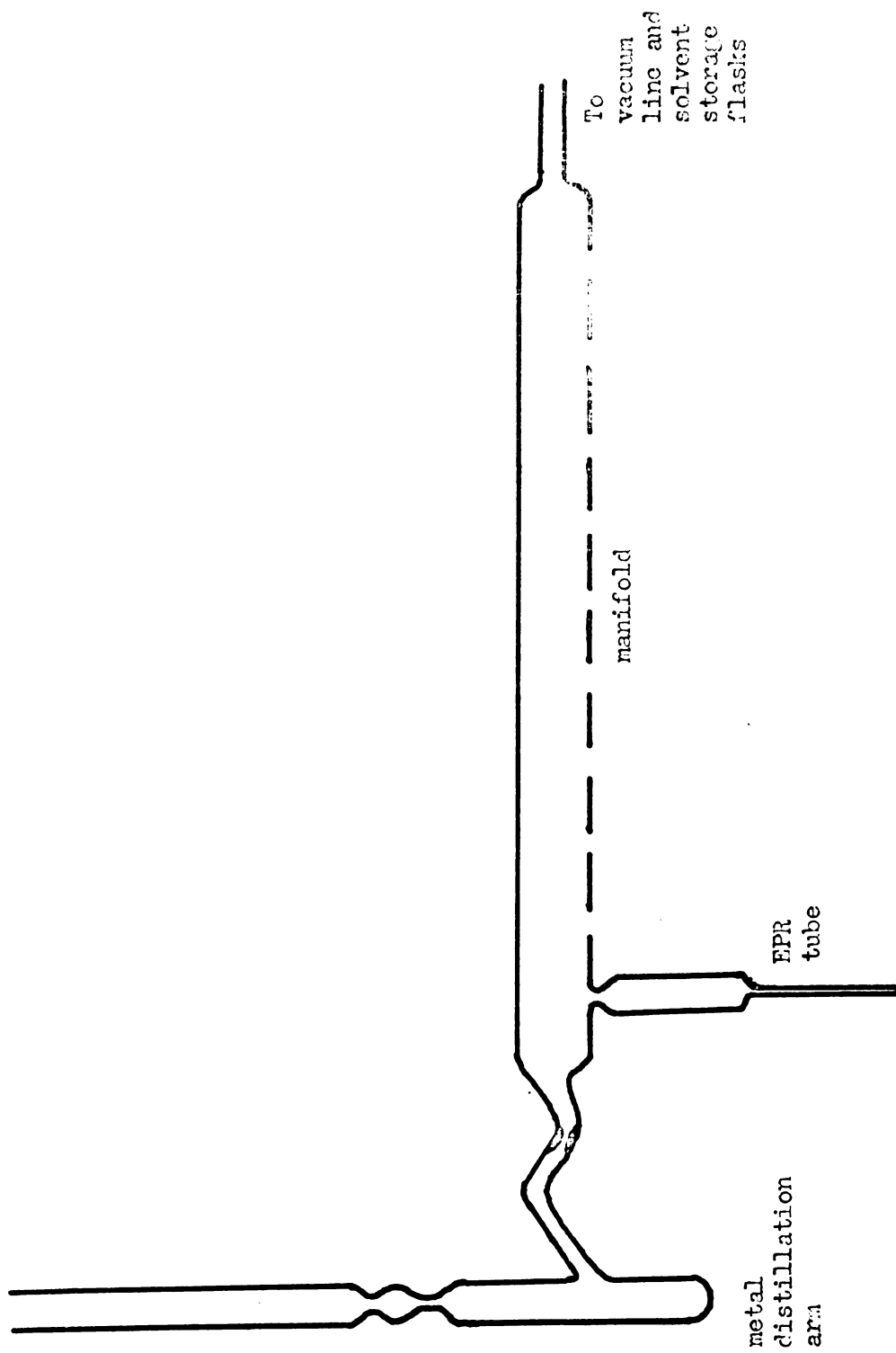


Figure 5. Vessel used to prepare solutions of sodium, potassium, rubidium, and cesium in amine solvents for EPR measurement.

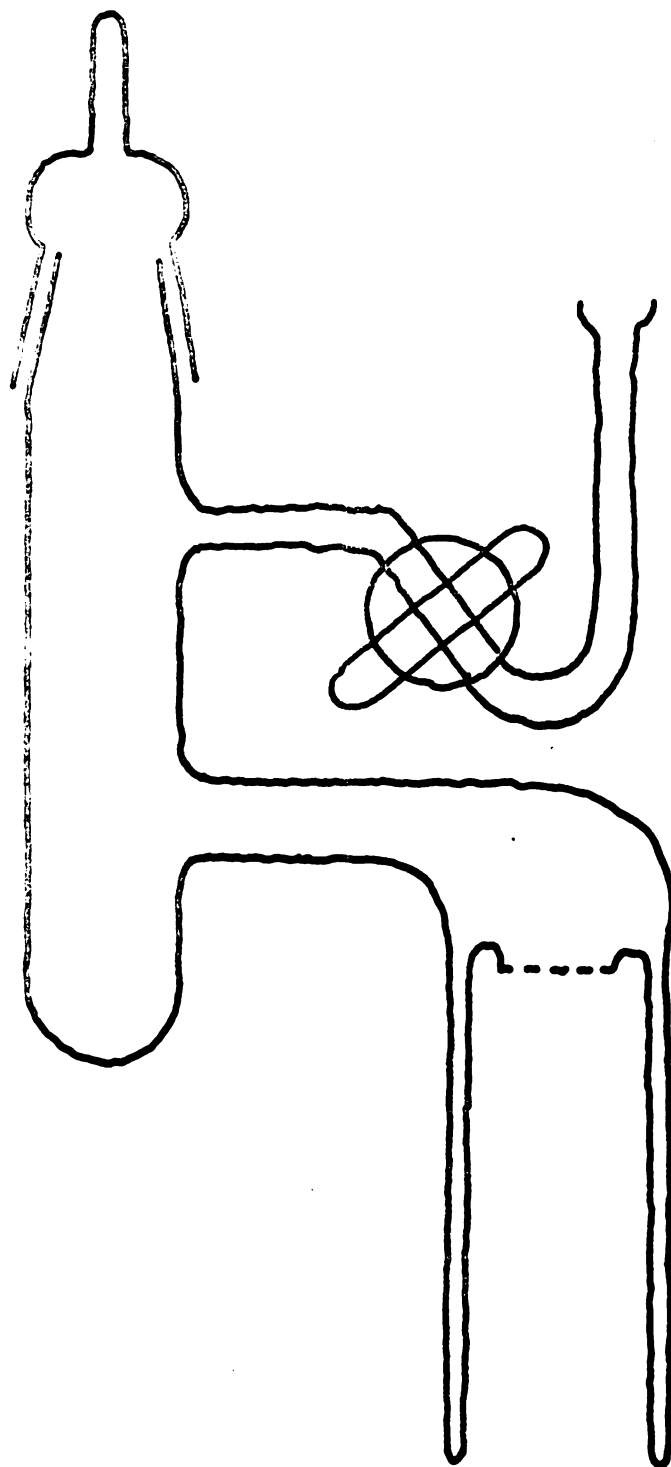


Figure 6. Vessel used to prepare lithium-amine solutions for EPR studies.

lithium. The apparatus was then disconnected from the vacuum line, the metal-amine solution tipped into the EPR tubes, and the tubes sealed off.

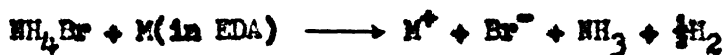
2. Preparation of metal-mixed solvent solutions for EPR measurement. The preparation of potassium-ethylamine-ammonia mixtures (42) and cesium-ethylamine-ammonia mixtures (41,42) has been described previously. To measure ammonia in small amounts, the volume of the manifold available to vapor was first determined. The ammonia reservoir was degassed and held at constant temperature to establish a known pressure of ammonia vapor in the manifold. This was then condensed into the sample tube using liquid nitrogen. For higher concentrations of ammonia, both liquid volumes were measured directly by determining the liquid height immediately after removal from a dry-ice bath. Mole fractions were calculated assuming no volume change upon mixing.

After measurements had been completed, the ammonia content was determined using an aerograph Model 90-P3 gas chromatograph. Analysis was accomplished by freezing the sample tube in liquid nitrogen, breaking it, and dropping it into a vessel which was quickly sealed off from the atmosphere. The sample was allowed to vaporize and fill the volumetric vessel; the needle of a volumetric syringe was inserted through an elastic membrane and a sample was removed. The chromatographic column was packed with 15% THEED and 5% tetrathylpentaamine on 60/80 Chromosorb W (72). The concentration of ammonia in these samples was determined by comparing the ratio of the peak areas of ammonia and ethylamine in the sample with the ratio of the areas of a number of standards.

Similar methods of preparation and analysis were used for other mixed solvent solutions.

3. Preparation of metal-amine and mixed solvent solutions for correlated EPR-optical measurements. When both EPR and optical spectra were desired using the same samples, Aminco cylindrical absorption cells were sealed above the 10-mm tubing of the solution make-up apparatus shown in Fig. 5 and the seal-off from the manifold was made on a side tube attached below the absorption cell. In this way the solution could be alternately tipped into the absorption cell and into the EPR sample tube. For absorption spectra, path lengths of 0.1, 0.3, 0.7, and 1.0 mm were used, depending on the expected concentration of the saturated solution.

4. Preparation of sodium-ethylenediamine solutions for correlated EPR-conductance measurements. When conductance measurements were desired in addition to EPR measurements, a series of platinum electrodes was attached to an EPR cell. Dilute solutions of sodium in ethylenediamine were prepared in an intermediate vessel and forced into the EPR-conductance cell with gaseous nitrogen. The total metal concentration was determined by decomposing a sample of each preparation and measuring the hydrogen liberated by the reaction



Correlated EPR-conductance measurements were made by alternately tipping the solution into the conductance cell and into the EPR tube.

5. Preparation of metal-amine solutions for spin concentration measurements. Although this matter will be discussed in greater detail later it is well at this point in the dissertation to describe one of the vessels used. Fig. 7 shows a solution make-up vessel which allowed the EPR reference sample to be placed inside of the metal-amine solution.

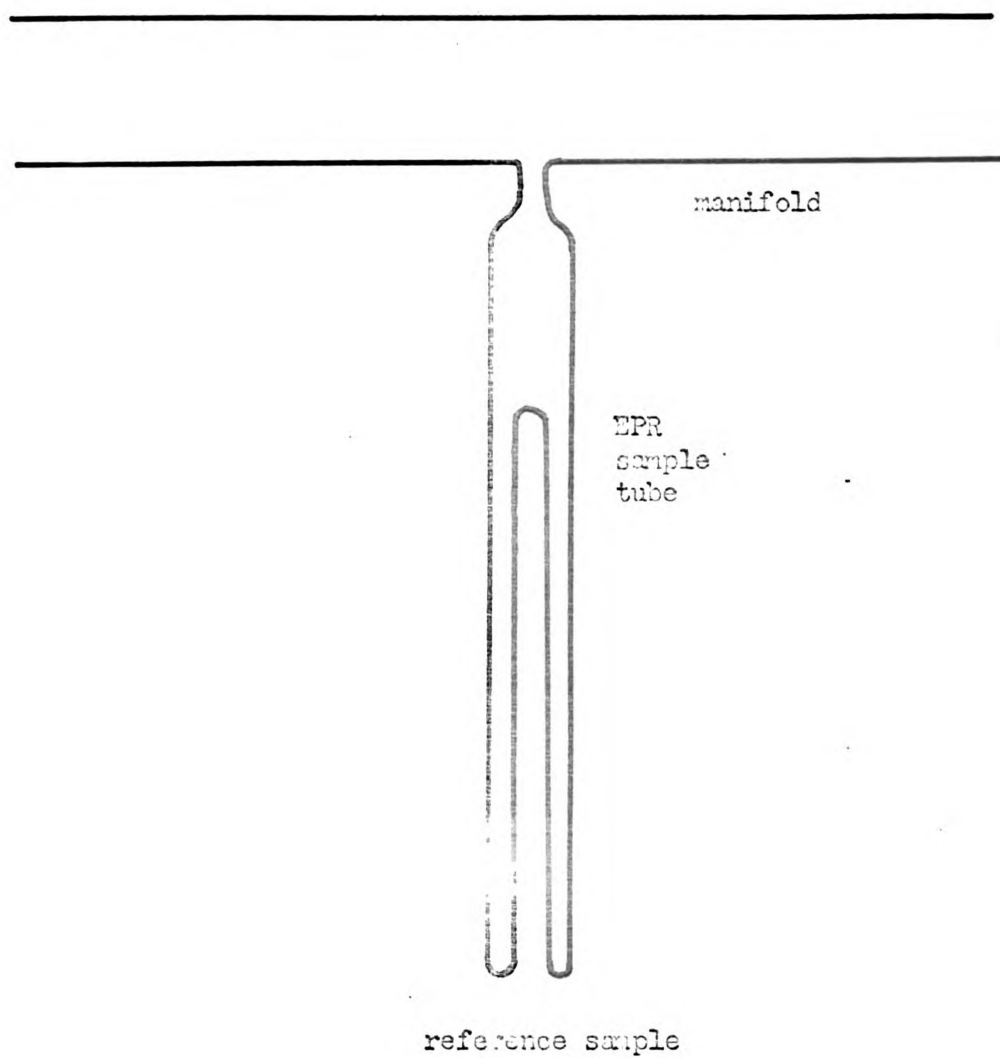


Figure 7. Vessel used to prepare sample for measurement of H_1 inside of metal-amine sample.

This permitted a measurement of the rotating magnetic field, H_1 , inside the sample.

6. EPR Measurements at X- and KU-band frequencies. For measurements at the higher frequencies, Pyrex tubing was found to be too glassy; hence, for measurements at these frequencies the EPR cells were constructed of high quality quartz tubing (Engelhard Suprasil).

B. EPR Measurements

1. The spectrometer. Four different EPR spectrometers were employed in obtaining the electron paramagnetic resonance data reported in this thesis. The instrument upon which the vast majority of measurements were taken was a Varian Model V-A500-10A X-band EPR spectrometer. The spectra taken using this instrument were recorded on an X-Y recorder whose X-axis is proportional to the magnetic field. This is accomplished by use of a Hall probe as a field sensor. This instrument employs 100-kc/sec modulation.

A second EPR spectrometer, located at Stauffer Laboratory for Physical Chemistry, Stanford, California, was made available to the author by Professor H. M. McConnell of Stanford University. This instrument is a Varian V-A503 35-Gc spectrometer equipped with fielddial and 100-kc/sec modulation.

The use of a third Varian EPR spectrometer was provided courtesy of Professor C. Kikuchi of the Department of Nuclear Engineering of the University of Michigan. This spectrometer was equipped with separate, interchangeable klystrons permitting measurements to be made at 17.5, 24.3, and 35.5 kmc/sec. This instrument also employed 100-kc/sec modulation and was equipped with fielddial.

The use of a fourth instrument was authorized by Professor J. Cowen of the Physics Department of Michigan State University. This instrument was so equipped as to afford either crystal or superheterodyne detection and permitted the use of several modulation frequencies.

2. Temperature regulation. Measurements were made over a temperature range from 4.2 to 378°K. EPR measurements at 4.2 and 77°K were made using V-4545A and V-4546 liquid helium and liquid nitrogen Dewar accessories respectively. For measurements between 90 and 378°K, temperature regulation was achieved using a V-4540 variable temperature control unit. This unit allows the temperature to be selected within $\pm 3^\circ\text{K}$ and maintained within $\pm 1^\circ\text{K}$. Temperatures were measured during the EPR measurement with a copper-constantan thermocouple.

3. The time averaging computer. The field stability of our X-band spectrometer (better than one part in 10^5) allowed the use of a Varian C-1024 time averaging computer in studying samples displaying very weak signals.

4. Measurement of hyperfine splitting and g-values. Both first and second derivative operations were employed in measuring the spectra. Hyperfine splitting was measured using a Hewlett-Packard Model 524C Frequency Counter and was checked against the hyperfine splittings of aqueous vanadyl sulfate, aqueous $\text{K}_3\text{Cr}(\text{CN})_6\text{NO}$, and aqueous peroxyamine disulphonate which are known to have hyperfine splitting values of 116.13 gauss (42) between the fourth and fifth lines of the eight line pattern, 5.260 gauss (73), and 13.0 gauss (74) respectively. For measurement of peak separations, pins corresponding to measured proton frequencies were placed at 1 to 10 gauss intervals directly on the recorded spectrum by simultaneously recording the second derivative of the EPR and proton signals.

The determination of g-values was carried out using the following formula (75).

$$g = 0.714489 \left[\nu \text{ (Klystron frequency in megacycles)} / B_0 \text{ (magnetic field in gauss)} \right] \quad (18)$$

where

$$B_0 = 2.3486855 \times 10^{-4} \nu_{\text{proton}}$$

Klystron frequencies were measured by beating with a harmonic of a Micro-Now Model 101 Frequency Calibrator and tuning the difference frequency with a communications receiver. Under optimum conditions, accuracies of one part in 10^5 were obtained. A second method of obtaining g-values consisted of simultaneously recording the spectra of a metal-amine solution and that of a material whose g-value was previously known. Reference samples included phosphorus doped silicon in polyethylene ($g = 1.99875$), pitch in KCl ($g = 2.00280$), DPPH in benzene ($g = 2.00354$), peroxyamine disulphonate ($g = 2.00550$), and aqueous $\text{K}_3\text{Cr}(\text{CN})_5\text{NO}$ ($g = 1.99454$). Since many of the hyperfine splittings observed in this work are large, the high field approximation is no longer rigorously valid. For cases where nuclear hyperfine interactions are large, the paramagnetic electron spin operators will not lie along the direction of the applied magnetic field as in the high field approximation but will rather lie along the resultant of the applied magnetic field and nuclear magnetic moment vectors. The perturbation on the Zeeman transition resulting from hyperfine interaction was corrected for as follows:

For g isotropic

$$B_0 = B_0(m) + A_F m_I + A_F^2 [I(I+1) - m_I^2] / 2B_0(m) \quad (19)$$

where $B_0(m)$ is the magnetic field position of the EPR line due to the

component m_I of the nuclear magnetic moment I , and A_I is the nuclear hyperfine interaction constant. The derivation of Eq. 19 may be seen as follows;

The spin Hamiltonian appropriate for metal-amine solutions is

$$\mathcal{H} = g\beta\vec{B}_0 \cdot \vec{S} + A\vec{I} \cdot \vec{S} \quad (20)$$

In the presence of a strong external magnetic field the appropriate representation, in which S_z and I_z are diagonal. The external field defines the z-axis. In this representation the spin Hamiltonian may be divided into a diagonal part

$$\mathcal{H}_0 = g\beta B_0 S_z + A I_z S_z$$

and an off-diagonal part

$$\mathcal{H}' = A(I^+S^- + I^-S^+)/2$$

In order to solve the above Hamiltonian we must resort to perturbation theory. The reader should note that this implies that the resultant magnetic vector is "perturbed" only a slight distance from the magnetic field vector. If the hyperfine interaction is comparable to the applied field, the resultant vector will be considerably removed from the direction of the applied field vector and one obviously cannot treat the problem in terms of the S, I, m_S, m_I representation or by means of perturbation theory.

Applying perturbation theory, we find that the contribution $B_0(m)$ to the energy is, to second order,

$$\begin{aligned} W^{(2)}(m_S, m_I) = -A^2/4g\beta B_0(m) \left\{ -[S(S+1) - m_S(m_S-1)] \times [I(I+1) - m_I(m_I+1)] \right. \\ \times \left[1 + \sum_{n=1}^{\infty} [A(m_S - m_I - 1)/g\beta B_0(m)]^n + [S(S+1) - m_S(m_S+1)] \right. \\ \times [I(I+1) - m_I(m_I-1)] \times \left. \left(1 + \sum_{n=1}^{\infty} (-1)^n [A(m_I - m_S - 1)/g\beta B_0(m)]^n \right) \right\} \end{aligned}$$

This is seen to be an expansion in $\Lambda[A/g\beta B_0(m)]^q$. For the purposes of our derivation we need only consider the terms for which $q = 1$, but in order that the reader may receive an idea of the importance of higher order terms we shall consider terms of the expansion through $n = 2$.

These terms, taken with the diagonal part of the Hamiltonian, yield the following expression for the frequency of the transition

$$m_S = -\frac{1}{2} \longrightarrow m_S = +\frac{1}{2} :$$

$$\begin{aligned} &= g\beta h^{-1} B_0(m) + \Lambda m_I + \Lambda^2 [I(I+1) - m_I^2] / 2g\beta h^{-1} B_0(m) \\ &\quad + \Lambda^3 [I(I+1) - 3m_I^2] / 4[g\beta h^{-1} B_0(m)]^2 \\ &\quad + \Lambda^4 m_I [2I(I+1) - 4m_I^2 - \frac{1}{2}] / 4[g\beta h^{-1} B_0(m)]^3 \end{aligned}$$

It is assumed in this expression that $S = \frac{1}{2}$. This equation can be immediately related to Eq. 19 if one drops the last two terms and notes that $\Lambda(\text{sec}^{-1}) = g\beta h^{-1} A_F(\text{gauss})$.

Many workers prefer to use an approximate form of Eq. 19 by assuming that $B_0(m) = B_0 + \Lambda_F m_I$; thus obtaining

$$B_0(m) = B_0 - \Lambda_F m_I - \Lambda_F^2 [I(I+1) - m_I^2] / 2B_0$$

If the paramagnetic entity which we are considering can exist in more than one form we must consider dynamic as well as static second-order effects. Let us assume that the paramagnetic species can exist in two forms, A and B, with splitting constants Λ_A and Λ_B . Each form will give rise to its own spectrum, one with frequencies $\omega_A^0(m)$ and the other with frequencies $\omega_B^0(m)$. These are obtained from Eq. 19 by replacing the splitting constant Λ_F with Λ_A and Λ_B , respectively.

If rapid interconversion of the two forms takes place, the average frequencies are obtained;

For long correlation times, $(\omega_0 \tau)^2 \gg 1$,

$$j(0) = \tau g(0),$$

and

$$\begin{aligned} k(\omega_0) &= \omega_0^{-1} g(0) \\ &= (\omega_0 \tau)^{-1} j(0) \end{aligned}$$

The second-order correction terms in Eq. 21 are replaced by

$$[|\gamma_0| (I^2/2B_0(m)) + \frac{1}{2}k(\omega_0)] [I(I+1) - m^2],$$

where now the dynamic shift applies to any type of modulation, not only a two-jump model. In the particular case of the two-jump model we have

$$\begin{aligned} \frac{1}{2}k(\omega_0) &= (\gamma_0^2/2\omega_0) p_A p_B (\lambda_A - \lambda_B)^2 \\ &= (|\gamma_0|/2B_0(m)) \langle (\delta\lambda)^2 \rangle \end{aligned}$$

and Eq. 21 is obtained.

An analysis of metal-amine solutions has provided evidence which indicates that Eq. 21 rather than Eq. 19 should be used. Because the assignment of λ_A and λ_B is not certain it was felt that the use of Eq. 19 would constitute the most desirable method of obtaining second-order corrections. However, with further refinement of the model of Dalton et al., (42) Eq. 21 should be used. Because Eq. 19 involves successive reiteration a computer program was written which allowed a Control Data 3600 Computer to perform the necessary second-order corrections.

Eq. 19 is reasonably accurate for hyperfine splittings up to 150 gauss. In several cesium-amine solutions and in the gas phase, the cesium electron-nuclear hyperfine interaction exceeds 200 gauss. For these cases it is obvious that we must proceed from a different framework.

For long correlation times, $(\omega_0 \tau)^2 \gg 1$,

$$j(0) = \tau g(0),$$

and

$$\begin{aligned} k(\omega_0) &= \omega_0^{-1} g(0) \\ &= (\omega_0 \tau)^{-1} j(0) \end{aligned}$$

The second-order correction terms in Eq. 21 are replaced by

$$[|\gamma_0| (A^2/2B_0(m)) + \frac{1}{2}k(\omega_0)] [I(I+1) - m^2],$$

where now the dynamic shift applies to any type of modulation, not only a two-jump model. In the particular case of the two-jump model we have

$$\begin{aligned} \frac{1}{2}k(\omega_0) &= (\gamma_0^2/2\omega_0) p_A p_B (A_A - A_B)^2 \\ &= (|\gamma_0|/2B_0(m)) \langle (\Delta A)^2 \rangle \end{aligned}$$

and Eq. 21 is obtained.

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In general the nuclear interactions of an atom in a magnetic field are the combination of the several interactions of the Hamiltonian,

$$\mathcal{H} = h\bar{I} \cdot \bar{S} - \mu_S \bar{S} \cdot \bar{B}_0 / S - \mu_I \bar{I} \cdot \bar{B}_0 / I$$

With several such interactions present simultaneously it is not in general possible to select a priori a representation for which the energy matrix is diagonal. Often it is possible to select a representation in which the largest matrix elements are diagonal, in which case a standard form of perturbation calculation can be used to make corrections for the effect of the non-diagonal matrix elements. Such a procedure was used to derive Eq. 19. In many cases, however, the non-diagonal matrix elements are comparable to the diagonal one, in which case the perturbation is unsatisfactory. In this case the best procedure is to calculate all the matrix elements from the interaction Hamiltonian in any convenient representation. The energy levels of the system may then be obtained by a solution of the corresponding secular equation. An example of the solution of the secular equation for an intermediate coupling problem is the solution of the intermediate field problem given by H. F. Ramsey (81). In this case and if the z-axis is taken in the direction of the external field B_0 , the Hamiltonian of the system is

$$\mathcal{H} = -dI_z - cS_z + h\bar{I} \cdot \bar{S}$$

$$\mathcal{H} = -dI_z - cS_z + hI_z S_z + \frac{1}{2}h(I_+ S_- + I_- S_+)$$

where $d = \mu_I B_0 / I$ and $c = \mu_S B_0 / S$

As discussed in Section III of Reference 81, an Fm (where $\bar{F} = \bar{I} + \bar{S}$ and $m = m_I + m_S$) representation is most convenient when B_0 is small and an $m_I m_S$ representation is most convenient when B_0 is large.

However, in intermediate magnetic fields the matrix is not even approximately diagonal in either representation, so that the secular equation must be solved. As a result it makes little difference which representation is chosen in the calculation of the complete matrix and the secular equation will, of course, be independent of this choice even though the matrices are quite different in form. For the calculation given in Reference 81, Ramsey chose the $m_I m_S$ representation; a calculation with an Fm representation has been published elsewhere (82). For the case where $S = \frac{1}{2}$, Ramsey obtained for the contribution to the energy in the limit of $B_0 = 0$ (in the Fm representation),

$$W(F, m) = -\Delta W / 2(2I + 1) - \mu_I B_0 / I \pm \Delta W / 2(1 + 4mx / (2I + 1) + x^2) \quad (22)$$

where $x = (-\mu_S / S + \mu_I / I) B_0 / \Delta W = (g_S - g_I) \mu_B B_0 / \Delta W$

with $g_I = -\mu_I / I \mu_B$

where μ_B is the Bohr magneton and g_S is the electron g-factor.

Eq. 21 was first derived by Breit and Rabi (83). Fessenden and Schuler (84) have simplified the Breit-Rabi equation by expanding the square-root term in the formula. This expansion results in an equation for the various transitions of the form

$$\gamma = g h^{-1} B_0 + m a + C_2 a^2 / D + C_3 a^3 / D^2 + C_4 a^4 / D^3 + \dots \quad (23)$$

where

$$D = (g - g_I) h^{-1} B_0,$$

$$C_2 = \frac{1}{2} I(I + 1) - \frac{1}{2} m^2,$$

$$C_3 = m \left[\frac{1}{2} m^2 + \frac{1}{2} - \frac{1}{2} I(I + 1) \right],$$

$$C_4 = -[I(I + 1) - 6m^2] [I(I + 1) - 1] + 5m^4$$

Eqs. 19, 22, and 23 were used when appropriate. As with Eq. 19, Eqs. 22 and 23 should be modified to include the effects of dynamic as well as static shifts.

5. Measurement of spin concentrations. There are two main parts to the problem of determining spin concentration: first, the relation between certain presumably measurable quantities and the actual number of unpaired spins; and second, the accurate measurement of these quantities.

If an EPR absorption line in the absence of saturation satisfies the Bloch equations modified for a linearly polarized field,(85), the static spin susceptibility χ_0 is given by

$$\chi_0 = 2/\pi\omega \int_0^\infty \chi'' d\omega, \quad (24)$$

where ω is the angular frequency of the rf field of amplitude H_1 , $\omega_0 = \gamma B_0$ is the precession angular frequency, and χ'' is the absorptive part of the total spin susceptibility. χ'' is related to the actual power absorbed by the sample P_a , by $\chi'' = 2P_a/\omega B_1^2$, so that

$$\chi_0 = \frac{4\gamma}{\pi\omega B_1^2} \int_0^\infty P_a dB_0. \quad (25)$$

However, this relation will be applicable only if the following conditions are met: (1) The spin system must be in thermal equilibrium with its surroundings, i.e., saturation must be absent; (2) The line width must be small compared to H_0 at resonance; (3) The modulation amplitude must be small compared to the linewidth; and (4) skin effects must be absent.

If P_a is small compared to the total power impinging on the sample, the change in crystal detector signal will be directly proportional to P_a and the necessary data (except for a constant of proportionality) for performing the required integration would be available from a plot of crystal signal versus magnetic field H_0 . If a

magnetic field modulation scheme is used in which the modulation amplitude is small compared to the linewidth, a quantity proportional to dP_H/dB_0 is measured so that a double integration is necessary. A susceptibility determination thus depends upon the measurement of four quantities: γ (or the g factor), the microwave frequency ω , B_1 inside the sample, and P_A or dP_A/dB_0 as a function of B_0 . Assuming almost free spins, the spin concentration is then given by the expression

$$N = \chi_0 [3kT/g^2 \beta^2 S(S+1)] \quad (26)$$

It should be emphasized that the foregoing simple combination of quantities usually measured in an EPR experiment cannot, in general, be identified with a static susceptibility. The exact form of the Kramig-Kroners relations (86) applies strictly only to the case where the magnetic field is constant and frequency is the variable. Altshuler (87) has attempted to derive similar relations for the case in which frequency is constant and the magnetic field is the variable; however, these relations cannot be obtained in explicit form. Of course, if the EPR line is narrow compared to B_0 at resonance, approximations of the Kramig-Kroners relations lead to the expression (24).

If an EPR curve can be shown to satisfy the modified Bloch equations, an increase in both simplicity and accuracy can be achieved in determining the spin concentration. For example, if the EPR curve can be shown to be the first derivative of a Lorentzian curve, the integrated absorption, which is proportional to $S_P^2 D$ can be compared directly with a Lorentz-shaped curve for a standard sample of known susceptibility without resorting to numerical integration procedures (88).

The method of line shape analysis used was similar to that used by Singer (89) and by Weidner (90) for an absorption curve. The widths at various fractional heights on the derivative curve were plotted against the corresponding widths for a Gaussian and a Lorentzian curve (see Fig. 8). The slope of this line yields a reliable average value for the linewidth S_p . Line shape analyses were performed on all the curves used to obtain spin concentrations. In the case of metal-amine-ammonia solutions of high ammonia concentration the high electrical conductance results in a microwave skin depth. As Bloembergen (91) and Feher and Kip (65) have shown, a mixture of χ' and χ'' results when the sample dimensions are comparable to the skin depth. It was found that this effect could be eliminated by using sample tubes of 1.5 mm I.D. or less.

It can be seen from Eq. 25 that χ_p and thus the spin concentration is inversely proportional to the square of the rf magnetic field amplitude B_1 inside the sample. Because of the difficulty of accurately determining the absolute magnitude of this quantity, a comparison method was used in which only relative values were required. It has been found that the signal from a number of paramagnetic materials cemented along side of the metal-amine sample provides a convenient monitor of B_1 in the cavity.

One complication in any determination of spin concentration is the difference between B_1 inside a sample and B_1 immediately outside the sample. Since all materials have a real part of the dielectric constant greater than unity, the density of the E field and B_1 inside will always be somewhat larger than that immediately outside the sample.

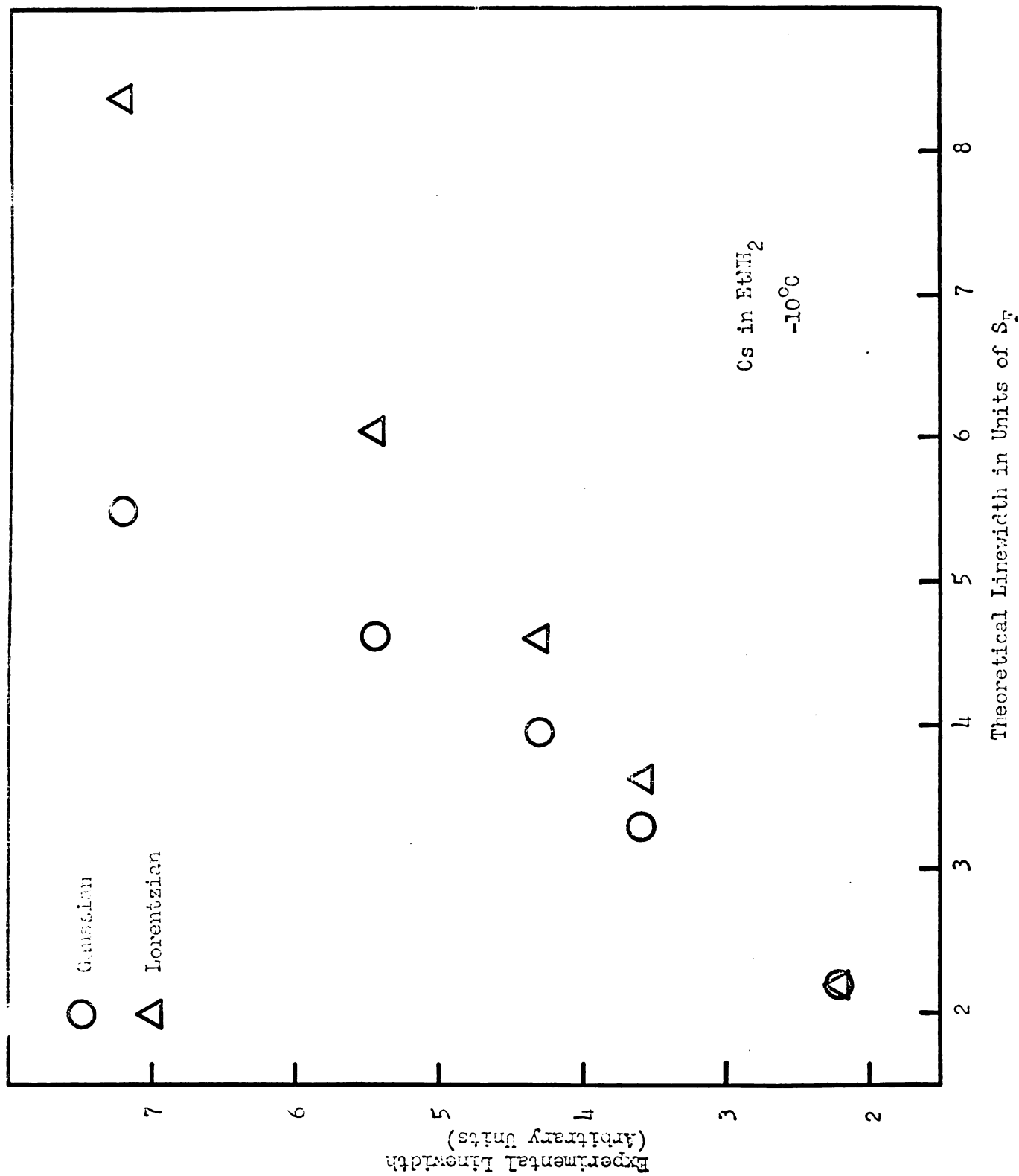


Figure 8a. Line shape analysis of a typical spectrum of Cs in EtNH₂.

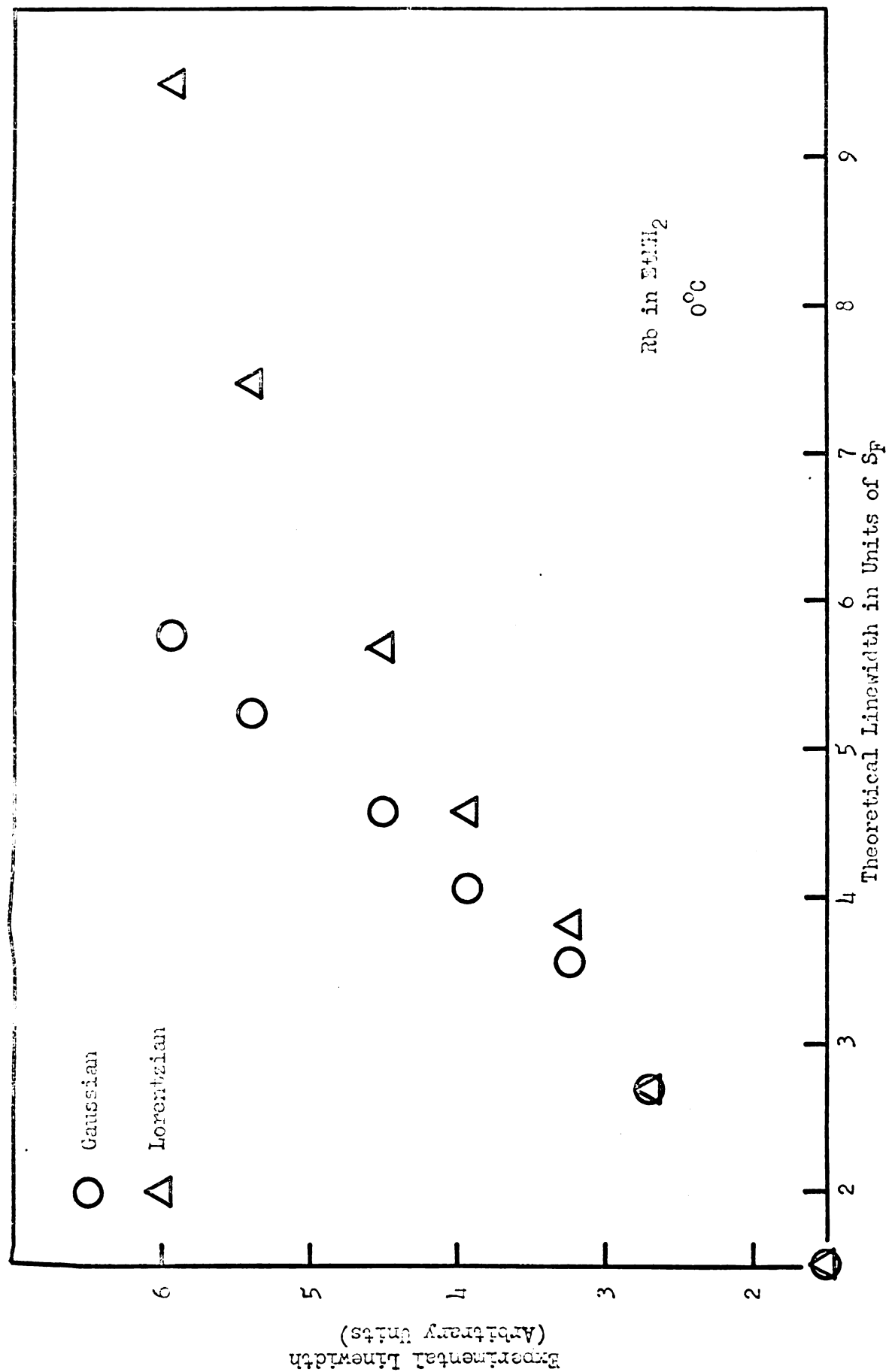


Figure 8b. Line shape analysis of a typical spectrum of Rb in $EtMl_2$.

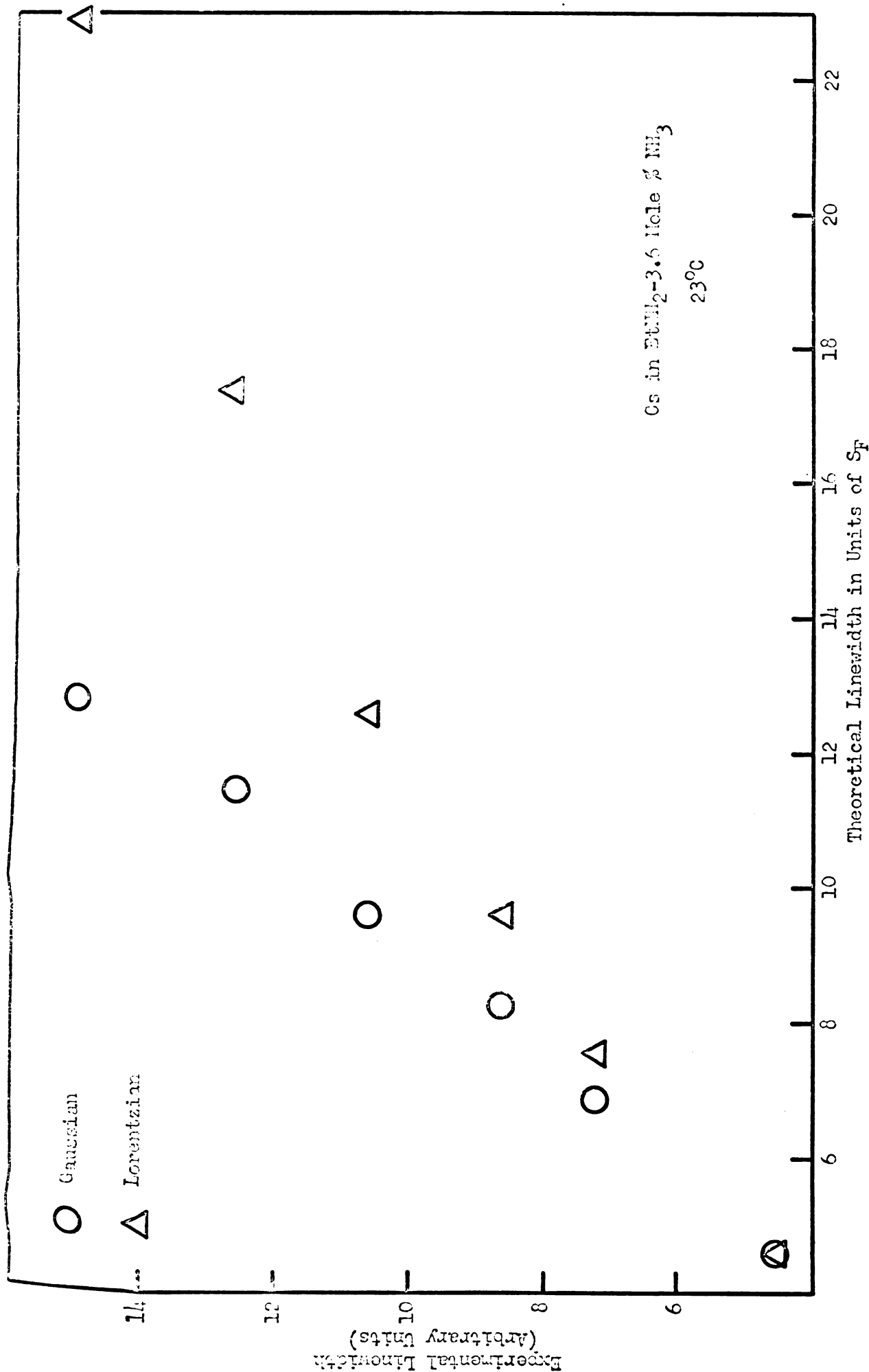


Figure 8c. Line shape analysis of a typical spectrum of Cs in an EtNH₂-NH₃ mixture.

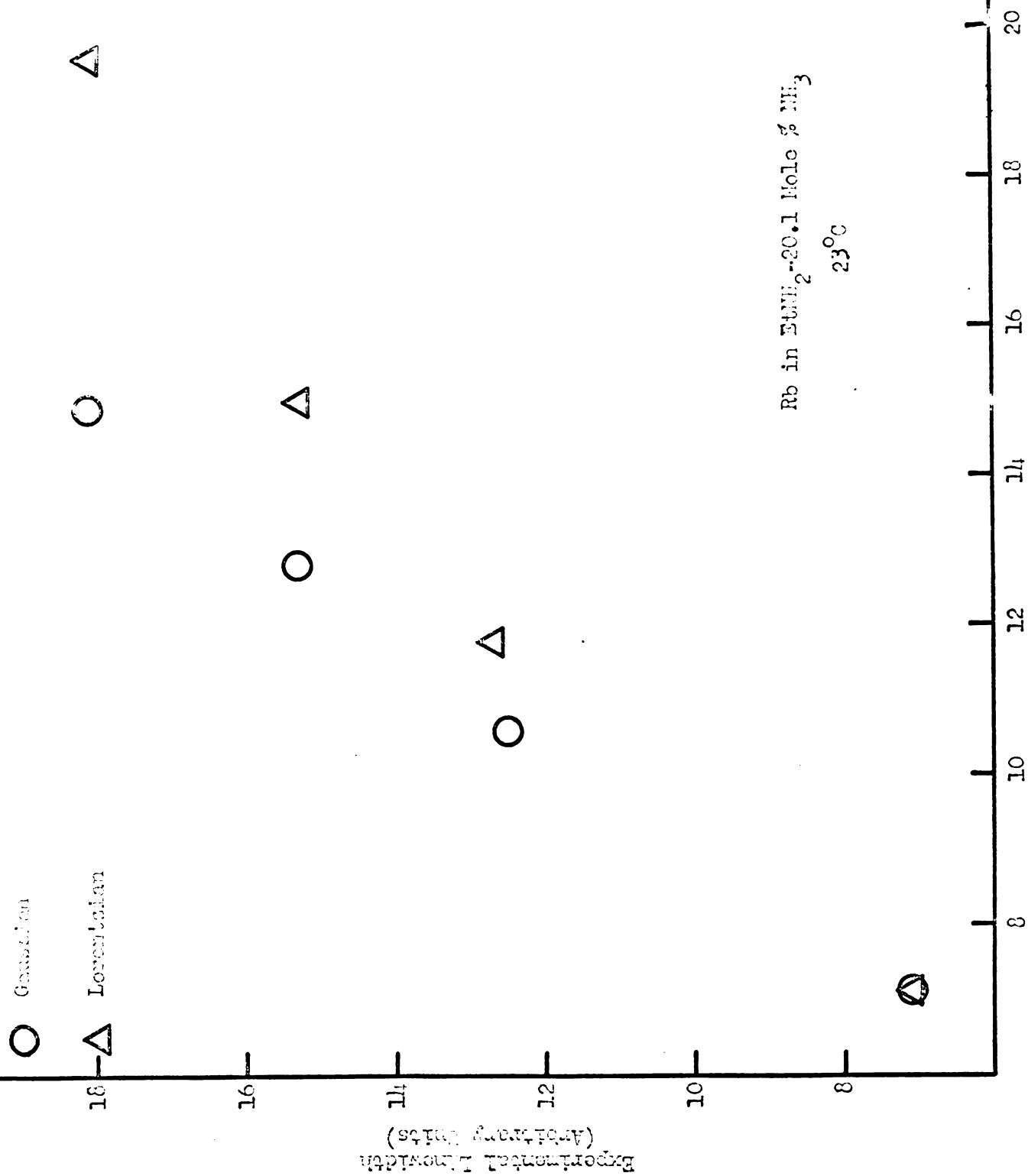


Figure 8d. Line shape analysis of a typical spectrum of Rb in an EtNH₂-NH₃ mixture.

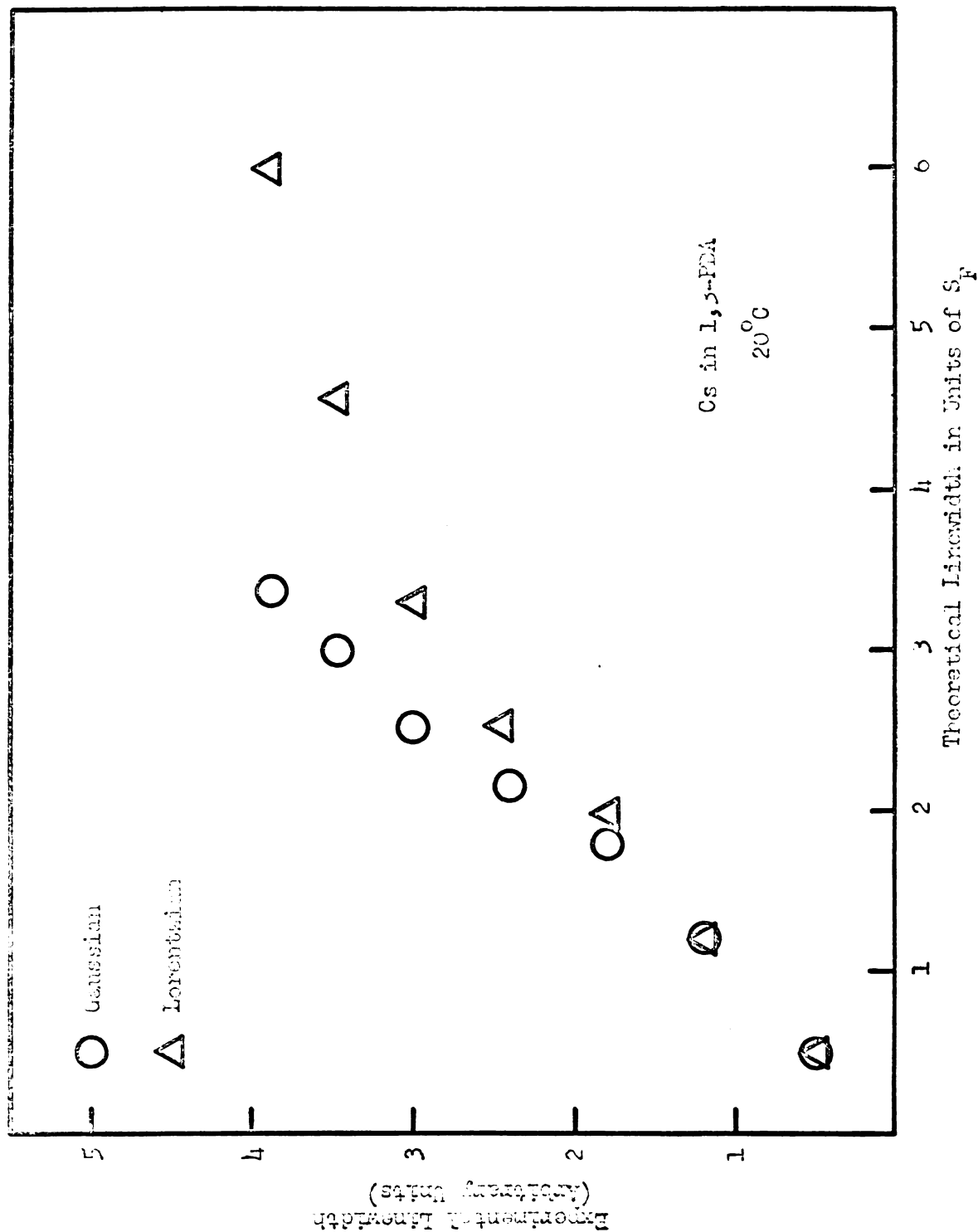


Figure 6e. Line shape analysis of a typical spectrum of Cs in 1,3-PDA.

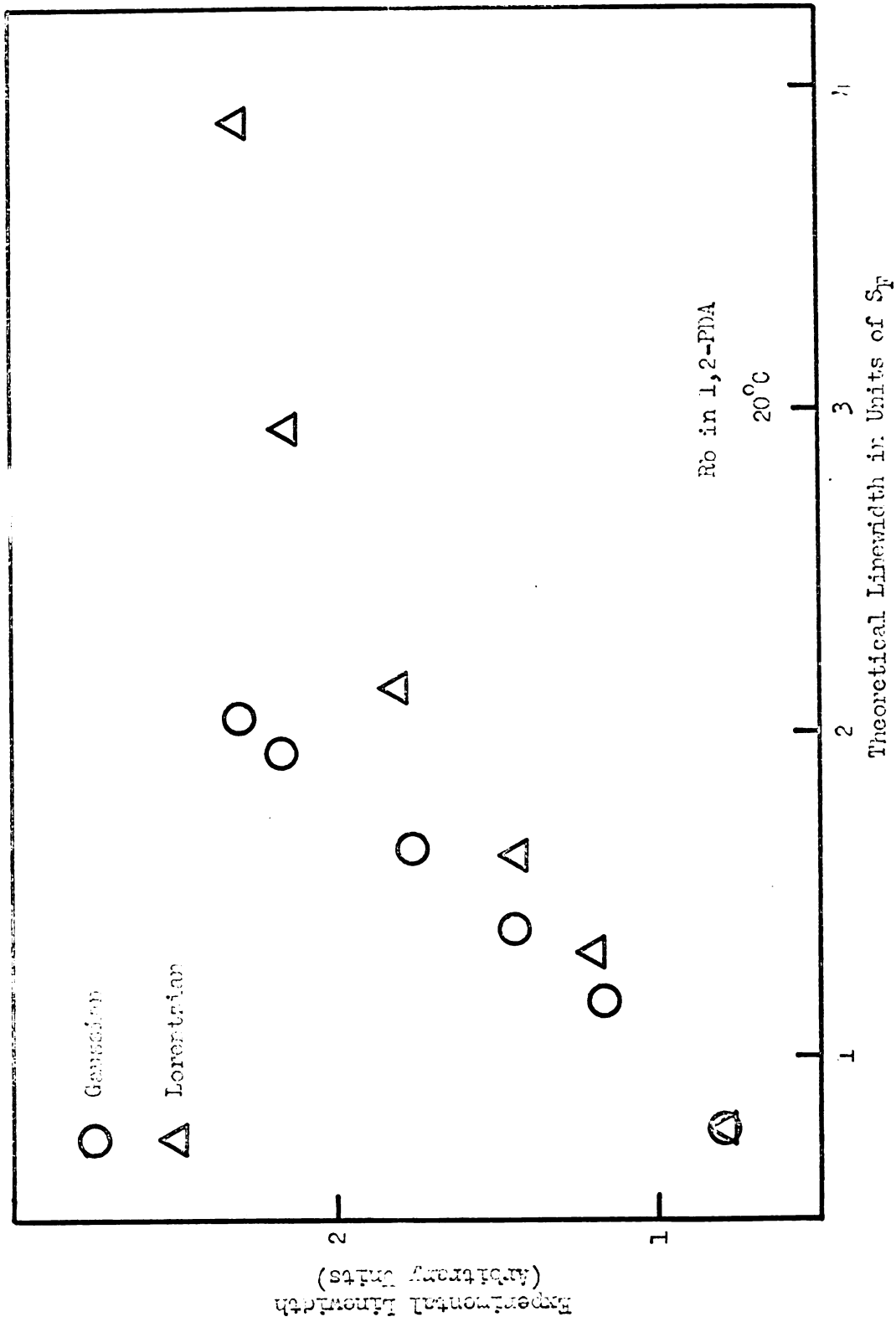


Figure 8f. Line shape analysis of a typical spectrum of Rb in 1,2-PDA.

This means that the effective filling factor of the cavity will be considerably enhanced by samples of sizable dielectric constant. One method of correcting for this "sucking in" of the microwave field is to place the reference material inside the sample. This was done by use of the apparatus shown in Fig. 7.

The magnitude of this "sucking in" which of course also depends upon the type and thickness of sample tubes, can be estimated by extrapolating the apparent spin concentration to samples of infinitesimal size. Only a slight size effect was observed for the materials reported here.

As mentioned previously, an accurate spin concentration measurement requires the determination of both the signal properties and H_1 , in the absence of saturation. Saturation curves (92) were, therefore, run on both reference and sample at the lowest temperatures used and the maximum allowable microwave power level was determined.

When the electrical properties of the sample, conditions for measurement, and the EPR line shape were taken into account as already described, the susceptibility was then calculated from the expression

$$\chi/\chi_0 = \chi_0/\chi_0^0 = K(g/g^0)(D/D^0)(G/G^0)(H_m^0/H_m)(S_p/S_p^0)^2 \quad (27)$$

in which D is the signal height, G the relative amplifier gain, H_m the modulation amplitude, and S_p the linewidth. K is a factor dependent upon the line shapes of the reference and the sample. Equating χ/χ_0 to χ_0/χ_0^0 assumes that both systems would obey Curie's law at fixed spin concentrations.

Measurement of K , which relates the line shape of the reference sample to that of the unknown, is required for the evaluation of spin

concentration. A convenient material to use for the evaluation of K is $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ in single crystal form. It has a very small Weiss constant so that expression 25 is applicable. Single crystals of convenient size (a few hundred micrograms) can be grown, weighed on a microbalance, and then imbedded in paraffin. No change in the EPR properties has been observed for such standard samples over a period of several years. The EPR linewidth and g factor are both orientation dependent; however, the described method of determining spin concentrations takes into account both these parameters. The line is very nearly Lorentzian so that the expression 27 could be used accurately for all the measurements reported in this paper. From a signal-to-noise standpoint, it was found worthwhile to rotate the standard sample in the field until a fairly narrow line with S_y approximately 30 gauss was obtained since the signal height D is inversely proportional to S_y^2 .

Measurements were made on the reference and sample simultaneously. This was done by attaching the reference material to the sample in either of two ways. Powdered samples, dispersed in polyethylene or paraffin were cut into sleeves that fitted snugly around the sample tubes. Reference samples in solution were sealed in tubes of various diameters and taped to the sample tubes. A summary of the reference samples used along with pertinent information about their preparation and EPR characteristics is given in Table V. Obviously, not all references were applicable in every case. The references used were selected to match the spin concentration range of the samples without serious overlap with the lines of the sample. Some of the materials listed were used as checks on secondary reference standards.

6. Measurement of paramagnetic relaxation or line widths.

There are two reasons for discussing relaxation phenomena in EPR. The first is that the nature of these phenomena must be properly taken into account if one wishes to make a significant measurement of spin susceptibility or spin concentration. The second reason is that relaxation phenomena in themselves can be a valuable indication of the nature of the unpaired spins and their interactions with their surroundings.

Practically all relaxation phenomena can be discussed conveniently by starting with Bloch's phenomenological description of magnetic resonance (68). Bloch defines a longitudinal or spin-lattice relaxation time T_1 and a transverse or spin-spin relaxation time T_2 and then shows that the imaginary or absorptive part of the susceptibility is given by

$$\chi'' = \frac{1}{2} \chi_0 \omega_0 T_2 / [1 + (\omega - \omega_0)^2 T_2^2 + (\gamma B_1)^2 T_1 T_2 / 4] \quad (28)$$

where χ'' and P_n are related by

$$\chi'' = 2P_n / \omega B_1^2$$

The parameters T_1 and T_2 were introduced purely phenomenologically based on a fairly simple model. Therefore, it should be emphasized that for the EPR response of any real system, the definition of these parameters and their correspondence to measurable quantities must be closely examined.

The spin-lattice relaxation time T_1 was introduced as the time constant for an assumed first order rate of approach of an excited spin system to equilibrium, i.e. $dn/dt = (n_0 - n)/T_1$ where n is the population difference between the ground and the excited spin states

and n_0 is the equilibrium value of this quantity. The exponential degradation of the energy of a spin system to its immediate surrounding (lattice) has been shown to be a remarkably good approximation even for quite complicated and multilevel systems (94). This does not mean, however, that a single T_1 can adequately describe a system containing different kinds of spins or inhomogeneities in structures.

The significance of T_2 is even less straightforward. For an idealized spin system, the definition of T_2 in terms of a normalized shape function $g(\omega - \omega_0)$, viz. $g(0) = T_2/\pi$, leads to simple relations between T_2 and line width. For example, for a Lorentzian shape function, the half-width at half-height, $(\omega - \omega_0)_{1/2}$, is equal to $1/T_2$, while for a Gaussian shape function this width is given by $(\pi \ln 2)^{1/2}/T_2$ (95). In these cases, both T_1 and T_2 in Eq. 28 can thus be related simply to experiment.

For many paramagnetic materials, such simple correspondences do not exist. As Portis (96) has shown in his detailed study of spin relaxation of F-centers, the different interaction mechanisms which give rise to line broadening can cause drastic differences in the EPR behavior which do not permit the direct application of Eq. 28. The basis for these differences is most easily discussed by defining two types of broadening, homogeneous and inhomogeneous, which depend upon how fast these interactions are varying relative to the time of a spin transition. Portis (96) lists a number of sources of homogeneous broadening in which the interactions of the spins among themselves and with their surroundings are so fast that all the spins can be conveniently characterized by time-averaged interaction parameters. For these situations, Eq. 28 will be applicable.

In the case of inhomogeneous broadening, Portis (96) lists several interactions which vary slowly over the time required for a spin transition. As a result of these "inhomogeneous" interactions, the EPR signal will appear as the envelope of a number of spin packets as is shown in Fig. 9. The parameter T_2^* is now defined for the envelope distribution $h(\omega - \omega_0)$ by $h(0) = T_2^*/\pi$. It should be emphasized that T_2^* cannot in general be related to a line width since not only can the line shape deviate substantially from Lorentzian or Gaussian but it can also be asymmetric.

Portis (96) has also shown that the EPR saturation behavior of homogeneously and inhomogeneously broadened lines is quite different. As expression 28 indicates, the line width increases with microwave power (proportional to H_1^2); whereas in the inhomogeneously broadened case, the line shape is independent of the extent of saturation. The behavior of the peak absorption intensity for the two cases also indicates that one can clearly differentiate between the two types of line broadening by careful saturation studies.

Considerable caution must be exercised in the use of Portis's simplified Eq. 19, however. It is strictly applicable only to the case illustrated in Fig. 9 where the over-all broadening is large compared to the width of the spin packets and T_1 is identical for all the spin packets.

The preceding paragraphs emphasize that any analysis of paramagnetic relaxation must be performed with great care. For any analysis to be meaningful we must always establish the applicability of any mathematical relationship which we desire to use.

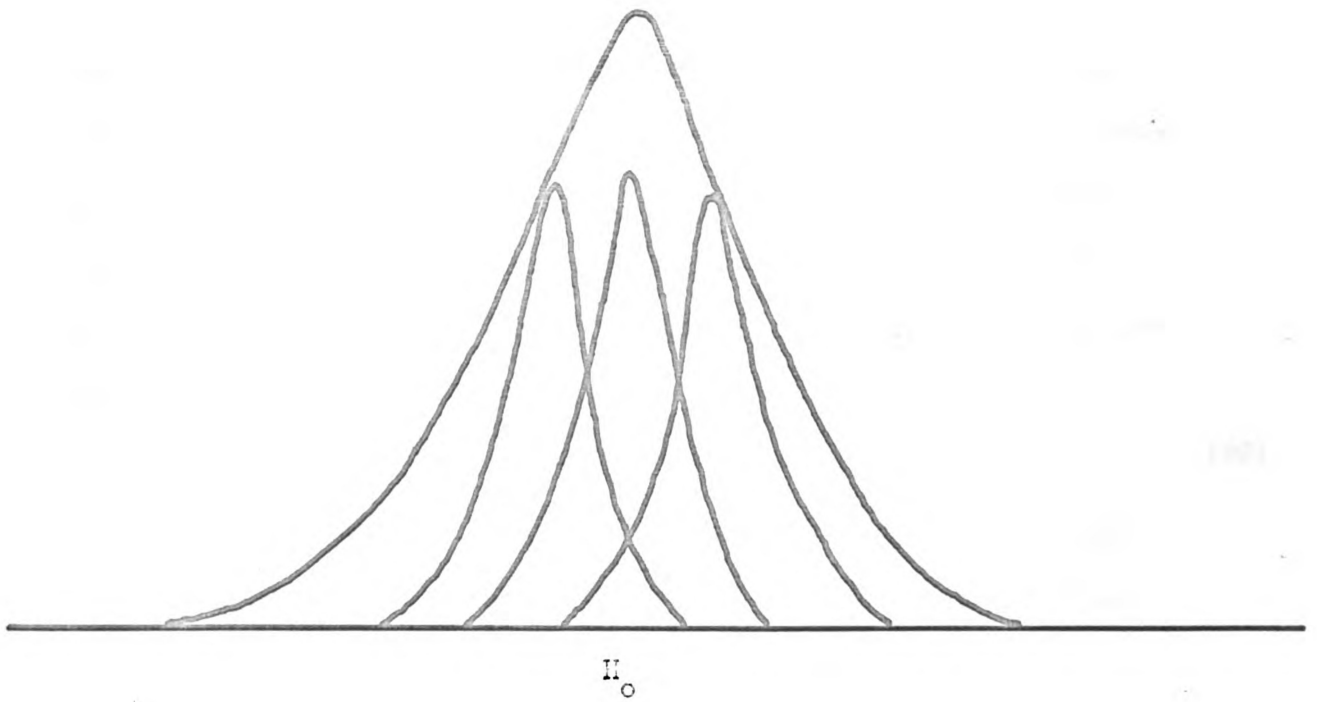


Figure 9. Inhomogeneously broadened resonance line.

As is also clear from the preceding paragraphs, the same considerations must be kept in mind when measuring T_1 and T_2 as when measuring spin concentrations. Let us first discuss the measurement of the spin-spin relaxation time T_2 . To accomplish this we must be able to relate the measured line shape to the Lorentzian or Gaussian shape function. If we are able to do this T_2 can be calculated from the two simple relationships already given. There are two experimental factors which must be carefully considered if one is to avoid distorting the true EPR line shape and thereby obtaining an erroneous measure of the half-width. The first of these is the modulatory amplitude, particularly if high-frequency modulation is used (97). E. R. Andrew (98) has shown that the second moment is related to the amplitude of the field modulation by

$$S_2^2 \text{ (observed)} = S_2^2 \text{ (intrinsic)} + \frac{1}{4} H_M^2 \quad (29)$$

It has been found by experience in this laboratory that the range of modulation $2 H_M$ may be set at about a quarter of the line width without introducing appreciable error. The line width, defined as the interval between maximum and minimum of the first derivative, is usually about twice the rms width (root second moment). From Eq. 29 it is seen that an error of about 2 percent is thus incurred in the second moment.

The second experimental factor which must be closely monitored is the scanning speed. Particularly with samples having very short relaxation times, scanning too fast can have the effect of distorting line shapes and widths. To guard against this possibility, line shapes were examined as a function of scanning speed.

There are a number of experimental methods which can be used to obtain T_1 . The particular method chosen depends upon both the absolute and relative magnitudes of T_1 and T_2 . A number of pulse techniques have been used (99), but these schemes are somewhat elaborate and may become exceedingly difficult for the shorter relaxation times. The saturation method is experimentally fairly simple but again requires the proof or assumption of certain characteristics of the EPR signal before T_1 can be determined. One simple way of obtaining absorption intensities as a function of microwave power is by using two attenuators, at least one of them calibrated. Known amounts of attenuation can be inserted in front of the cavity and identical amounts removed immediately before the detector. One can in this way insure a constant sensitivity of the system with change in microwave power. A single crystal of DPPH, for which T_1 and T_2 are known ($T_1 = T_2 = 6 \times 10^{-9}$ sec), can conveniently serve as a calibration material. If two attenuators are not available, one can also monitor H_1 in the cavity with one of the reference samples as described for the measurement of spin concentrations. Although the methods described above were employed by the author it may also be mentioned that Swidt (100) has used a method for determining H_1 which involves a direct measurement of the cavity Q.

An example of the results of saturation experiments on some metal-amine samples is shown in Fig. 10. The quantity D/D_0 is the extreme deflection on the derivative curve normalized to unity at zero microwave power. If Eq. 28 is applicable, the modulation frequency is not too large, and T_2 is known, a T_1 for each sample can be calculated from the expression

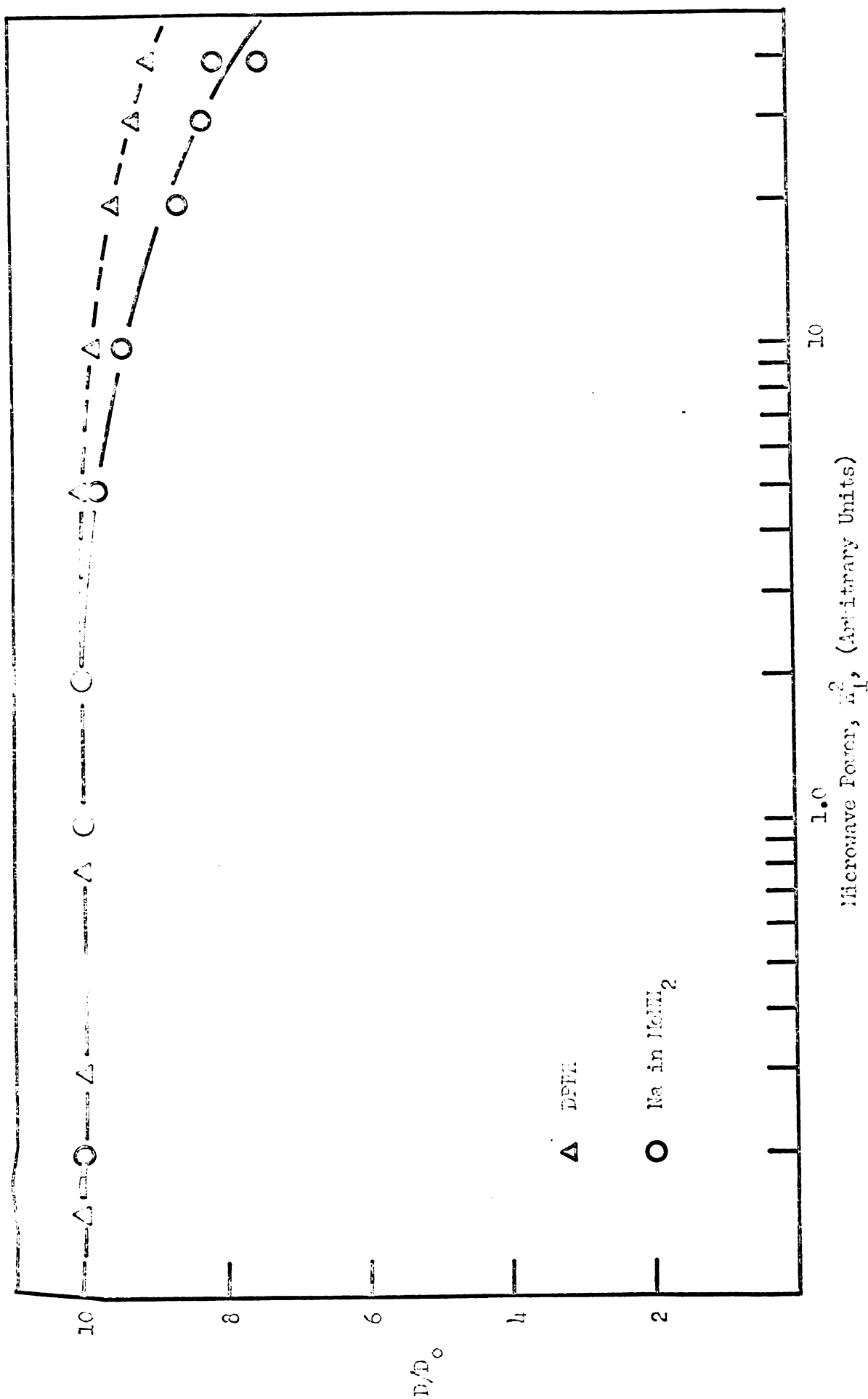


Figure 10. Saturation curve for a typical metal-amine sample and hydrazyl.

$$T_1 = (B_{1\text{DPPH}}^2 / B_1^2) T_{1\text{DPPH}}^2 T_2^{-1} \quad (30)$$

evaluated at the same percent of saturation.

In addition to the measurement of T_1 and T_2 we were faced in this work with the analysis of the anisotropic relaxation of hyperfine components. To insure that we were not measuring intermolecular spin-spin exchange effects only solutions dilute in metal were considered. Analysis showed that the integrated intensities (101) of the hyperfine lines of potassium, rubidium, and cesium solutions when normalized to unity are equal to within experimental accuracy. The absolute linewidth was determined from the $m_I = -3/2$ line and the relative widths so determined agreed with those obtained by direct linewidth measurements.

The analysis of the m_I -dependent relaxation observed in metal-saline solutions was carried out by evaluating the coefficients of T_2^{-1} to various powers of m_I .

C. Optical Measurements

Two optical systems were employed in taking the optical measurements reported in this thesis. When Amineo cylindrical absorption cells were attached to the EPR tubes optical spectra in the range 500 to 2000 mμ were taken using a Beckman DK-2 recording spectrophotometer. Temperature regulation was provided by a thermostat which has been previously described (102) and permitted control to $\pm 2^\circ\text{C}$.

Measurements at room temperature and in EPR tubes were taken employing a rapid scanning optical system constructed by Dye and Feldman (103). With the appropriate source and detector this instrument is usable over a range from 200 to 2500 mμ. Recently, Rynbrandt and

Dye have modified this system so that a Varian V-450 variable temperature control unit can be used to achieve temperature variation and regulation.

D. Conductance Measurements

Conductance measurements were attempted on sodium-ethylenediamine solutions using an EPR tube with conductance cell attached and employing a Wayne Kerr conductance bridge. The technique employed was similar to that used by Dewald (104).

E. Viscosity Measurements

The viscosities of methylamine and ethylamine were determined using the Ostwald viscometer arrangement shown in Fig. 11. The arrangement was so constructed that a solvent could be purified using high vacuum techniques, distilled into the viscometer, covered with pre-purified nitrogen, manipulated by means of a mercury leveling bulb, its viscosity measured, and finally distilled out to make way for another solvent. Temperature regulation was achieved by use of an evacuated Dewar filled with 2-propanol and cooled by the addition of dry-ice.

The viscometer was first calibrated using acetone and then the viscosities of methylamine and ethylamine were determined using the equation

$$\eta = \rho t \eta^* / \rho^* t^* \quad (31)$$

where η is the viscosity; ρ is the density; and t is the time in seconds required for the liquid to flow through the viscometer. The starred quantities refer to acetone.

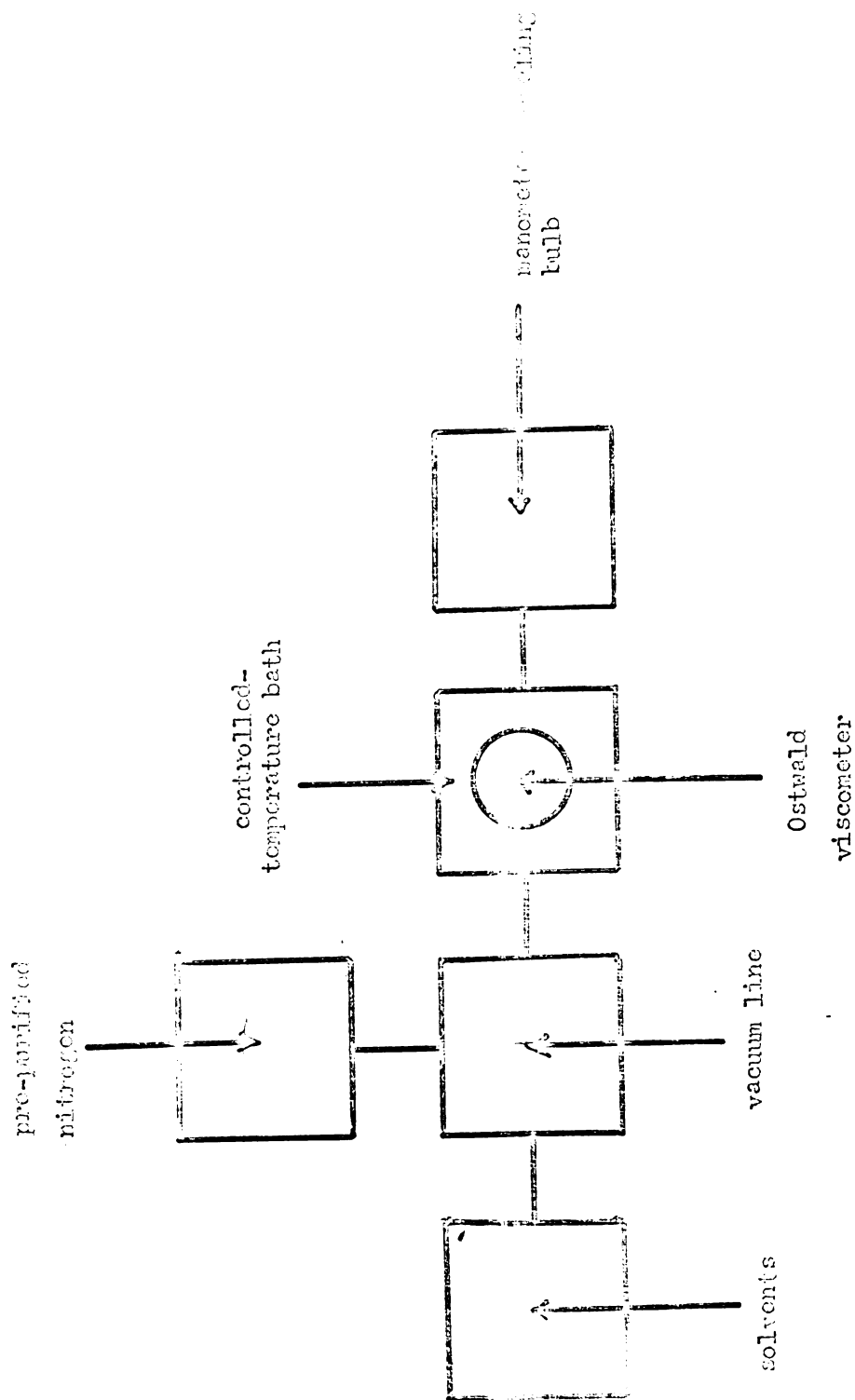


Figure 11. Block diagram of apparatus used to obtain the viscosities of methylamine and ethylamine as a function of temperature.

RESULTS

A. EPR Measurements on Metal-Amine Solutions

(Magnetic Parameters)

The qualitative observation of electron paramagnetic resonance in the metal-amine systems studied by the author are summarized in Table VI. In discussing these systems in detail we shall in general group them according to particular EPR characteristics; hence, our subheadings shall be the characteristic EPR absorptions or species.

1. The monomeric species. The characteristic EPR absorption of most potassium, rubidium, and cesium-amine solutions (also observed for some sodium solutions) is a hyperfine pattern arising from the interaction of a paramagnetic electron with a single alkali metal nucleus. The magnitude of this interaction is always less than the "free atom" value and is very sensitive to solvent as shown in Table VII. In general the hyperfine splitting increases as the ratio of alkyl character increases. This can also be viewed as the hyperfine interaction increasing as the solvating power of the solvent decreases.

Studies on dilute solutions show that the hyperfine splitting is independent of metal concentration.

Perhaps the most startling aspect of the hyperfine interaction is its marked dependence upon temperature. As seen in Table VIII, the hyperfine splitting may change by a factor of 4 over a one hundred degree temperature range. As can also be seen from Table VIII and from Fig. 12,

TABLE VI. Qualitative Nature of the Electron Paramagnetic Resonance Spectra of Metal-Amine Solutions^a

Solvent	Metal				
	Lithium	Sodium	Potassium	Rubidium	Cesium
NH_3	Single line ^d	Single line ^{c,d}	Single line ^{c,d}	Single line ^d	Single line ^d
ND_3			Single line ^c		
MeNH_2	Single line ^d	Single line ^{b,d}	Single line ^{b,d}	Hf's from metal nucleus ^{b,d,f} ; Single line ^{b,d}	Hf's from metal nucleus ^{b,d,f} ; Single line ^{b,d}
$\text{MeNH}_2/\text{NH}_3$	Not studied	Not studied	Not studied	Hf's from metal nucleus ^b ; Single line ^b ; Broad extra line ^b	Hf's from metal nucleus ^b ; Single line ^b ; Broad extra line ^b
$\text{MeNH}_2/\text{Me}_2\text{NH}$	Hf's from 4 equiv. nitrogens ^b ; Single line ^b				
EtNH_2	Hf's from 4 equiv. nitrogens ^{b,c} ; Single line ^{b,c,d,f}	No spectra ^{b,c}	Hf's from metal nucleus ^{b,h,i} ; Single line ^{b,h}	Hf's from metal nucleus ^{b,i} ; Single line ^{b,i}	Hf's from metal nucleus ^{b,i} ; Single line ^{b,i}
$\text{EtNH}_2/\text{NH}_3$	Hf's from 4 equiv. nitrogens ^b ; Single line ^b	Not studied	Hf's from metal nucleus ^b ; Broad extra line ^b	Hf's from metal nucleus ^b	Hf's from metal nucleus ^b ; Broad extra line ^b

TABLE VI. Continued

Solvent	Metal				
	Lithium	Sodium	Potassium	Rubidium	Cesium
EtNH ₂ /MeNH ₂	Single line ^a	Hfs from metal nucleus ^b ; b Single line ^b	Hfs from metal nucleus ^c	Not studied	Not studied
EtNH ₂ /iPr	Not studied	Not studied	Hfs from metal nucleus ^b ; b Single line ^b	Not studied	Not studied
n-PeNH ₂	Not studied ^j	Not studied	Hfs from metal nucleus ^b ; b ₁ , b ₂ Single line ^b	Hfs from metal nucleus ^b	Hfs from metal nucleus ^b ; b Single line ^b
iPrPeNH ₂	Not studied ^j	Not studied	Hfs from metal nucleus ^b ; b ₁ , b ₂ Single line ^b	Hfs from metal nucleus ^b ; b ₁ , b ₂ , b ₃	Hfs from metal nucleus ^b ; b ₁ , b ₂ , b ₃
EtNH ₂ /1-PeNH ₂			Hfs from metal nucleus ^b		
EDA	Single line ^d	Single line ^{d,m}	Single line ^{d,m}	Single line ^{d,m}	Single line ^d
1,2 PDA	Not studied ^j	Not studied	Hfs from metal nucleus ^b ; b Single line ^b	Hfs from metal nucleus ^b ; b Single line ^b	Hfs from metal nucleus ^b ; b Single line ^b
1,3 PDA	Not studied ^j	Not studied	Hfs from metal nucleus ^b ; b Single line ^b	Hfs from metal nucleus ^b ; b Single line ^b	Hfs from metal nucleus ^b ; b Single line ^b

TABLE VI. Continued

Solvent	Metal				
	Lithium	Sodium	Potassium	Rubidium	Cesium
3-MPA	Not studied ^j	Not studied	Hfs from metal nucleus ^{b,1,4,6,1} Single line	Hfs from metal nucleus ^{b,1,4,6,1} Single line ^{b,1}	Hfs from metal nucleus ^{b,1,4,6,1} Single line ^{b,1}
1,2 PDA/3-MPA	Not studied	Not studied	Hfs from metal nucleus ^{b,1} Single line ^b	Not studied	Not studied
n-BuMg ₂	Not studied ^j	Not studied	Hfs from metal nucleus ^{b,4,6,1} Single line ^{b,4}	Hfs from metal nucleus ^{b,1}	
n-BuMg ₂ /EtMg ₂	Not studied	Not studied	Hfs from metal nucleus ^{b,1} Single line ^b	Not studied	Not studied
Hexamethyl- phosphoric triester	Not studied	Not studied	Complex spectra ^a	Not studied	Not studied
1,2-Dimethoxy- ethane	Not studied	No signal ^{b,6}	No signal ^b	No signal ^b	Not studied
Hfs (2-(2-methoxy- ethoxy)ethyl) ether	Not studied	Not studied	No signal ^b	Single line ^b	Not studied

TABLE VI. Continued

- ^aOnly the characteristic absorptions are given.
- ^bThis work.
- ^cReferences 6 and 7.
- ^dReferences 37 and 63.
- ^eReference 43.
- ^fReference 11^b.
- ^gSodium does not appear to be soluble in ethylamine.
- ^hReferences 51 and 52.
- ⁱReference 11⁵.
- ^jAlthough no electron paramagnetic resonance spectra have been taken, the author has observed this anion to form the characteristic blue solution upon dissolution of lithium.
- ^kSolution was metastable.
- ^lSolution was very unstable.
- ^mReference 31.
- ⁿReference 29.
- ^oSodium-potassium alloy was used.

TABLE VII. The Hyperfine Splitting, A_H , of the Monomeric Species as a Function of the Metal and Solvent Employed.^a

Solvent	A_H (Gauss) ^b			
	^{23}Na	^{39}K	^{85}Rb	^{133}Cs
MeNH_2			25.60 ± 0.3 (23°C)	55.89 ± 0.8 (23°C)
EtNH_2		13.00 ± 0.1 (50°C)	64.06 ± 0.3 (23°C)	127.6 ± 0.6 (23°C)
$\text{EtNH}_2/\text{MeNH}_2$	5.79 ± 0.1 (23°C)			
$n\text{-PrNH}_2$		14.00 ± 0.1 (23°C)	33.91 ± 0.4 (23°C)	171.5 ± 2.0 (23°C)
1-PrNH_2		18.25 ± 0.1 (23°C)	99.2 ± 3.0 (0°C)	240.7 ± 5.0 (20°C)
3-MPA		5.17 ± 0.3 (-16°C)	99.19 ± 2.0 (23°C)	71.46 ± 1.0 (-40°C)
$1,2\text{-PDA}$		2.82 ± 0.3 (0°C)	30.55 ± 0.3 (20°C)	67.30 ± 0.6 (20°C)
$3\text{-MPA}/1,2\text{-PDA}$ (1/1)		5.45 ± 0.2 (10°C)		
$1,3\text{-PDA}$		2.74 ± 0.3 (-10°C)	30.81 ± 0.3 (20°C)	67.47 ± 0.6 (20°C)

^aOnly values obtained by the author or by the author and V. A. Nicely are reported.

^bIt is often convenient to express hyperfine splittings as percent free atom splitting. This is accomplished by dividing the observed splitting by the free atom splitting. The free atom splittings for the alkali metals are as follows: $A_{\text{Li}} = 143$ G; $A_{\text{Na}} = 316$ G; $A_{\text{K}} = 82.5$ G; $A_{\text{Rb}} = 363$ G; $A_{\text{Cs}} = 818$ G.

TABLE VIII. The Hyperfine Splitting, A_H , of the Monomeric Species as a Function of Temperature.

<u>Nethylefine</u>					
Rubidium (^{85}Rb)					
T($^{\circ}\text{C}$)	A_H (Gauss)	T($^{\circ}\text{C}$)	A_H (Gauss)	T($^{\circ}\text{C}$)	A_H (Gauss)
90	36.8	43	27.8	-5	18.0
85	35.9	40	25.6	-20	15.0
80	34.6	25	24.0	-25	15.0
70	33.0	23	25.6	-30	13.6
60	31.1	19	23.2	-40	10.0
57	30.0	10	21.5	-45	11.2
50	28.6	-2	20.0	-75	6.1
Cesium (^{133}Cs)					
T($^{\circ}\text{C}$)	A_H (Gauss)	T($^{\circ}\text{C}$)	A_H (Gauss)	T($^{\circ}\text{C}$)	A_H (Gauss)
75	84.2	22	55.7	-50	20.6
70	83.5	22	52.8	-60	18.3
68	78.2	7	44.3	-73	15.2
60	75.0	6	45.0	-75	15.0
50	70.2	-5	39.0	-100	12.9
40	63.7	-12	35.8	-100	14.3
30	58.2	-21	33.4		
23	52.9	-35	26.0		

TABLE VIII. Continued.

<u>Ethylamine</u>					
Rubidium (^{85}Rb)					
$T(^{\circ}\text{C})$	$\lambda_H(\text{Gauss})$	$T(^{\circ}\text{C})$	$\lambda_H(\text{Gauss})$	$T(^{\circ}\text{C})$	$\lambda_H(\text{Gauss})$
50	78.8	0	49.6	-80	55.14
40	72.8	0	43.9	-80	54.63
35	69.8	-10	43.5	-80	55.78
30	66.5	-20	37.8	-90	50.71
23	64.1	-30	34.1	-90	50.71
23	65.0	-40	25.4	-90	50.69
20	61.0	-50	20.0	-100	46.21
15	57.5	-70	99.28	-100	49.02
10	55.0	-70	99.35		
5	52.0	-70	99.15		
Cesium (^{133}Cs)					
$T(^{\circ}\text{C})$	λ_H	$T(^{\circ}\text{C})$	$\lambda_H(\text{Gauss})$	$T(^{\circ}\text{C})$	$\lambda_H(\text{Gauss})$
85	205	10	118.8	-30	83.25
80	197	10	117.8	-30	82.93
70	185	10	117.8	-40	77.30
60	173	0	109.6	-40	76.90
50	161.8	0	107.5	-40	77.71
40	149.6	0	108.6	-50	71.64
40	150.2	-10	98.99	-50	71.55
30	138.7	-20	90.46	-50	70.34
10	138.7	-20	89.87	-60	64.61
20	127.8	-20	90.67	-60	64.86
20	127.7	-30	82.81	-60	65.06

TABLE VIII. Continued.

<u>Proxylamine</u>					
Potassium (^{39}K)					
$T(^{\circ}\text{C})$	$A_H(\text{Gauss})$	$T(^{\circ}\text{C})$	$A_H(\text{Gauss})$	$T(^{\circ}\text{C})$	$A_H(\text{Gauss})$
80	21.8	30	14.6	-10	9.4
70	20.3	23	14.0	-20	8.3
60	18.9	20	13.2	-30	7.2
50	17.5	10	11.9	-35	6.6
40	15.9	0	10.5		
<u>Rubidium (^{85}Rb)</u>					
$T(^{\circ}\text{C})$	$A_H(\text{Gauss})$	$T(^{\circ}\text{C})$	$A_H(\text{Gauss})$	$T(^{\circ}\text{C})$	$A_H(\text{Gauss})$
40	91.5	29	86.5	10	79.1
38	91.0	25	85.7	0	75.0
35	89.0	23	83.9	-10	70.5
32	88.0	20	83.0		
<u>Cesium (^{133}Cs)</u>					
$T(^{\circ}\text{C})$	$A_H(\text{Gauss})$	$T(^{\circ}\text{C})$	$A_H(\text{Gauss})$	$T(^{\circ}\text{C})$	$A_H(\text{Gauss})$
50	204	30	180	-10	135
45	197	23	172	-20	125
40	193	10	157	-30	116
35	186	0	145		
<u>Isoxanzoline</u>					
Potassium (^{39}K)					
$T(^{\circ}\text{C})$	$A_H(\text{Gauss})$	$T(^{\circ}\text{C})$	$A_H(\text{Gauss})$	$T(^{\circ}\text{C})$	$A_H(\text{Gauss})$
30	19.4	23	18.3	15	16.9
25	18.5	20	17.5	0	14.1

TABLE VIII. Continued.

<u>Isonononamide</u>					
Cesium (^{133}Cs)					
$T(^{\circ}\text{C})$	$A_H(\text{Gauss})$	$T(^{\circ}\text{C})$	$A_H(\text{Gauss})$	$T(^{\circ}\text{C})$	$A_H(\text{Gauss})$
20	241	10	231	0	220
<u>3-Nitro-L-nononamide</u>					
Cesium (^{133}Cs)					
$T(^{\circ}\text{C})$	$A_H(\text{Gauss})$	$T(^{\circ}\text{C})$	$A_H(\text{Gauss})$	$T(^{\circ}\text{C})$	$A_H(\text{Gauss})$
-20	82.0	-30	77.8	-42	69.1
-25	80.3	-40	71.5	-45	69.5
<u>1,2-Propanediolamine</u>					
Potassium (^{39}K)					
$T(^{\circ}\text{C})$	$A_H(\text{Gauss})$	$T(^{\circ}\text{C})$	$A_H(\text{Gauss})$	$T(^{\circ}\text{C})$	$A_H(\text{Gauss})$
50	5.91	10	3.82	-20	2.75
40	5.35	0	3.25	-20	2.55
30	4.55	0	2.81		
20	4.42	-10	2.75		
Rubidium (^{85}Rb)					
$T(^{\circ}\text{C})$	$A_H(\text{Gauss})$	$T(^{\circ}\text{C})$	$A_H(\text{Gauss})$	$T(^{\circ}\text{C})$	$A_H(\text{Gauss})$
60	38.6	25	30.5	0	26.6
50	37.0	20	30.6	-10	23.9
40	36.1	15	29.2	-20	21.9
30	32.4	10	27.7		

TABLE VIII. Continued.

<u>1,2-Propylenimine</u>					
Cesium (^{133}Cs)					
T($^{\circ}\text{C}$)	$A_H(\text{Gauss})$	T($^{\circ}\text{C}$)	$A_H(\text{Gauss})$	T($^{\circ}\text{C}$)	$A_H(\text{Gauss})$
60	83.5	30	71.7	-10	57.5
50	82.0	20	67.3	-20	54.2
45	76.7	10	63.1	-30	50.5
40	75.5	0	60.8		
<u>3-Methoxy-n-propylamine/ 1,2-Propylenimine</u>					
Potassium (^{39}K)					
T($^{\circ}\text{C}$)	$A_H(\text{Gauss})$	T($^{\circ}\text{C}$)	$A_H(\text{Gauss})$	T($^{\circ}\text{C}$)	$A_H(\text{Gauss})$
10	5.45	5	5.16	0	4.94
<u>1,3-Propylenimine</u>					
Potassium (^{39}K)					
T($^{\circ}\text{C}$)	$A_H(\text{Gauss})$	T($^{\circ}\text{C}$)	$A_H(\text{Gauss})$	T($^{\circ}\text{C}$)	$A_H(\text{Gauss})$
50	5.90	10	3.80	-20	2.83
40	5.35	0	3.40	-20	2.63
30	4.75	-10	2.72		
20	4.25	-20	2.48		
Rubidium (^{85}Rb)					
T($^{\circ}\text{C}$)	$A_H(\text{Gauss})$	T($^{\circ}\text{C}$)	$A_H(\text{Gauss})$	T($^{\circ}\text{C}$)	$A_H(\text{Gauss})$
45	35.0	30	32.1	15	28.6
40	34.0	20	30.8	0	23.6
35	33.0				

TABLE VIII. Continued.

<u>1,3-Propanediamine</u>					
Cesium (^{133}Cs)					
$T(^{\circ}\text{C})$	$\lambda_H(\text{Gauss})$	$T(^{\circ}\text{C})$	$\lambda_H(\text{Gauss})$	$T(^{\circ}\text{C})$	$\lambda_H(\text{Gauss})$
60	82.4	10	64.6	-20	52.7
40	74.4	0	60.5	-30	50.3
20	67.5	-11	54.3		

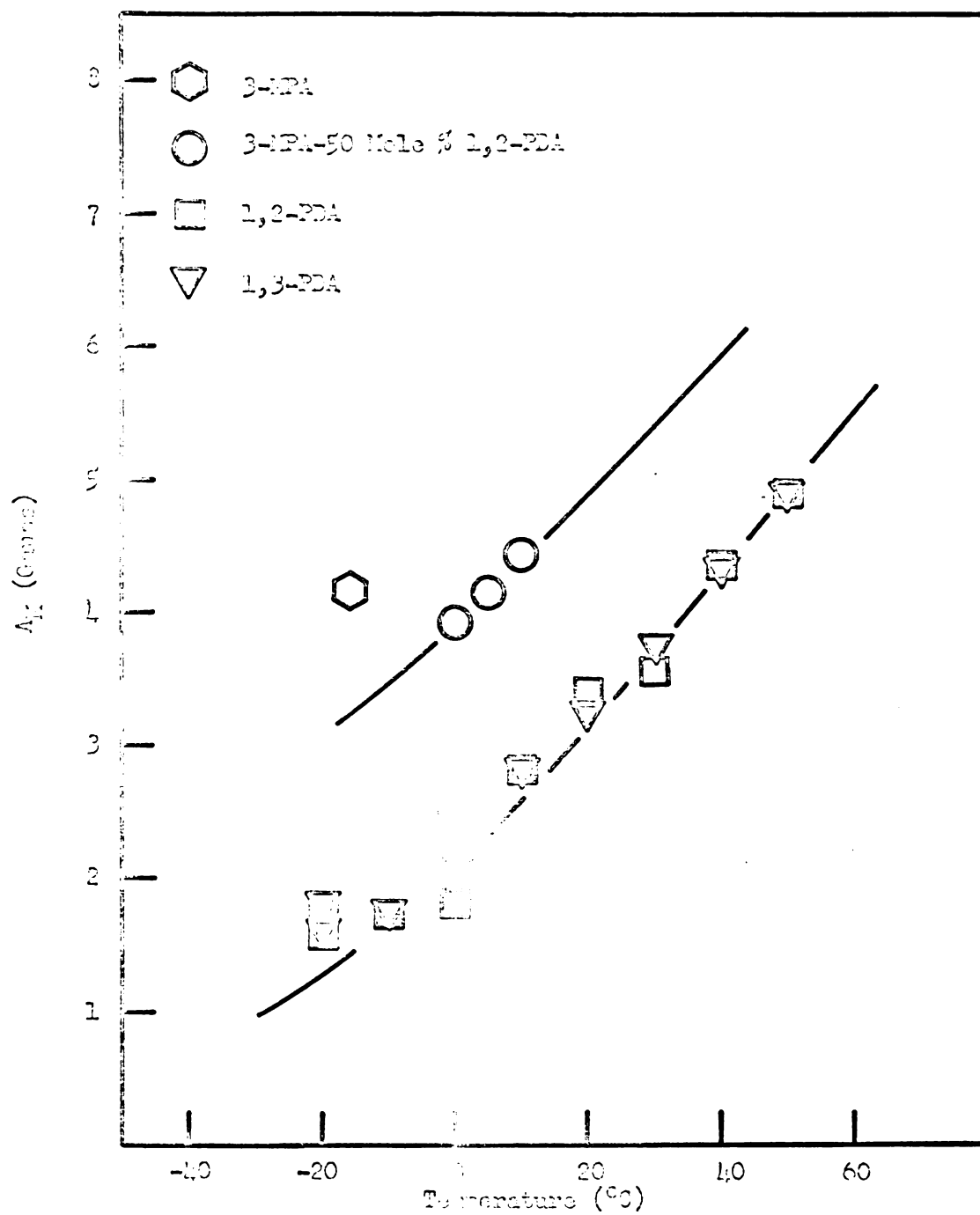


Figure 12a. Hyperfine splitting for some potassium solutions as a function of solvent and temperature.

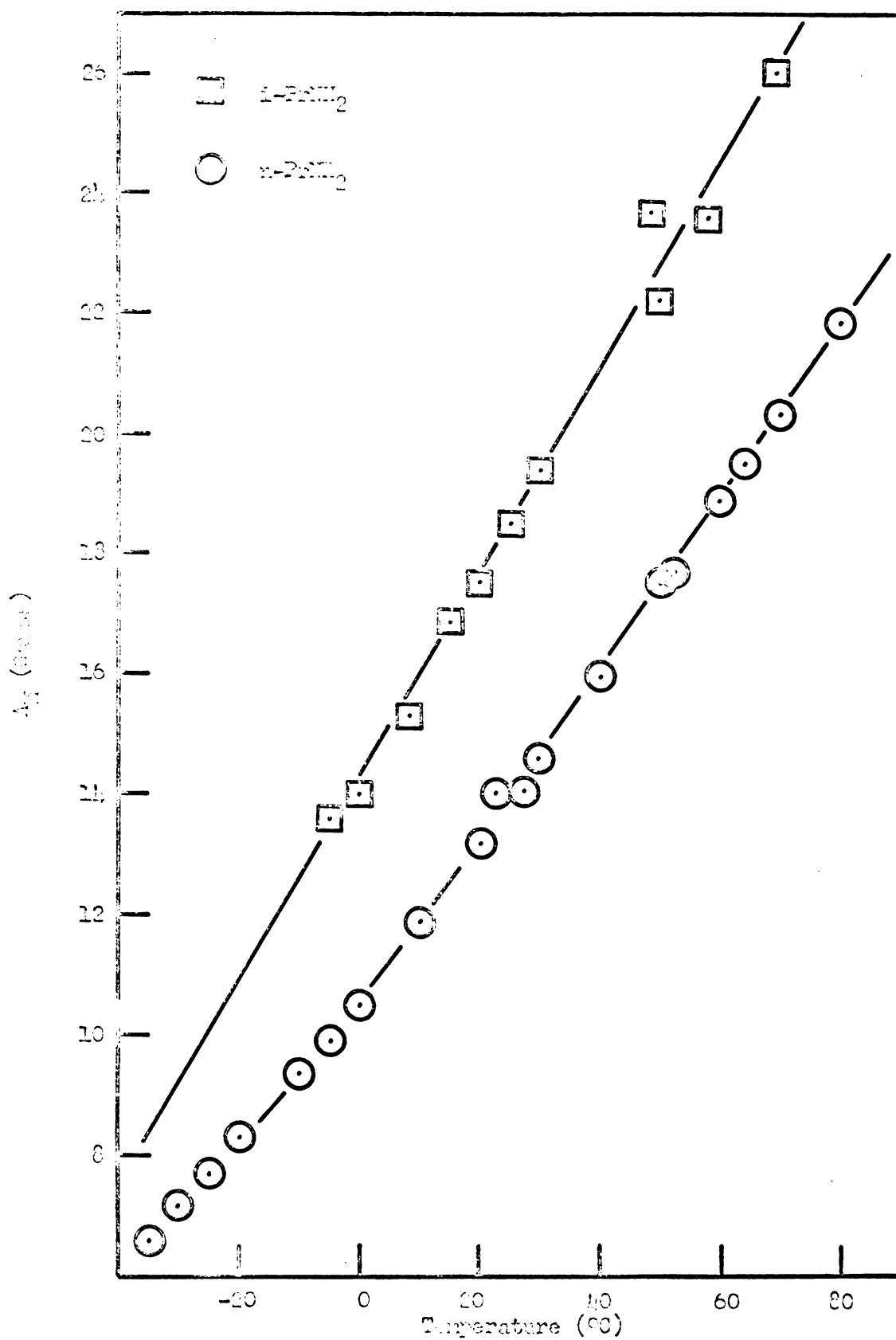


Figure 12b. Hyperfine splitting for some potassium solutions as a function of solvent and temperature.

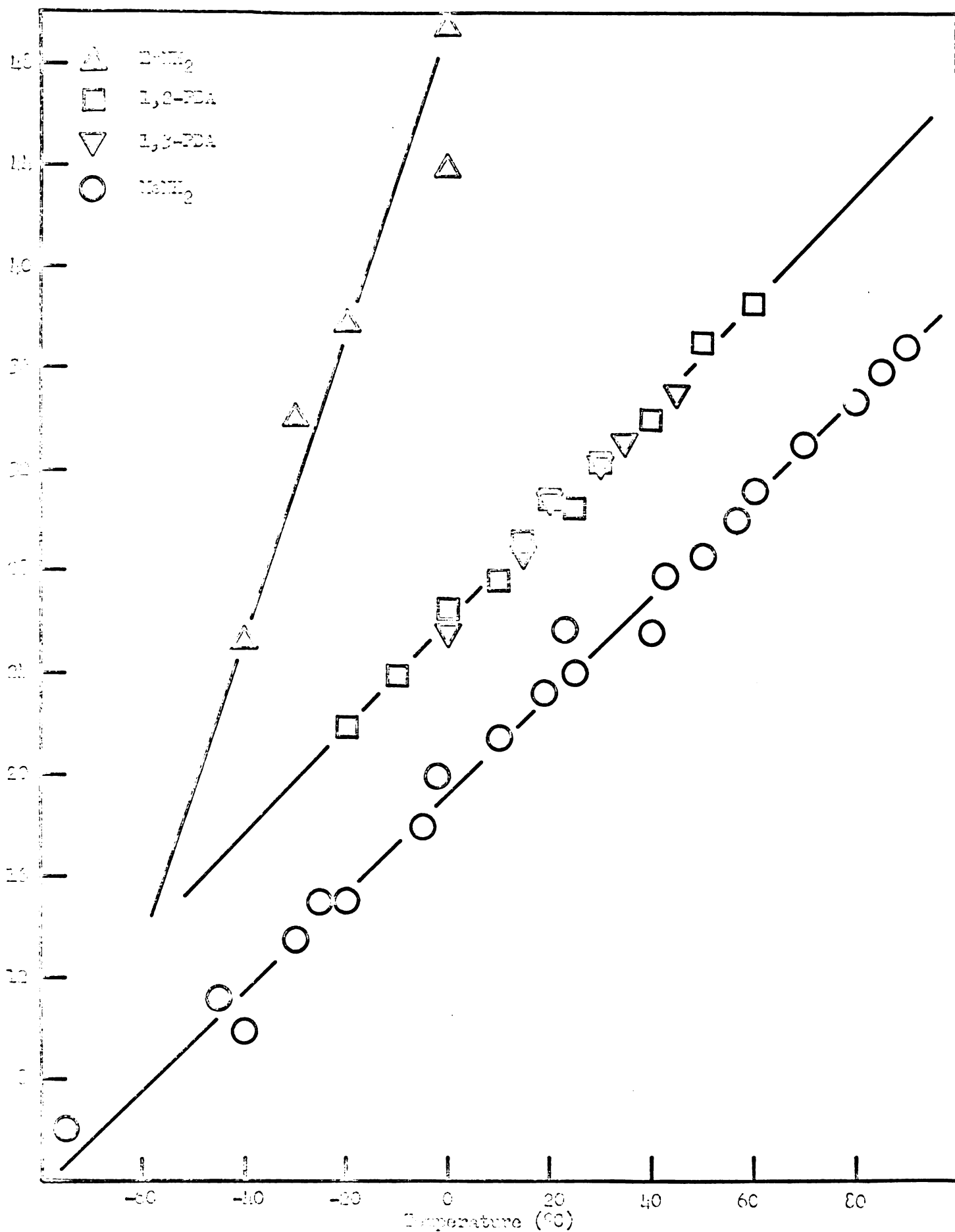


Figure 12c. Hyperfine splitting for some rubidium (^{85}Rb) solutions as a function of solvent and temperature.

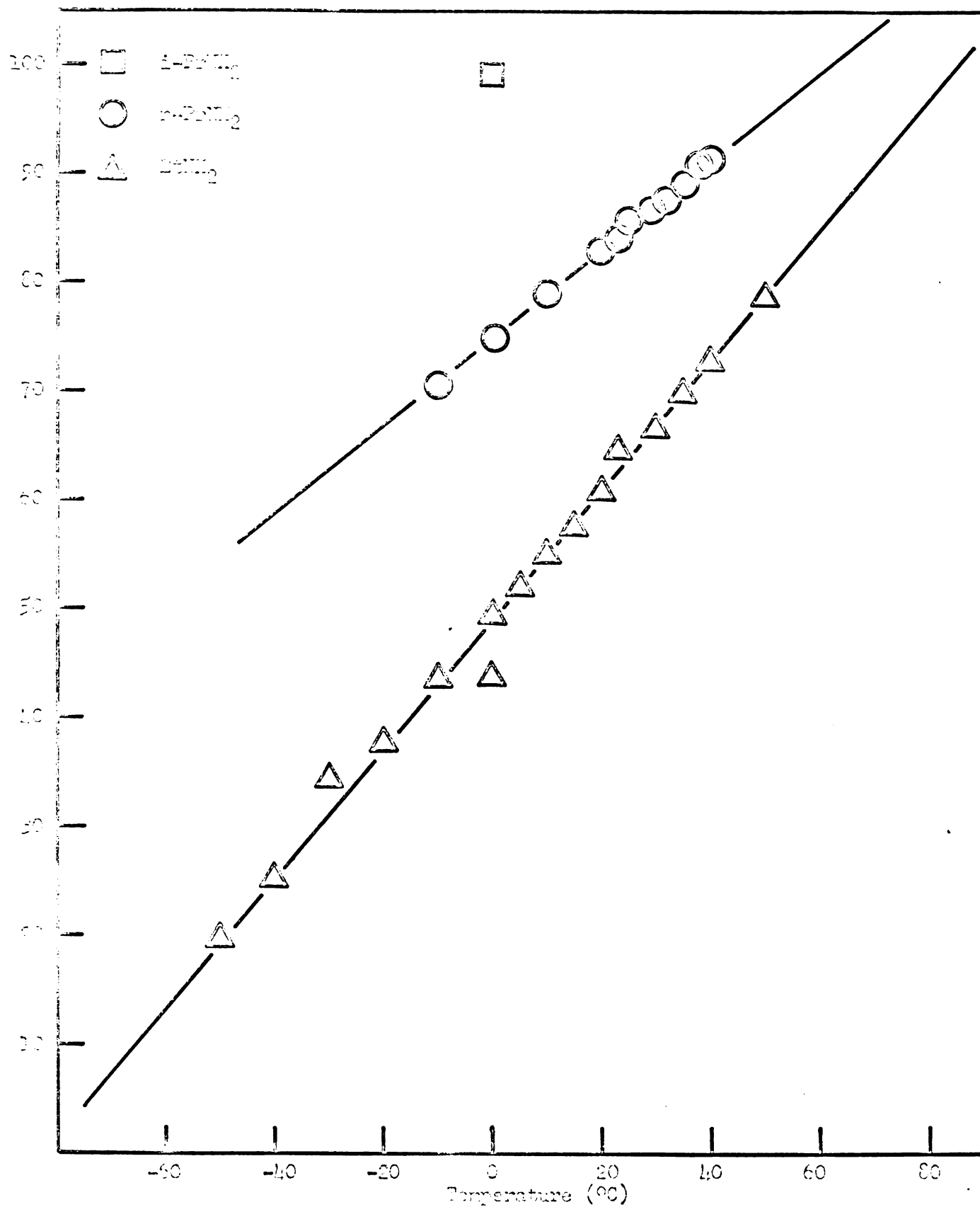


Figure 12d. Hyperfine splitting for some rubidium (⁸⁵Rb) solutions as a function of solvent and temperature.

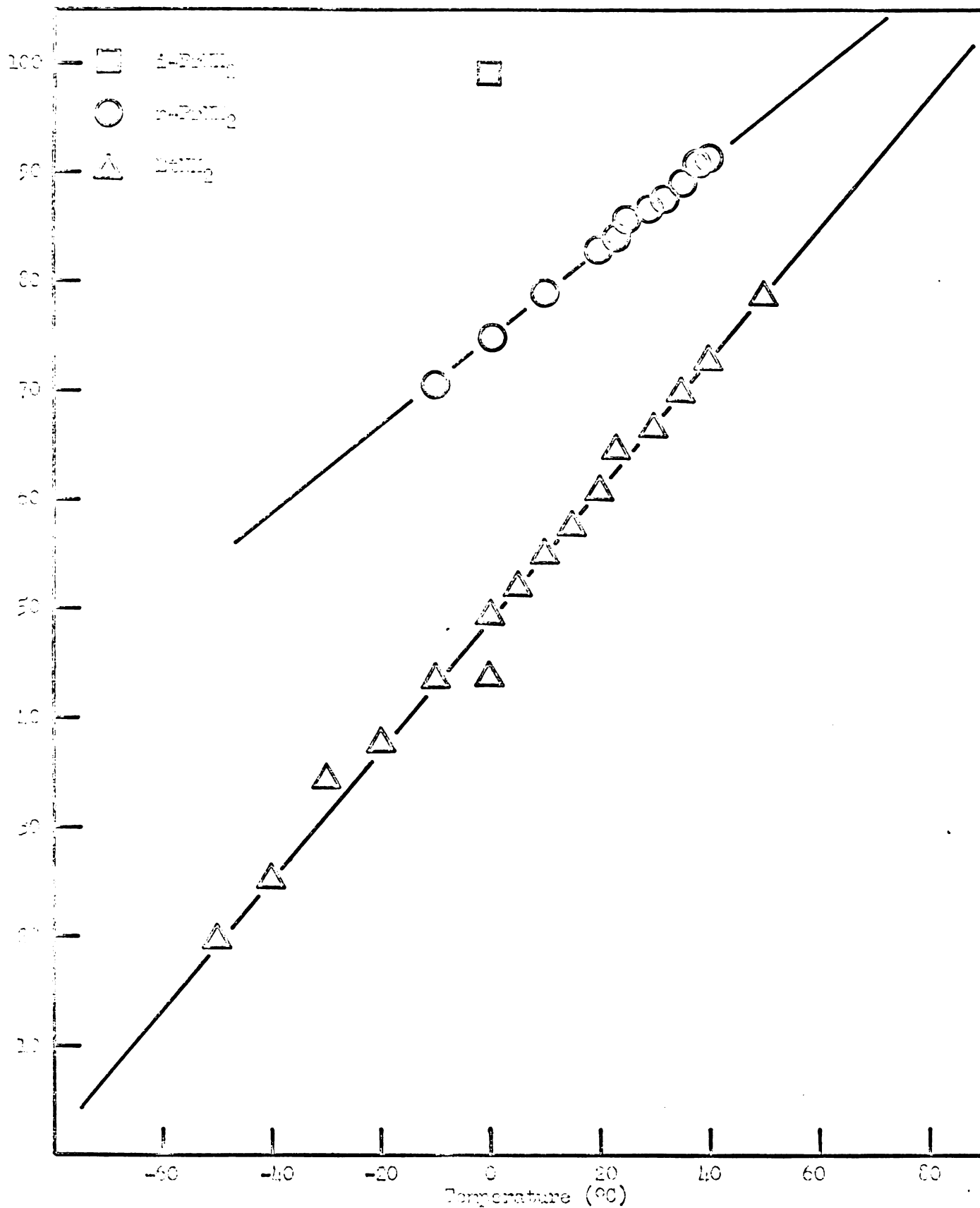


Figure 12d. Hyperfine splitting for some rubidium (^{85}Rb) solutions as a function of solvent and temperature.

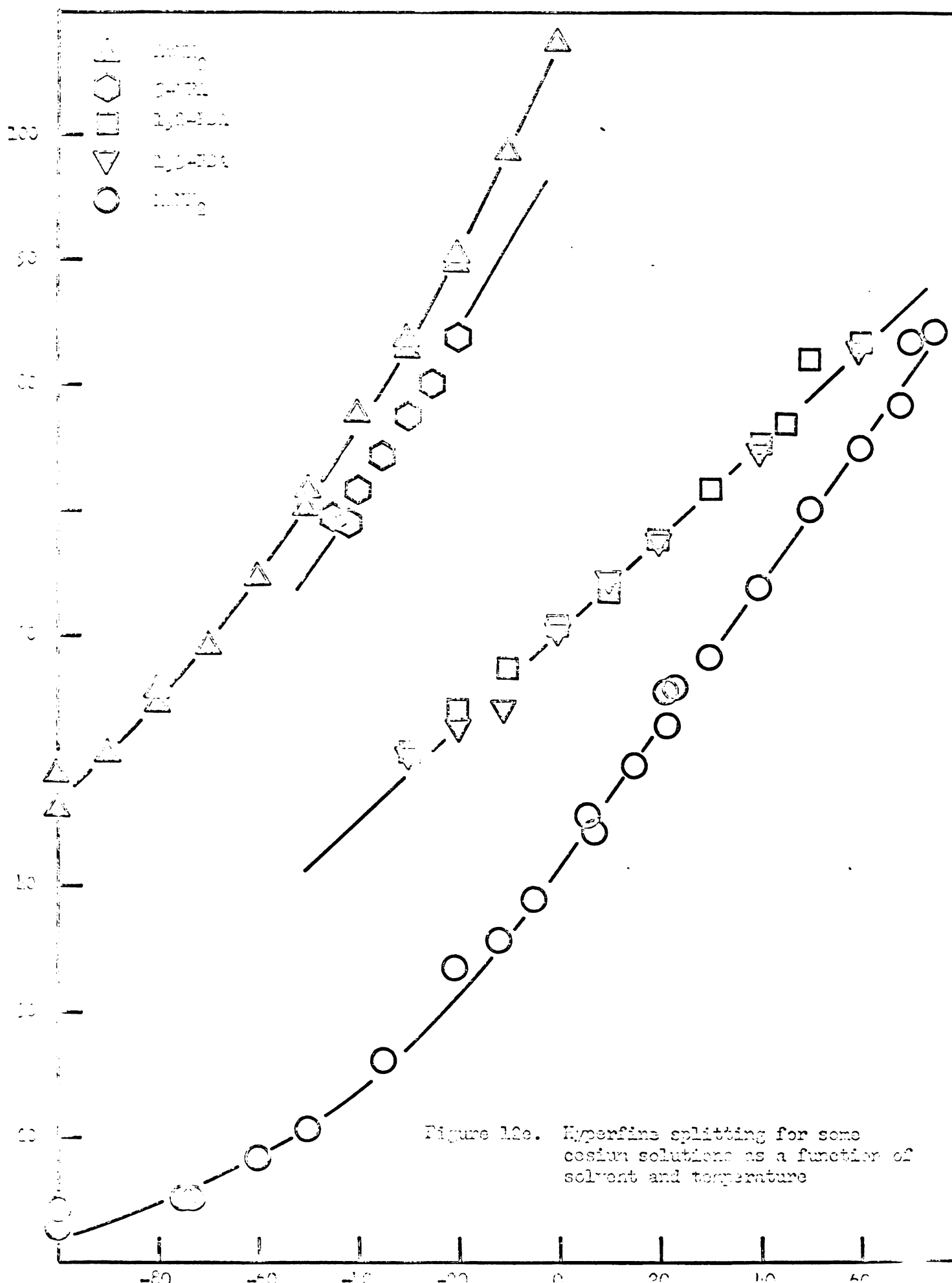


Figure 12e. Hyperfine splitting for some cesium solutions as a function of solvent and temperature

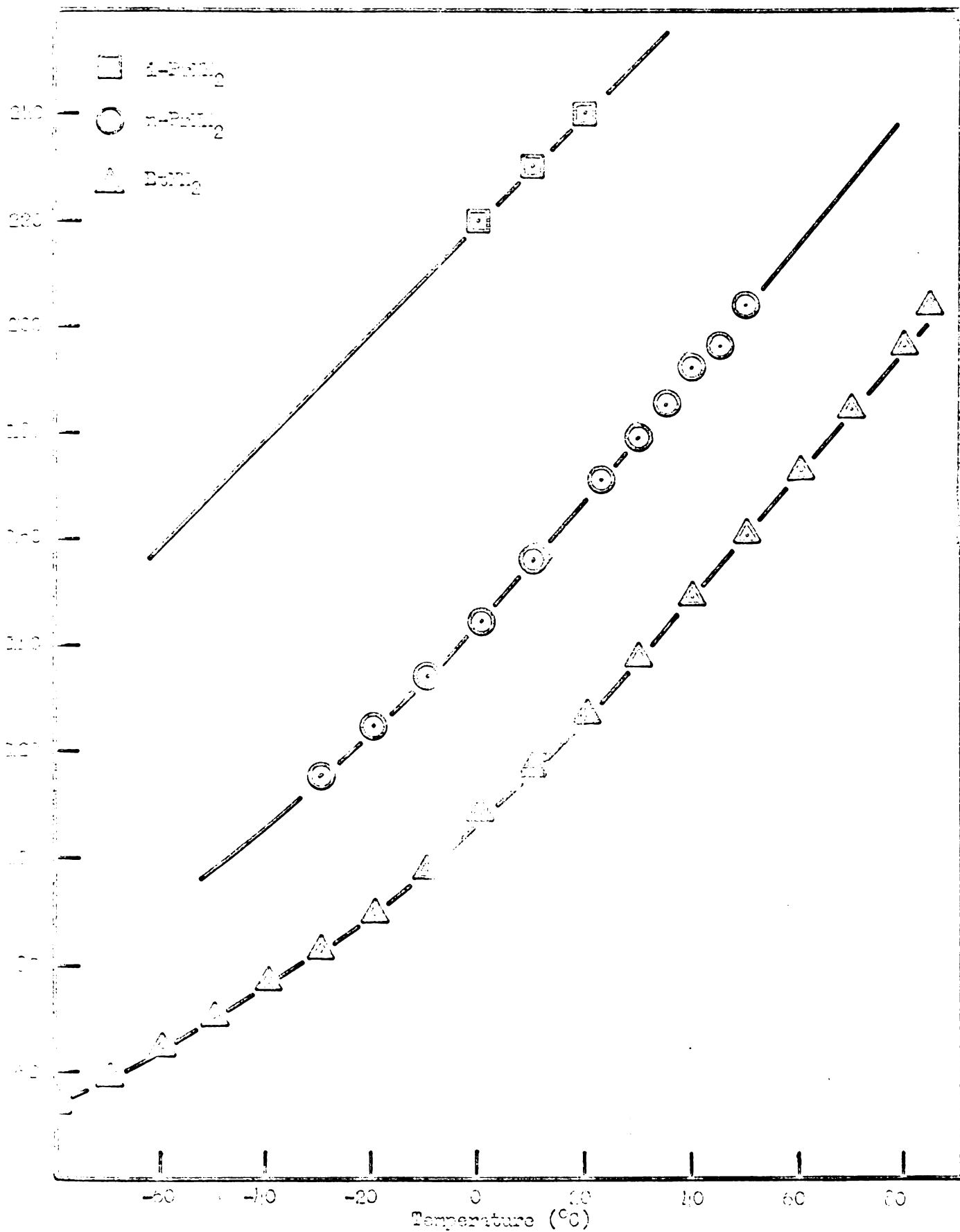


Figure 12f. Hyperfine splitting for some cesium solutions as a function of solvent and temperature.

the functional dependence of A_M upon temperature is not always the same. However, in no instance has the hyperfine interaction been observed to increase with decreasing temperature.

As can be observed from Table VII and Fig. 13, the effect of mixing two amines or of mixing ammonia with an amine is to yield a value of A_M intermediate between the values for the metal dissolved in the pure solvents. However, the temperature dependence of A_M for the mixed solvent may or may not be the same as for the pure solvents as can be seen from Fig. 14.

The g -value of the monomeric species as can be noted from Table IX appears to be nearly independent of the solvent used but appears to be a strong function of the alkali metal investigated.

The temperature dependence of the g -value also varied from metal to metal as can be seen from Fig. 15 and Table X. For solutions of potassium in the amines, g_M is nearly independent of temperature while the g -value for rubidium and cesium solutions decreases markedly with increasing temperature over the range from -100°C to room temperature. The scatter of the data prevents the establishment of a definite pattern for rubidium and cesium solutions above room temperature.

The g -value of the monomeric species is independent of metal concentration and is only slightly affected by the addition of ammonia or a second amine to the solution under investigation.

The spin concentration of the monomeric species in saturated metal-amine solutions as a function of metal and solvent used is given in Table XI. The concentration of the monomeric species is observed to decrease as the temperature is decreased. The relative magnitude of this decrease is similar to that reported in Ref. 42.

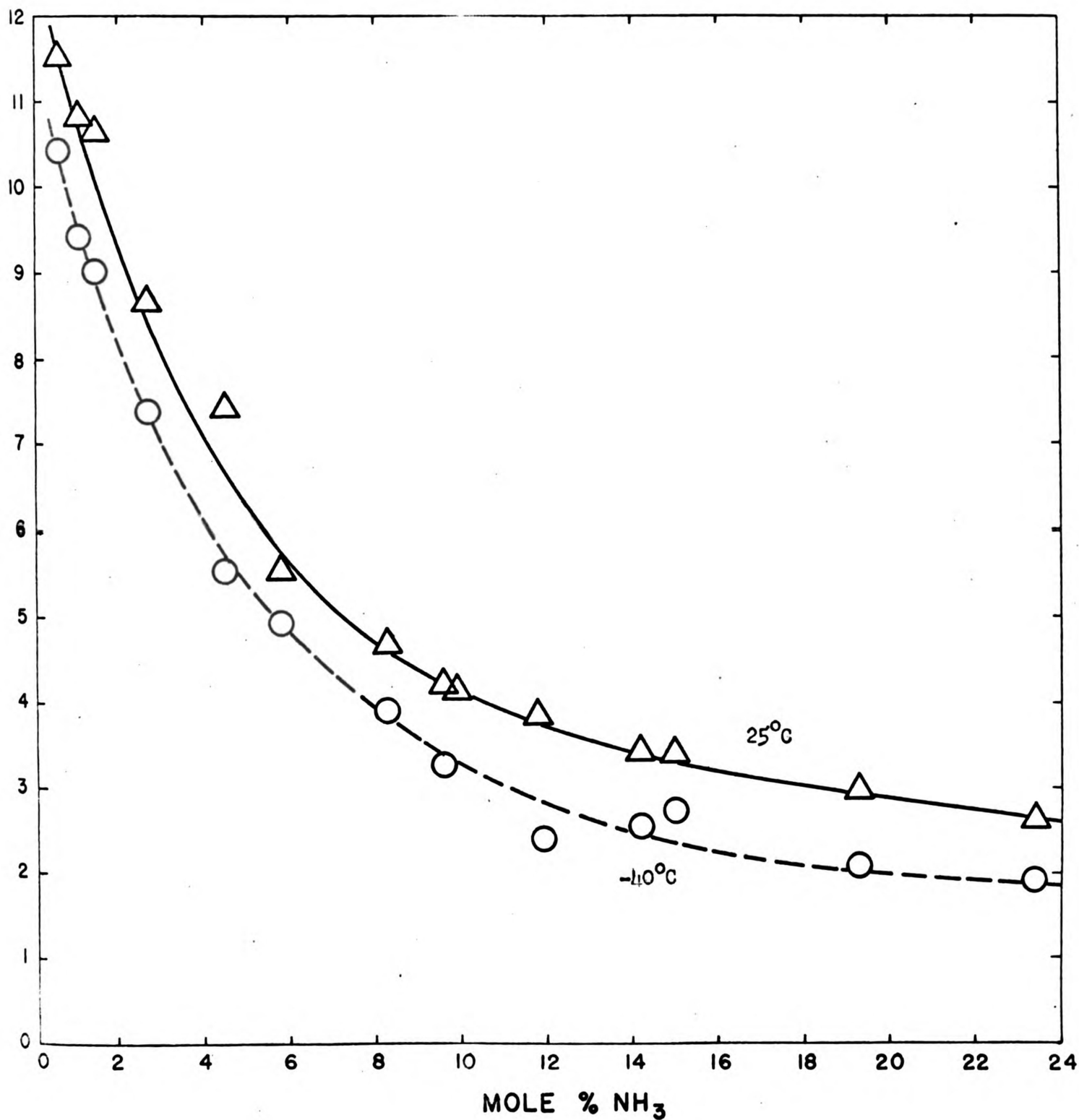


Figure 13a. The hyperfine splitting, A_M , of the monomeric species as a function of ammonia concentration for some potassium-ethylamine solutions.

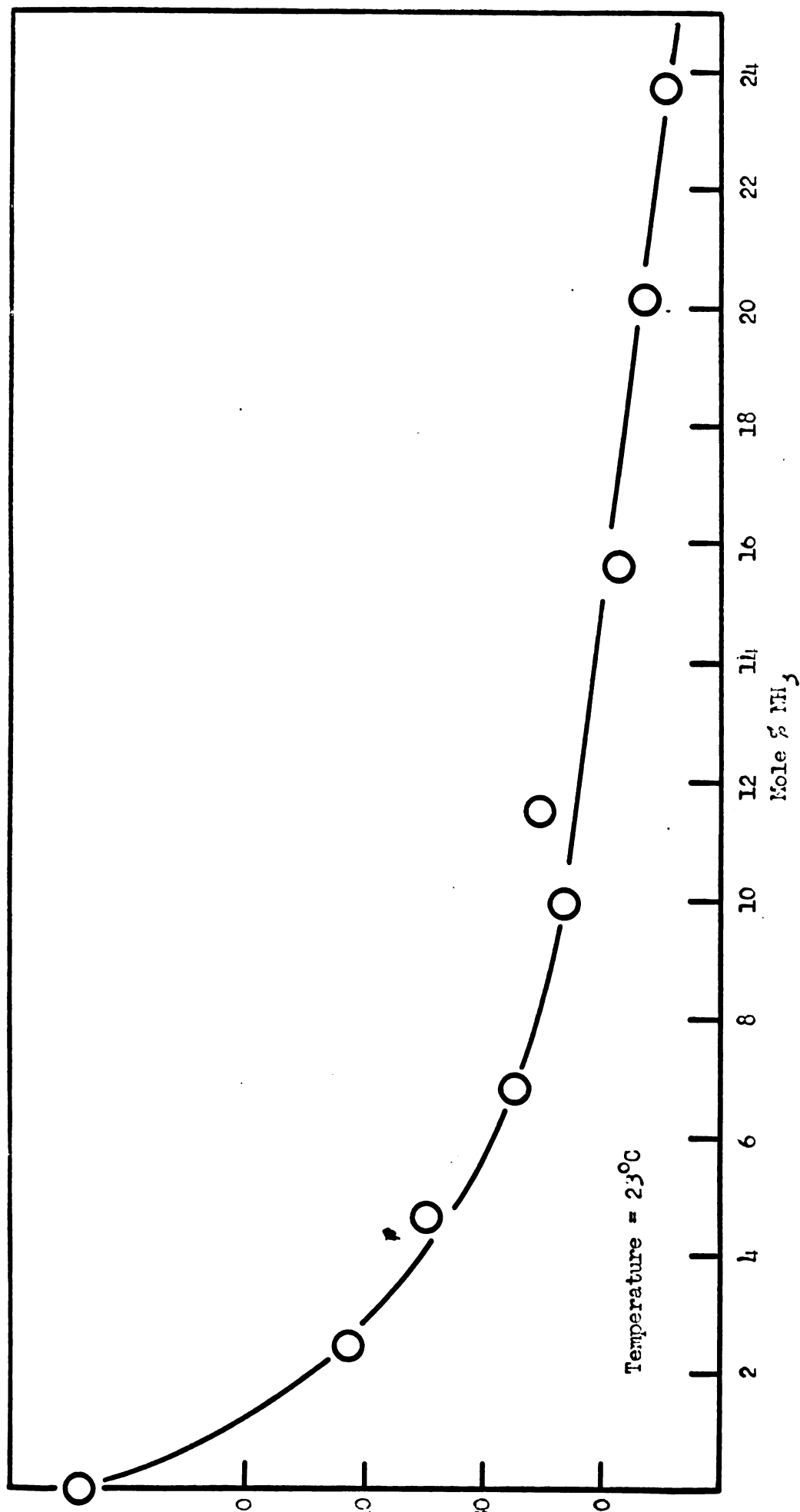


Figure 13b. The hyperfine splitting, A_M , of the monomeric species as a function of ammonia concentration for some rubidium (^{85}Rb) solutions.

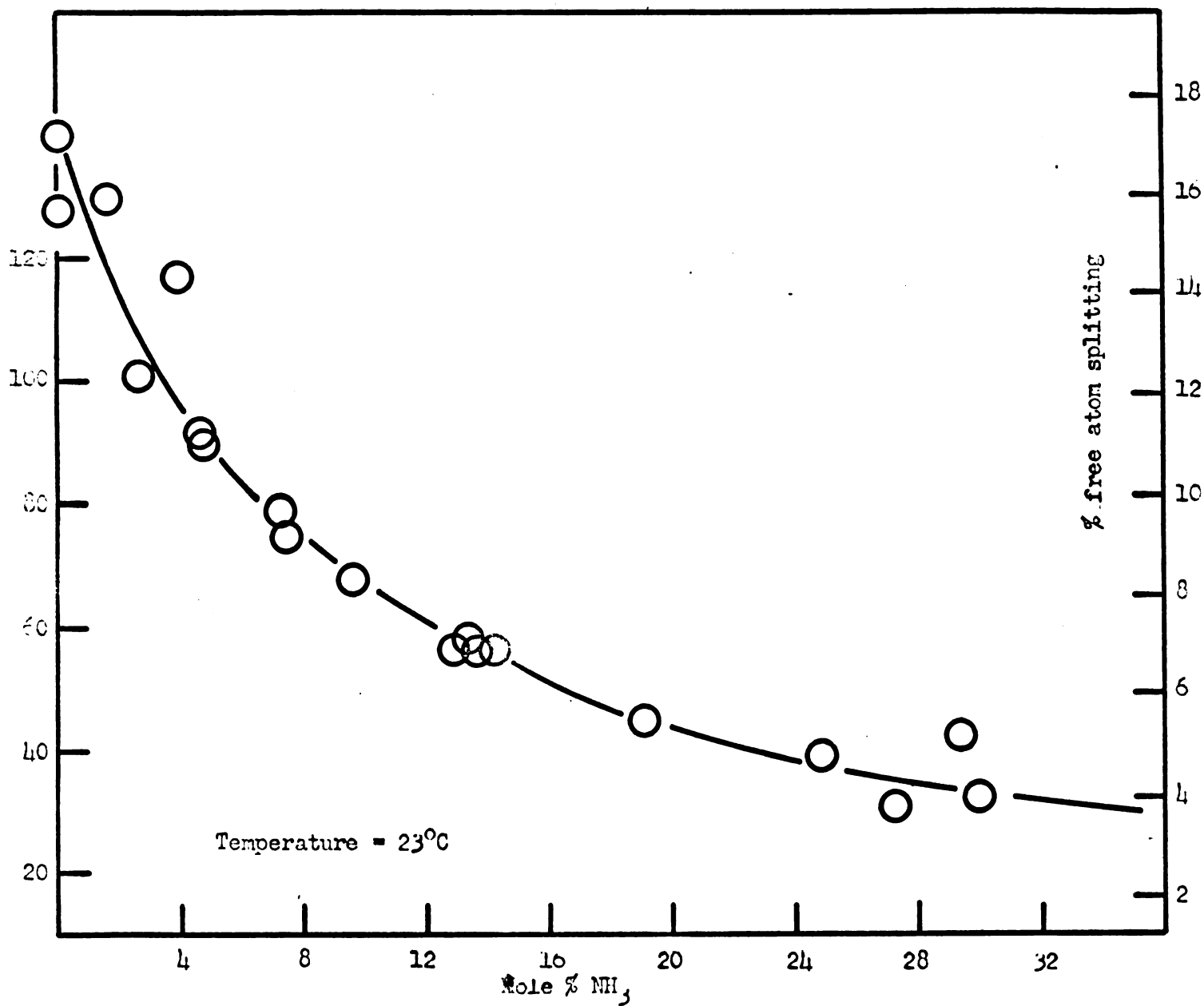


Figure 13c. The hyperfine splitting, A_M , of the monomeric species as a function of ammonia concentration for some cesium-ethylamine solutions.

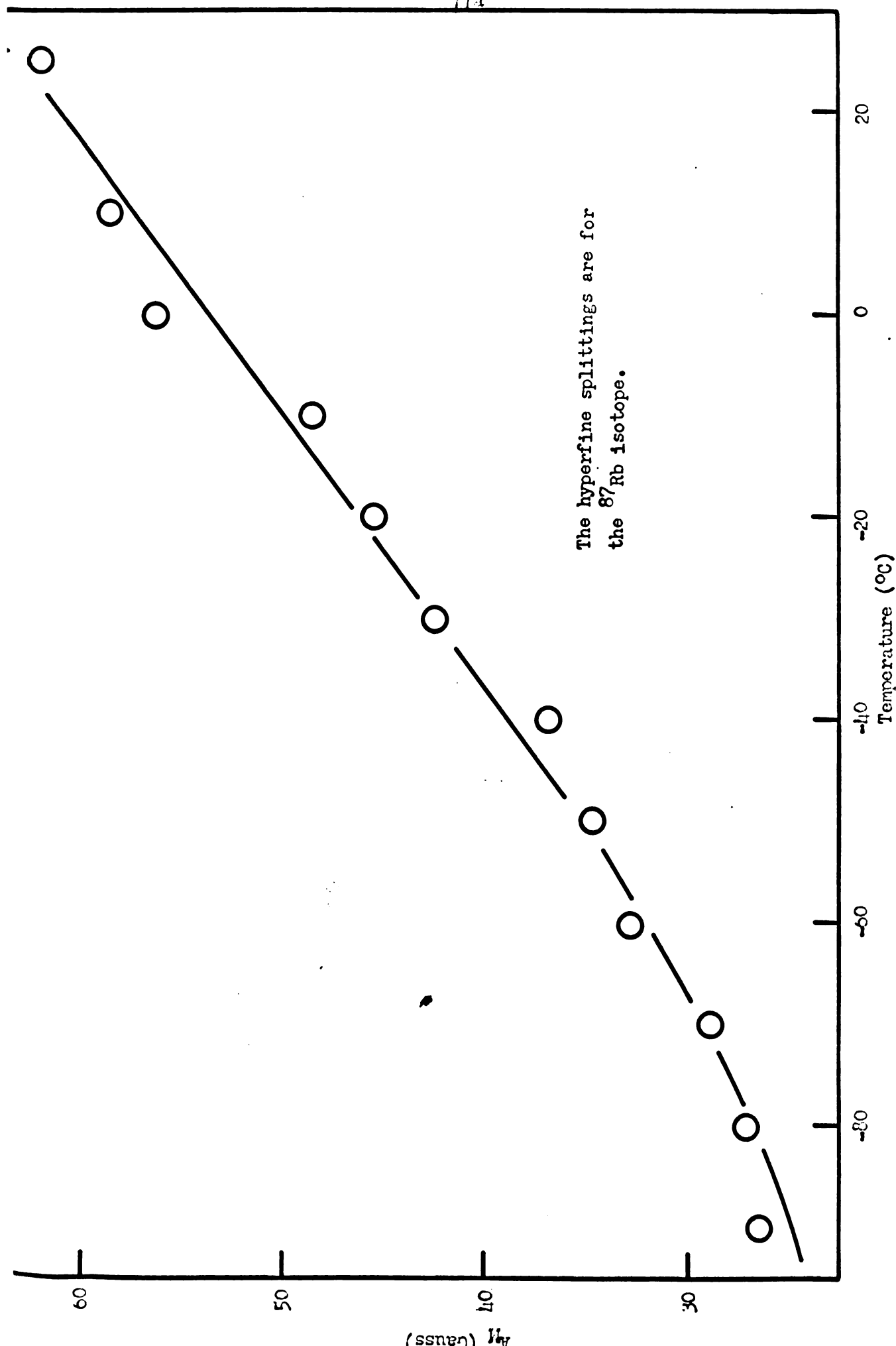


Figure 14a. The temperature dependence of A_{hf} for a solution of rubidium in an ethylamine-ammonia mixture containing 11.5 mole % NH_3 .

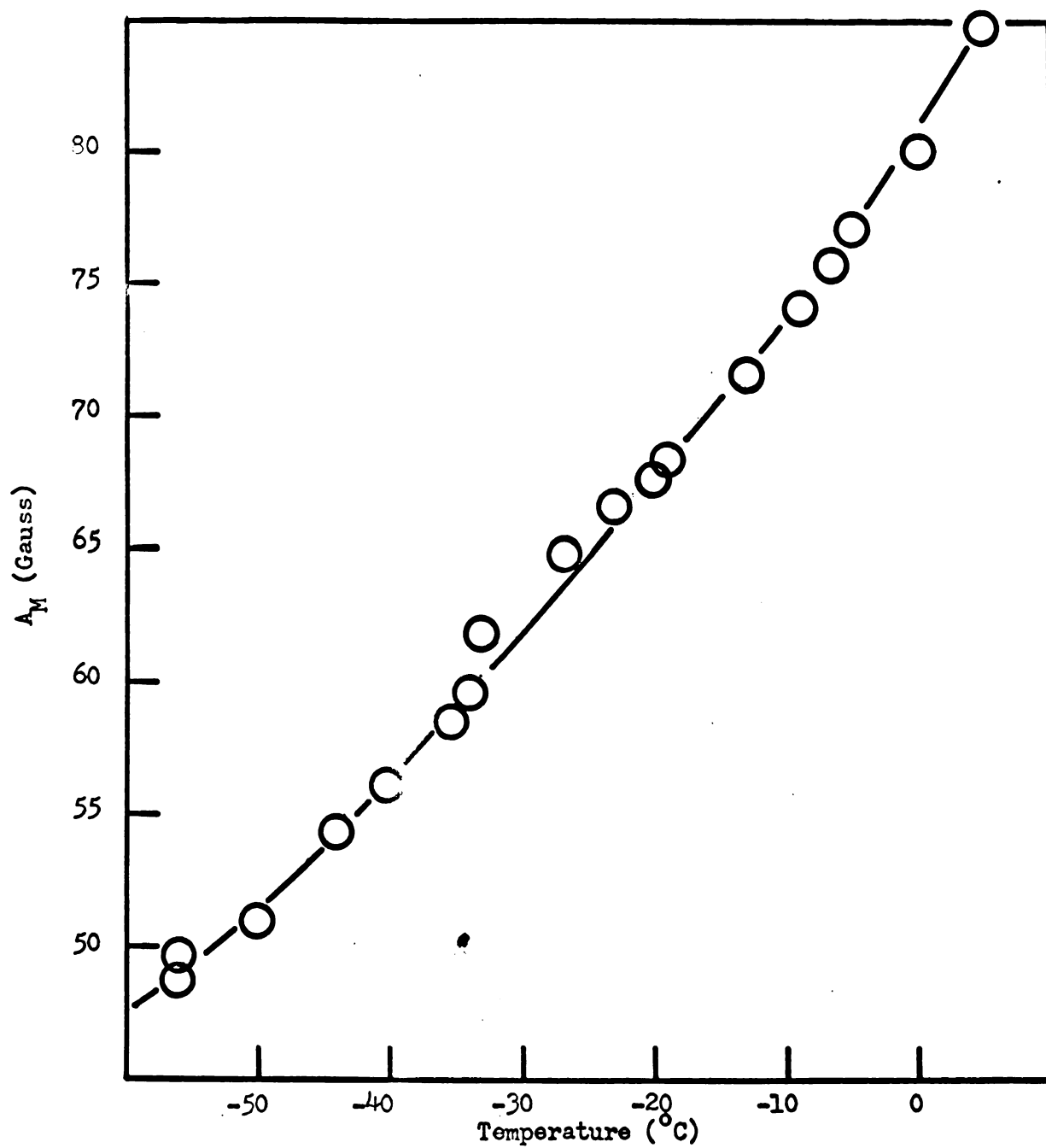


Figure 14b. The temperature dependence of A_M for a solution of cesium in an ethylamine-ammonia mixture containing 3.6 mole % NH_3 .

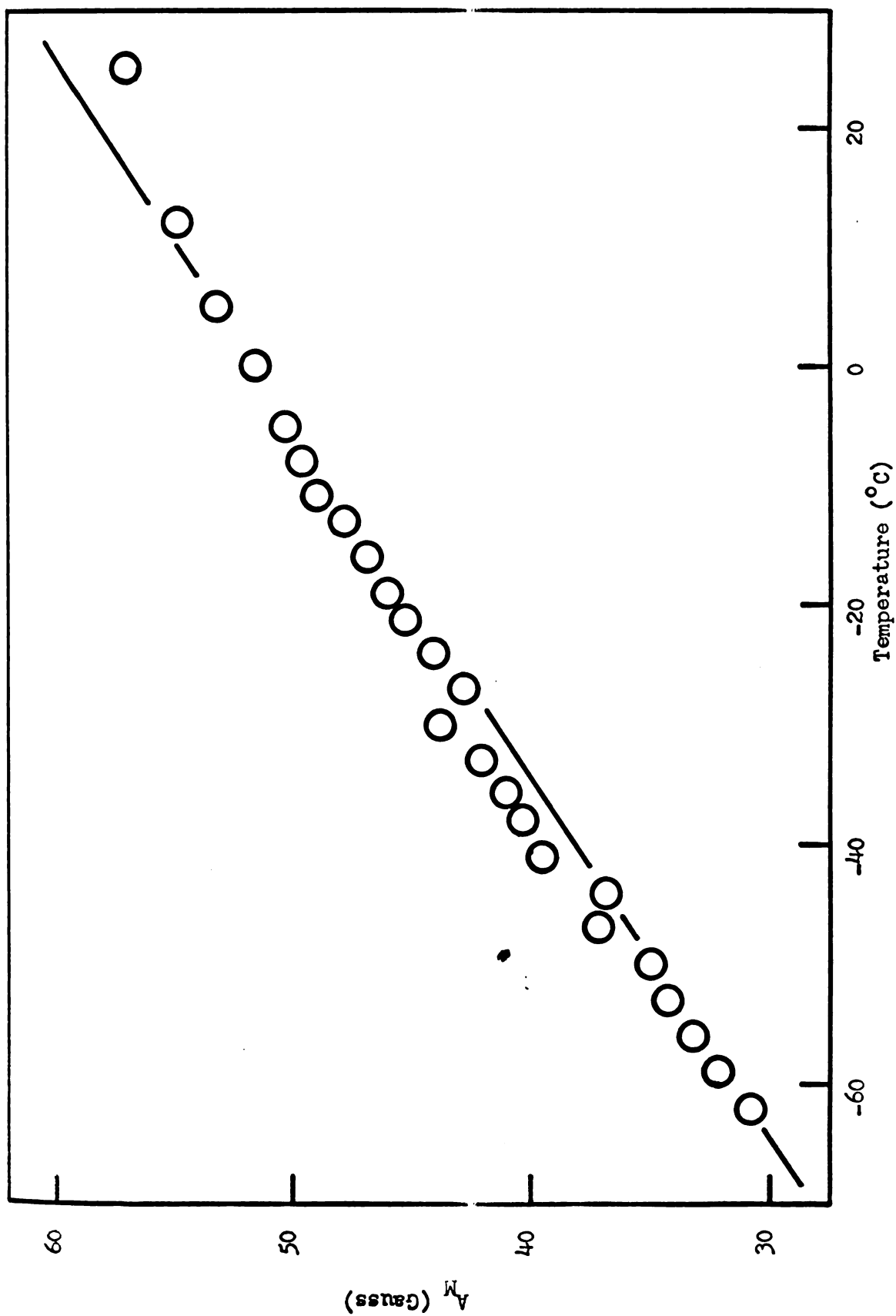


Figure 14c. The temperature dependence of A_M for a solution of cesium in an ethylamine-ammonia mixture containing 14.3 mole % NH_3 .

TABLE IX. The g -value, g_{M^+} of the Monomeric Species as a Function of Alkali Metal and Solvent for a Number of Metal-Amine Solutions.

Solvent	Metal			
	^{23}Na	^{39}K	^{85}Rb	^{133}Cs
MeNH_2			1.99986 $\pm$ 0.0005 (23°C)	1.99481 $\pm$ 0.0007 (23°C)
EtNH_2		2.00140 $\pm$ 0.0002 (0°C)	1.99982 $\pm$ 0.0002 (23°C)	1.99484 $\pm$ 0.0002 (23°C)
$\text{EtNH}_2 /$ MeNH_2	2.00149 $\pm$ 0.0002 (23°C)			
$n\text{-PrNH}_2$		2.0015 $\pm$ 0.0002 (23°C)	1.99979 $\pm$ 0.0005 (23°C)	1.99479 $\pm$ 0.0007 (23°C)
$i\text{-PrNH}_2$		2.0013 $\pm$ 0.0002 (23°C)	1.9998 $\pm$ 0.0006 (0°C)	1.9946 $\pm$ 0.0008 (20°C)
3-HPA		2.0013 $\pm$ 0.0005 (-16°C)		1.997 $\pm$ 0.002 (-40°C)
1,2-PDA				1.996 $\pm$ 0.001 (20°C)
1,3-PDA				1.996 $\pm$ 0.001 (20°C)

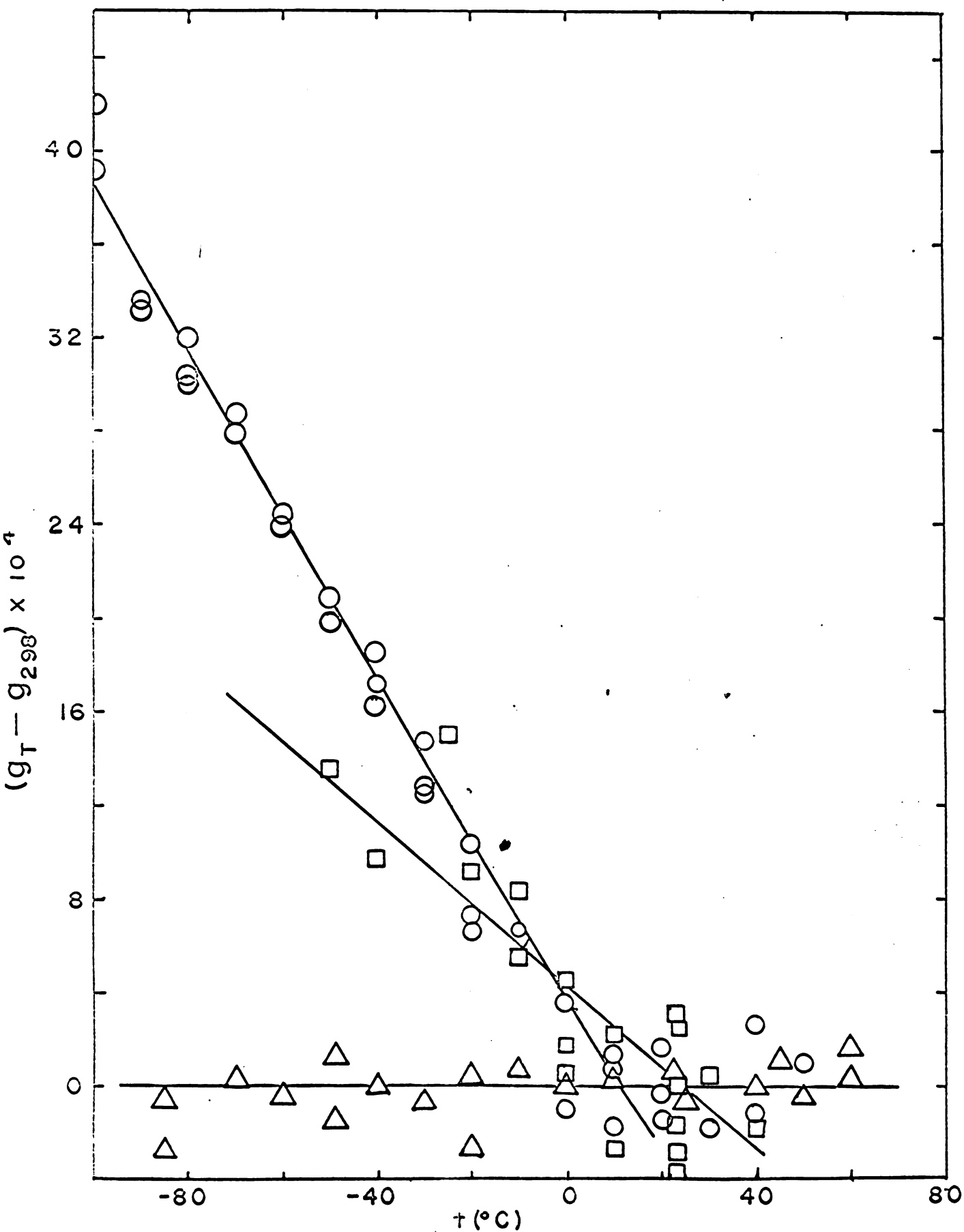


Figure 15. Variation of g-value with temperature for ^{39}K , Δ ; ^{85}Rb , $\square$; and ^{133}Cs , $\circ$ in ethyl alcohol.

TABLE I. The g-value, g_{H} , of the Monomeric species as a Function of Temperature.

<u>Ethylamine</u>			
Potassium		Rubidium	
<u>T(°C)</u>	<u>g-value</u>	<u>T(°C)</u>	<u>g-value</u>
60	2.00157	50	2.00002
60	2.00144	45	1.99986
50	2.00136	40	2.00000
40	2.00140	30	1.99989
23	2.00146	23	1.99982
0	2.00140	0	1.99874
-20	2.00148	0	1.99685
-20	2.00112	-20	1.99902
-40	2.00140	-30	1.99921
-60	2.00136	-30	1.99935
-70	2.00142	-40	2.00080
-75	2.00165	-40	2.00082

<u>Cesium</u>			
<u>T(°C)</u>	<u>g-value</u>	<u>T(°C)</u>	<u>g-value</u>
50	1.99495	20	1.99470
40	1.99511	20	1.99502
40	1.99473	20	1.99481
30	1.99477	10	1.99490
30	1.99466	10	1.99467

TABLE I. Continued.

Cesium			
<u>T(°C)</u>	<u>g-value</u>	<u>T(°C)</u>	<u>g-value</u>
10	1.99497	-50	1.99683
0	1.99474	-60	1.99725
0	1.99521	-60	1.99729
-10	1.99551	-60	1.99721
-20	1.99583	-70	1.99773
-20	1.99553	-70	1.99764
-20	1.99551	-70	1.99767
-30	1.99612	-80	1.99805
-30	1.99609	-80	1.99790
-30	1.99632	-80	1.99784
-40	1.99657	-90	1.99821
-40	1.99669	-90	1.99816
-40	1.99647	-100	1.99878
-50	1.99634	-100	1.99905
-50	1.99692		

TABLE XI. The Spin Concentration (at 23°C) of the Monomeric Species as a Function of Metal and Solvent for a Number of Saturated Metal-Amine Solutions^a.

Solvent	Spin Concentration			
	Sodium	Potassium	Rubidium	Cesium
MeNH ₂			$1 \times 10^{-3}M$	$8 \times 10^{-3}M$
EtNH ₂		$1 \times 10^{-6}M$	$6 \times 10^{-5}M$	$5 \times 10^{-4}M$
EtNH ₂ / MeNH ₂	$2 \times 10^{-6}M$			
n-PrNH ₂		$9 \times 10^{-7}M$	$8 \times 10^{-6}M$	$2 \times 10^{-4}M$
1-PrNH ₂		$7 \times 10^{-7}M$	$5 \times 10^{-6}M$	$1 \times 10^{-4}M$
3-MPA		$1 \times 10^{-7}M$	$5 \times 10^{-7}M$	$5 \times 10^{-6}M$
1,2-PDA		$6 \times 10^{-5}M$	$1 \times 10^{-5}M$	$1 \times 10^{-3}M$
1,3-PDA		$9 \times 10^{-5}M$	$4 \times 10^{-5}M$	$2 \times 10^{-3}M$

^aThe concentration of the saturated solution appears to be sensitive to the method of solvent purification used. This may cause as much as a ten-fold variation in the measured spin concentration.

2. The solvated electron. To distinguish this absorption from the broad extra absorption detected by computer analysis we shall mean by the electron absorption the line located at $g = 2.00190 \pm 0.0002$ and of linewidth comparable to that of the hyperfine pattern. The spin concentration of this species and the ratio of its concentration to that of the monomeric species varies from solvent to solvent and from metal to metal as can be seen from Table XII. In general one can say that this species is favored by polarizable or ionizing solvents such as methylamine or the diamines. The temperature dependence of the spin concentration of the solvated electron varies markedly from one metal solution to the next.

In solutions of potassium in the amines the concentration of the solvated electron is observed to decrease slightly with decreasing temperature. On the other hand, the absorption due to the solvated electron is observed to increase with decreasing temperature for solutions of rubidium and cesium in the amines. The behavior of the extra line in solution of lithium in ethylamine and ethylamine-ammonia mixtures will be discussed later.

In general it has been found that the electron absorption is favored by conditions indicative of decomposition, e.g., standing at room temperature or above for prolonged periods of time. This could however be because equilibrium is attained very slowly in these solutions.

The addition of ammonia has the effect of suppressing the solvated electron absorption relative to the monomer absorption.

The g -value of the solvated electron is independent of metal and solvent used, metal concentration, and temperature as can be seen from Table XII.

TABLE XII. The Spin Concentration (at 23°C) and g-value of the Solvated Electron for a Number of Metal-Amine Systems.

Solvent	g_0			
	Sodium	Potassium	Rubidium	Cesium
MeNH_2			2.0018 ± 0.0002 $1 \times 10^{-5} \text{M}$	2.0018 ± 0.0002 $8 \times 10^{-3} \text{M}$
EtNH_2		2.0019 ± 0.0002 $5 \times 10^{-7} \text{M}$	2.0019 ± 0.0002 $5 \times 10^{-7} \text{M}$	2.0019 ± 0.0002 $1 \times 10^{-6} \text{M}$
$\text{EtNH}_2 /$ MeNH_2	2.0019 ± 0.0002 $2 \times 10^{-6} \text{M}$			
3-KPA		2.0019 ± 0.0002 $1 \times 10^{-7} \text{M}$	$5 \times 10^{-7} \text{M}$	2.0019 ± 0.0002 $1 \times 10^{-6} \text{M}$
1,2-PDA		$1 \times 10^{-6} \text{M}$	$5 \times 10^{-5} \text{M}$	2.0019 ± 0.0002 $1 \times 10^{-3} \text{M}$
1,3-PDA		$1 \times 10^{-6} \text{M}$	$7 \times 10^{-5} \text{M}$	2.0019 ± 0.0002 $2 \times 10^{-3} \text{M}$

3. Extra absorption detected by computer analysis. Computer analysis of potassium-ethylamine-ammonia solutions showed the building in of an additional broad absorption at higher ammonia concentrations (42). The results of this analysis on a typical spectrum are shown in Fig. 16 and the parameters of the extra absorption for potassium-ethylamine-ammonia solution are shown in Table XIII. As can also be seen from Fig. 16, this absorption is also present in other amine-ammonia solutions. At the time of this writing computer analysis had not been performed upon these solutions.

4. Lithium-ethylamine and lithium-ethylamine-ammonia solutions. Several aspects of the behavior of lithium-ethylamine and ethylamine-ammonia solutions are unique; hence, these solutions will be discussed apart from other metal-amine solutions.

Lithium dissolves in ethylamine to give highly concentrated solutions which can not be studied because of their deleterious effect on the cavity Q. Resonances have been observed from diluted samples of these solutions.

The range of metal and solvent compositions which we studied are summarized in Table XIV. The qualitative nature of these spectra can be seen in Fig. 17.

At room temperature the resonance of a moderately dilute solution of lithium in pure ethylamine is a single line at $g = 2.0019 \pm 0.0002$ of width 0.3 gauss. The width of this line increases monotonically with decreasing temperature until at -80°C it measures 2.5 G. A precipitous drop in the line width to 0.1 G and a ten-fold decrease in the spin concentration occurs as the solution freezes just below -80°C .

TABLE XIII, EPR parameters of hfs pattern and extra absorption as obtained by computer analysis

<u>Sample K-12</u> <u>5.8 Mole percent ammonia</u>				
Temp.	A_F	S_F (hfs)	S_F (extra absorption)	$n_{\text{extra}}/n_{\text{hfs}}$
(°C)	(gauss)	(gauss)	(gauss)	
-38	5.08 ^b	1.25 ^b		
-72	4.24 ^b	1.17 ^b		
<u>Sample K-11</u> <u>9.6 Mole percent ammonia</u>				
-7	3.76 ^b	2.11 ^b	12.1 ^b	2.31 ^b
-15	3.66	2.18	10.3	1.28
	3.66 ^b	2.18 ^b	10.2 ^b	1.27 ^b
-41	3.24	1.76	12.7	4.94
	3.23 ^b	1.84 ^b	11.8 ^b	3.35 ^b
<u>Sample K-25</u> <u>9.9 Mole percent ammonia</u>				
-8	3.52	2.63	9.27	1.74
	3.52 ^b	2.64 ^b	2.24 ^b	1.70 ^b
-35	3.39	2.54	8.83	1.78
-68	2.97	2.24	7.87	1.88
	2.97 ^b	2.24 ^b	7.85 ^b	1.73 ^b
<u>Sample K-10</u> <u>11.8 Mole percent ammonia</u>				
-12	2.74	2.31	6.83	4.81
-42	2.36	1.97	5.95	6.45
-75	1.89	1.48	4.69	7.78

TABLE XIII. (continued)

<u>Sample K-9</u>		<u>14.2 Mole percent ammonia</u>		
Temp (°C)	A_F (gauss)	S_F (hfs) (gauss)	S_F (extra absorption) (gauss)	n_{extra}/n_{hfs}
-10	2.94	2.50	7.45	4.77
-41	2.54	2.16	6.51	4.31
-69	2.21	1.77	5.68	3.19

^aSpectra were fit by the superposition of two absorption patterns. One of these was the Gaussian hyperfine pattern arising from electronic interaction with the ³⁹K and ⁴¹K nuclei. The other was a single absorption of Gaussian shape. The routine alternately adjusted the parameters for both of these patterns. Except as noted, initial adjustment was made on the single absorption.

^bThe hyperfine pattern was adjusted first.

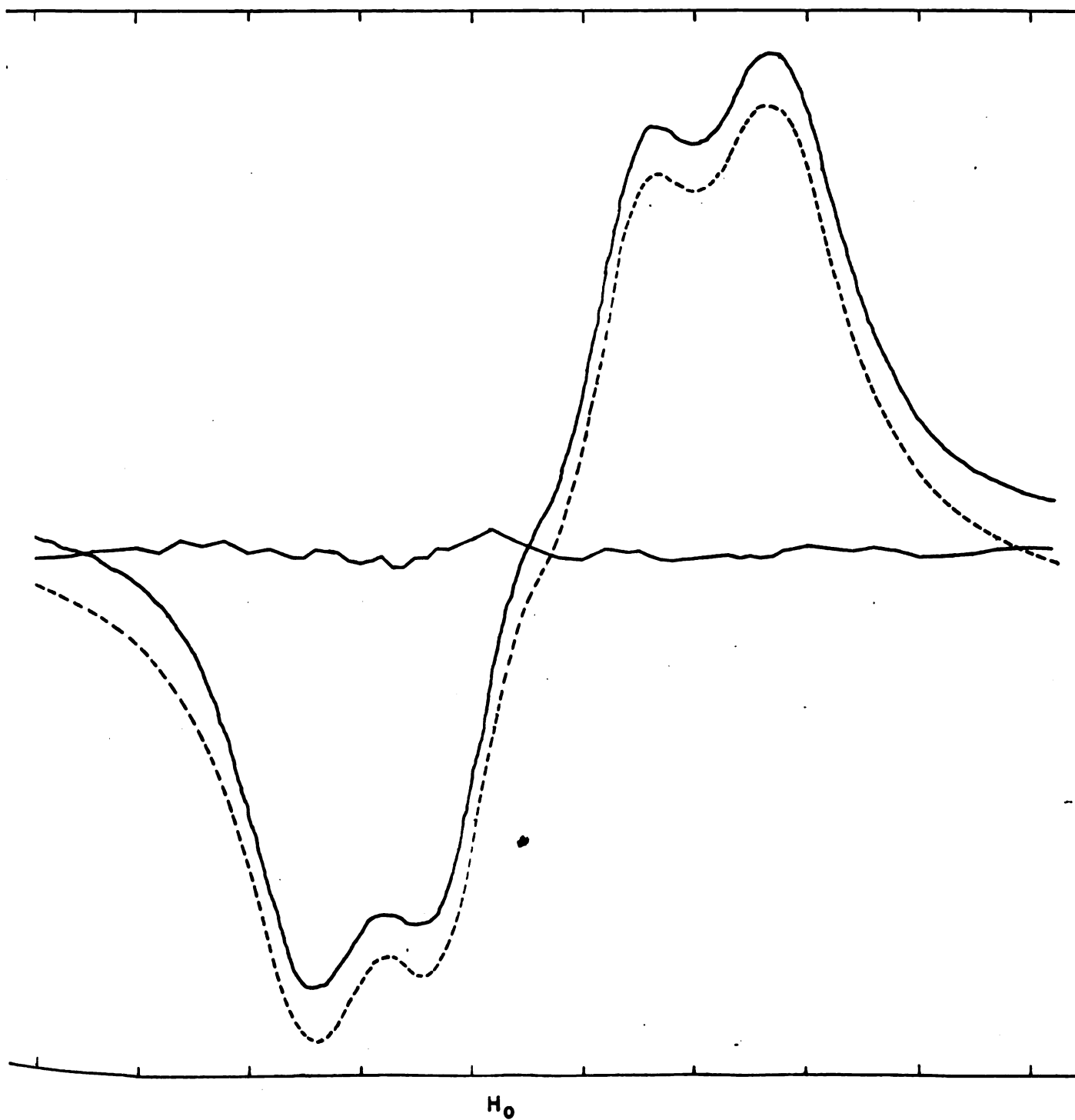


Figure 16. A potassium-ethylamine-ammonia solution showing the presence of the extra absorption

TABLE XIV. Summary of EPR Results for Lithium in Ethylamine-Ammonia Mixtures.

Sample	Mole Percent Ammonia	Estimated Metal Concentration Moles/liter	EPR Spectra
1	0.0	10^{-3} to 10^{-4}	Single line
2	0.5	10^{-5} to 10^{-6}	Nine line hfs + single line
3	1.3	10^{-4} to 10^{-5}	Nine line hfs + single line
4	2.1	10^{-3} to 10^{-4}	Single line
5	4.3	10^{-4} to 10^{-5}	Nine line hfs + single line
6	5.2	10^{-5} to 10^{-6}	Nine line hfs

LITHIUM

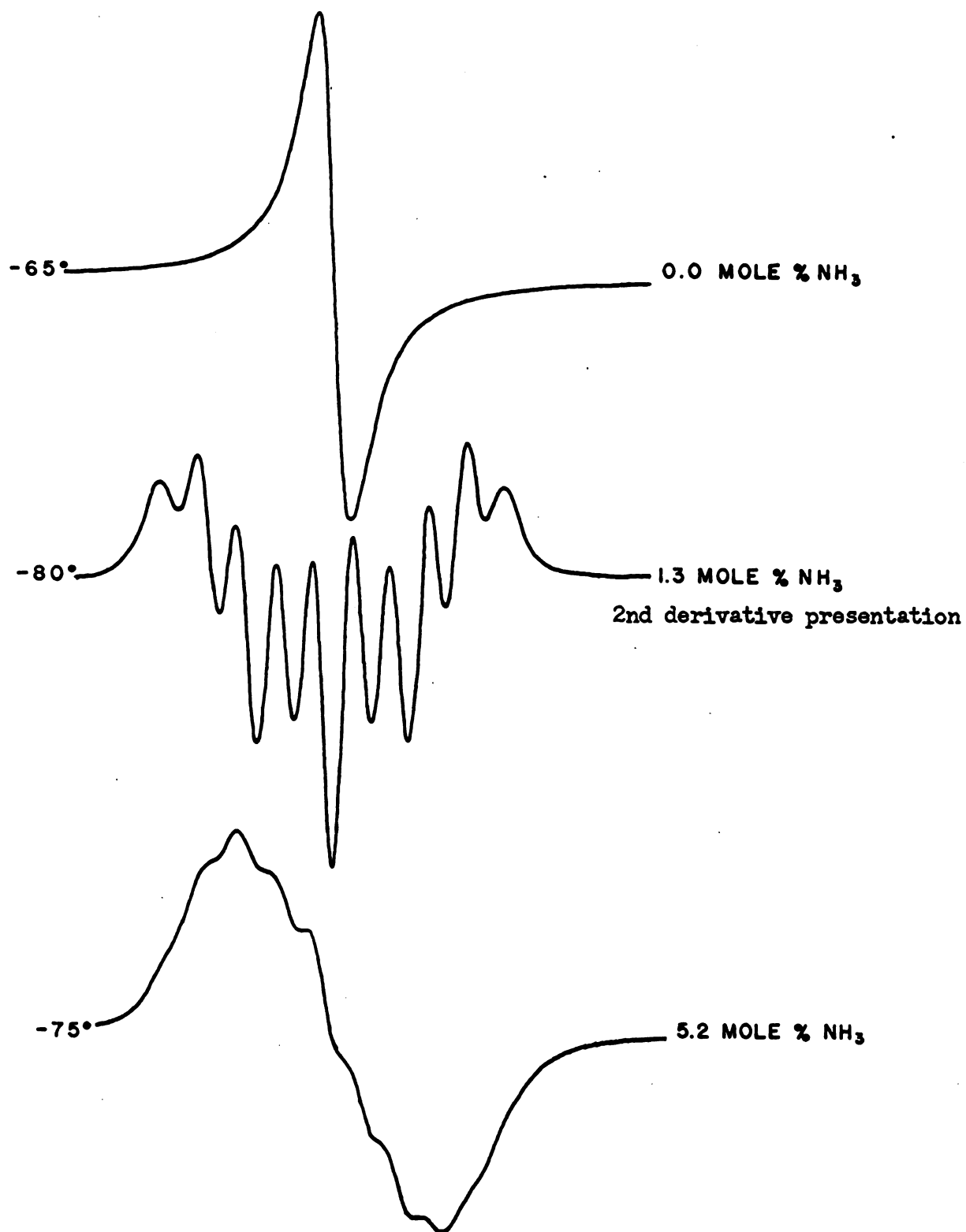


Figure 17. EPR spectra of lithium in some ethylamine-ammonia mixtures.

Below -90°C the line width increases as the temperature decreases; the spin concentration decreases over this same region.

In a more dilute solution of lithium in an ethylamine-ammonia mixture the author observed a spectrum consisting of nine lines spaced at intervals of 2.45 ± 0.1 G. The relative intensity of the eight outer lines indicate that the hyperfine splitting arises from interaction of a paramagnetic electron with four equivalent nitrogens. The central line is much more prominent than any of the others indicating the presence of an extra absorption. Careful analysis showed the g -value of these two patterns to be the same; namely, $g_{\text{H}} = g_{\text{e}} = 2.0019$. The g -values of the two species and the hyperfine interaction, A_{H} , are independent of temperature over a range from -50° to -98°C . At -80°C the line width of the hyperfine components is observed to be 1.84 G. The line width of the extra line appears to be slightly less than this. Both increasing temperature and increasing concentration have the effect of broadening the individual hyperfine lines and the extra line, the line width of the extra line being more sensitive to changes in these parameters. The addition of ammonia appears to result in a slight increase in the line width of these two species. Increasing the concentration of metal also has the effect of reducing the amplitude of the central line with respect to the hyperfine pattern. In the most dilute solutions the extra line was the predominant species. Upon freezing, the hyperfine pattern and extra line collapse to a single line ($S_{\text{F}} = 4.52$ G; $g = 2.0019$) at -98°C . Upon further cooling the line width increases (e.g., $S_{\text{F}} = 10.98$ G at -120°C) with decreasing temperature. Below -130°C it is clear that the spectrum consists of a single narrow absorption superimposed upon a broad absorption.

The broad absorption appears to consist of unresolved hyperfine splitting. The signal intensity decreases markedly at -98°C and continues to decrease as the temperature decreases. The low spin concentration made resolution below -150°C difficult. Upon warming, the single line reverts back to the hyperfine pattern and extra line at -85 to -87°C . Further warming results in smearing of the hyperfine pattern and extra line so that at -35°C only a single absorption with broad tails is observed. Above 0°C the line width of the absorption decreases very slightly. However it appears that unresolved hyperfine splitting may be present up to $+50^{\circ}\text{C}$.

The stability of our samples was much greater than that reported by other workers(43). The samples prepared by the author were stable for over a week. During this time they were stored at room temperature and were heated intermittently to temperatures as high as $+50^{\circ}\text{C}$.

5. Absorption of sodium in methylamine and the alkali metals in ethylenediamine. When only a single absorption is observed one is not justified in assigning this a priori to the monomer, solvated electron, or any other paramagnetic species. Thus we will group these spectra together until further evidence can be presented meriting their assignment to any given species. The g-values of several single absorptions are given in Table IV.

Solutions of sodium in methylamine give a weak signal (approximately 5×10^{-6} M) and display a g-value of 2.0017 ± 0.0002 and a line width of 1.45 G. The g-value is found to be independent of temperature. Above the melting point of the solution the linewidth increases with increasing temperature; moreover, below the melting point the linewidth was observed to decrease with decreasing temperature. There is however

TABLE IV. g-values of Solutions Exhibiting only a Single Line.

Solvent	Metal				
	Lithium	Sodium	Potassium	Rubidium	Cesium
NH_3	$2.001 \pm$	$2.0012 \pm$	$2.0012 \pm$	$2.0003 \pm$	
	0.001^a	0.0002^b	0.0002^b	0.0002^a	
	(23°C)	(23°C)	(23°C)	(23°C)	
MeNH_2	$2.0019 \pm$	$2.0017 \pm$	$2.0017 \pm$		
	0.0002^a	$0.0002^{a,c}$	$0.0002^{a,c}$		
	(23°C)	(23°C)	(23°C)		
EDA	$2.0021 \pm$	$2.0017 \pm$	$2.0018 \pm$	$2.0017 \pm$	$1.998 \pm$
	0.0002^a	0.0002^a	0.0002^a	0.0005^a	0.003^a
	(23°C)	(23°C)	(23°C)	(23°C)	(23°C)

^aReference 68.^bReference 6.^cThis work.

a discontinuity in the behavior of linewidth as a function of temperature at the melting point. As can be seen from Table XVI, the present data are in excellent agreement with those obtained previously by Vos (68).

The addition of ethylamine has the effect of broadening this line. At sufficiently high ethylamine concentrations, a composite pattern appears, consisting of a single narrow line superimposed upon what appears to be a four-line hyperfine pattern. The hyperfine splitting arising from the interaction of a single paramagnetic electron with a ^{23}Na nucleus is given in Table VII. The g-values of the hyperfine species and of the solvated electron are given in Tables IX and XII respectively. At room temperature the concentration of the monomeric species and the solvated electron were approximately the same.

6. Kinetics of decomposition as studied by EPR. With the exceptions of isopropylamine, n-butylamine, and 3-methoxy-n-propylamine the solutions of the alkali metals in amines prepared in this laboratory exhibited extremely good stability. Some of the solutions have been stable for as long as two years. The stability of the solutions appears to depend upon the metal. Lithium and cesium solutions were found to be considerably more unstable than potassium and rubidium solutions.

In general when a metal-amine solution was observed to decompose, the monomeric species exhibited a first-order decay.

The decomposition of cesium solutions is particularly interesting. Freshly prepared solutions of cesium in ethylamine and the higher alkylamines show only the eight-line hyperfine pattern due to the cesium monomer. When decomposition begins, as indicated by the decrease in the spin concentration of the cesium monomer, the building in of a single line (due presumably to the solvated electron) is observed. The electron

TABLE XVI. Linewidth of Sodium-Methylamine Solutions.

Temperature ($^{\circ}\text{C}$)	S_F (Gauss)	$\tau_2 \times 10^7$ (sec)	$\tau_1 \times 10^7$ (sec)
-140	1.72 ^b	1.75	
-135	1.77 ^a	1.70	
-130	1.81 ^a	1.66	
-120	1.89 ^a	1.59	
- 70	1.18 ^b	2.54	
- 60	1.23 ^b	2.44	
- 60	1.20 ^a	2.50	
- 50	1.24 ^a	2.42	
- 43	1.24 ^b	2.42	
- 40	1.27 ^a	2.46	
- 30	1.30 ^a	2.31	
- 22	1.34 ^b	2.24	
- 10	1.36 ^a	2.21	
0	1.39 ^a	2.16	2.17
+ 14	1.43 ^b	2.10	
+ 22	1.48 ^{a,b}	2.03	2.05
+ 40	1.54 ^a	1.95	

^aThis work.^bReference 68.

absorption continues to increase as the hyperfine pattern decreases in intensity until the hyperfine pattern can no longer be detected. At that point the electron absorption begins to decay. This process is shown in Fig. 18 for a solution of cesium in ethylamine.

B. EPR Measurements on Metal-Amine Solutions

(Paramagnetic Relaxation)

Measurement of T_1 and T_2 by the saturation method indicates that $T_1 = T_2$, at least in the vicinity of room temperature.

We shall now proceed to discuss the linewidth behavior of the broad extra line, the species in lithium-ethylamine-ammonia solutions, and of sodium in methylamine-ethylamine solutions has already been given.

1. The monomeric species. One of the most fascinating features of the EPR hyperfine spectra of metal-amine solutions is the dependence of the line width upon hyperfine component. This nuclear spin-dependent relaxation appears to be present in all solutions studied in this laboratory except for solutions of sodium in methylamine-ethylamine mixtures. It may well be present in these solutions but be obscured by other relaxation phenomena such as chemical or spin exchange processes. The effect is most pronounced in cesium solutions and becomes increasingly less pronounced as one goes to the lighter alkali metals. The effect appears to be slightly more in evidence in the higher alkylamines than in methylamine. (It is difficult to ascertain this with certainty since the apparent effect may in reality be a result of different metal concentrations.) The dependence upon the nuclear spin quantum number is definitely most pronounced in the diamines as can be seen by comparing Fig. 19 to Fig. 3. Unfortunately very little quantitative analysis of

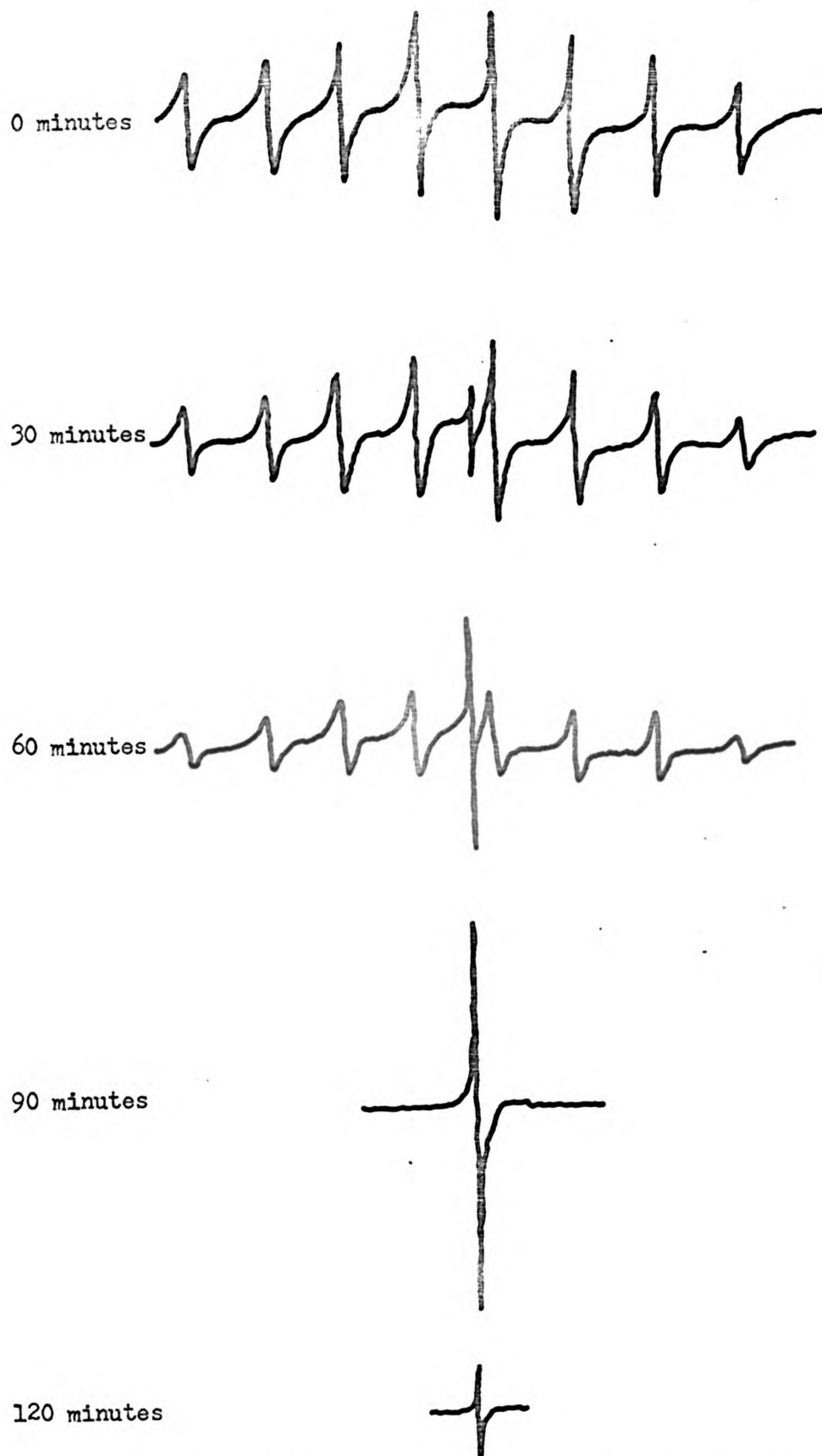


Figure 18. Decay of the EPR absorption of a cesium-ethylamine solution.

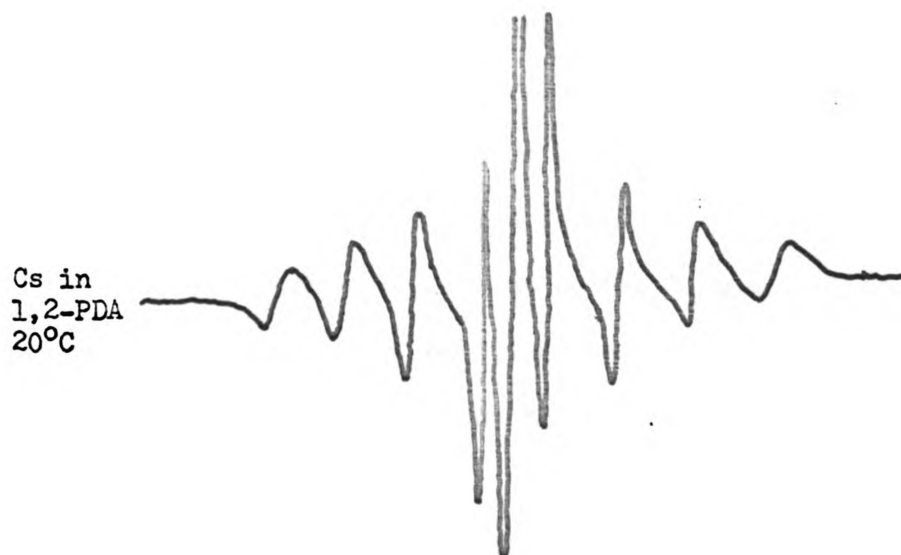
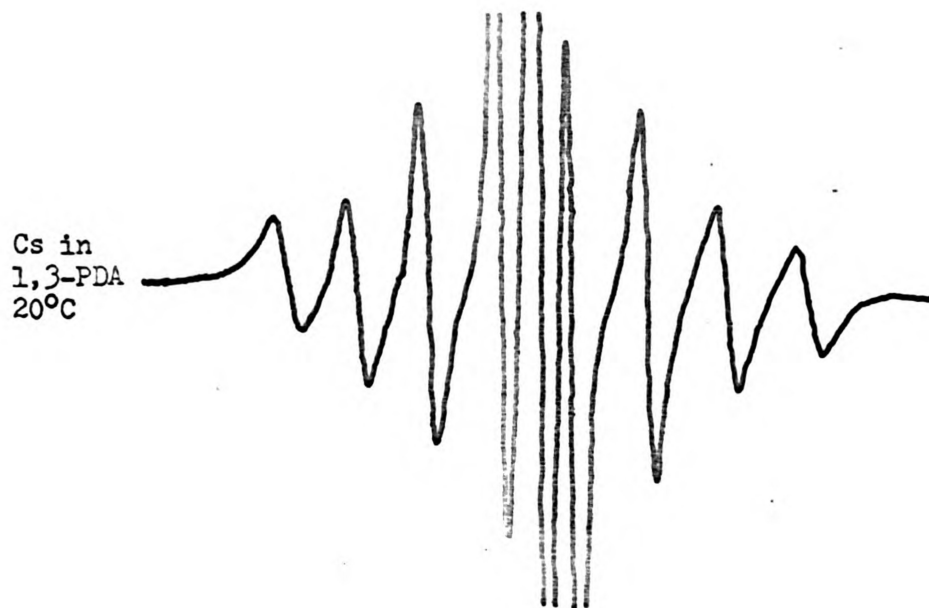


Figure 19. Cesium in 1,2- and 1,3-propanediamine.

this m_I -dependent relaxation has been performed to date. The experimentally determined values of the coefficients of the expression

$$\tau_2^{-1} = C_0 + C_1 m_I + C_2 m_I^2 + C_3 m_I^3$$

are given in Table XVII for those solutions upon which such an analysis has been applied.

The predominant coefficients appear to be C_0 and C_2 . The dependence upon m_I through third order is real but the deviations from a symmetric pattern are so small it is difficult to measure the coefficients of the first and third-order terms.

The addition of ammonia to ethylamine solutions of the metals broadens the lines and reduces the apparent dependence upon m_I . Since most of the studies were made on saturated solutions and the solubility is increased markedly upon addition of ammonia, it is difficult to separate contributions to the linewidth caused by m_I -dependent relaxation processes and from those due to exchange reactions. Indeed, the linewidth of samples with appreciable ammonia content was less for the unsaturated than for the saturated solutions.

The temperature dependence of the C_0 coefficient varies markedly from metal to metal. For potassium solutions C_0 is nearly independent of temperature while for cesium solutions it is a strong function of temperature.

2. The solvated electron. The behavior of the line width of the single absorption due to the solvated electron varies markedly from metal to metal. For solutions of lithium, rubidium, and cesium in the amines and diamines the line width increases with increasing temperature as can be seen from Table XVIII. As can also be seen from Table XVIII,

TABLE XVII. Analysis of Nuclear-Spin Dependent Relaxation for Several Metal-Amine and Metal-Amine-Ammonia Solutions.

Cesium in Ethylamine

Temperature °C	C_0 Gauss	C_1 Gauss	C_2 Gauss	C_3 Gauss
10	7.42	0.235	0.335	-0.021
0	6.75	0.323	0.336	-0.024
-10	5.73	0.322	0.354	-0.029
-20	5.16	0.341	0.384	-0.032
-30	4.95	0.327	0.406	-0.028
-40	4.53	0.299	0.433	-0.032
-50	4.42	0.221	0.442	-0.019
-60	5.12	0.198	0.453	-0.022
-80	4.57	0.006	0.392	-0.001

Cesium in Ethylamine-(5.6 Mole % Ammonia

Temperature °C	C_0 Gauss	C_1 Gauss	C_2 Gauss	C_3 Gauss
-45	10.79	0.287	0.608	-0.056
-50	9.94	0.075	0.617	-0.006
-55	9.87	0.082	0.436	-0.015

Rubidium in Ethylamine

Temperature °C	C_0 Gauss	C_1 Gauss	C_2 Gauss	C_3 Gauss
23	3.57	0.014	0.161	0.000

TABLE XVIII. Linewidths of the Solvated Electron.

Solution	S_{pe} Gauss
Cesium in Methyamine	40 (0°C) 20 (-40°C)
Potassium in Ethylamine	0.2 (25°C) 0.4 (-35°C)
Rubidium in Ethylamine	3.1 (0°C)
Cesium in Ethylamine	6.98 (10°C) 6.45 (0°C)
Cesium in Ammonia/Ethylamine (1/5)	6.6 (25°C)
Rubidium in 1,2-Propanediamine	5.1 (10°C)
Cesium in 1,2-Propanediamine	11.8 (20°C)
Cesium in 1,3-Propanediamine	21.0 (20°C)

the line width of the extra line decreases with increasing temperature for solutions of potassium in the amines.

At the time of this writing the dependence of the width of the extra line upon metal concentration had not been ascertained.

C. Optical Measurements on Metal-Amine Solutions

The results of qualitative optical spectra taken in this laboratory and elsewhere are summarized in Table XII.

The temperature and ammonia dependence of the visible, red, and infrared bands for solutions of rubidium and cesium in ethylamine-ammonia mixtures are similar to those observed for potassium solutions (42).

D. Conductance Measurements on Sodium- -Ethylenediamine Solutions

Because of experimental difficulties only one successful conductance measurement was obtained. This value is given in Table XI along with the values observed by Dewald (71).

E. Viscosity Measurements on Anhydrous Methylamine and Ethylamine

The viscosities of methylamine and ethylamine are given as functions of temperature in Table XII.

TABLE IX. Summary of the Optical Spectra of Methyl-L-lysine and Methyl-L-Aspartic Solutions.

Solvent	Metal	Temperature °C	Absorption Max. (nm)	Absorbance	Cell Path Length (mm)	Reference
NH ₃	Li	-70	1500	2.43	0.1	(1)
	Na	-62	1470	2.57	1.0	(1)
	K	-71	1480		0.1	(1)
	Rb		1500			
PEtH ₂	Cs		1500			
	Li	-55	1320	0.73	0.1	(1)
	Li		710 1500			(4)
	Li	-75	690			(5)
	Li	-70	650			(3)
	Li	-70	680, IR*			(6)
	Na	23	690			(2)
	Na	-30	655	0.45	1.0	(1)
	Na	-40	650			(3)
	Na	-70	650 690			(6) (4)

TABLE IX. Continued.

Solvent	Metal	Temperature °C	Absorption Max. (nm)	Absorbance	Cell Path Length (mm)	Reference
Me_2NH_2	K	-60	654 820			(1)
	K	-70	650 820 IR*			(6)
	K	-70	650	(3)		(3)
	Cs	-70	650			(3)
	Cs	-60	1000			(7)
+ 20% NH_3	Na		690 1320			(4)
+ 40% NH_3	Na		1250			(4)
	K	-67	660 800		1.0	(1)
	K		650			(3)
	Cs		650			(3)
Et_2NH_2	Li	23	700 1300			(2)
	Li	23	700 1300	1.3	0.2 0.2	(8) (8)
	Li	-40	1420	2.14	0.1	(3)

TABLE XIV. Continued.

Solvent	Metal	Temperature °C	Absorption Max. (mμ)	Absorbance	Cell Path Length (mm)	Reference
EtOH ₂	Li		600			(4)
	Na		680			(4)
	K	-40	640			(2)
	K	-64	650	1.66		(1)
	K	23	675	1.2	10	(8)
	Rb	23	630 950			(2)
Rb	Rb	23	630 930	1.6	10 10	(8) (8)
	Rb	-80	650		10	(8)
	Cs	23	710 1040 1300			(2)
Cs	Cs	23	710 1040 1300	0.8	10 10 10	(8) (8) (8)
	Cs	-80	675 940			(2,8) (2,8)
+ 10% m ₃ K	K	27	725 920 1340			(2) (2) (2)

TABLE XIX. Continued.

Solvent	Metal	Temperature °C	Absorption max. (mμ)	Absorbance	Cell Path Length (mm)	Reference
$\text{EtNH}_2 +$ 30% NH_3	Na		789 1300			(8)
	K	-32	1400			(2)
$+ 50\% \text{NH}_3$	Na		1250			(8)
	K		1400			(2)
	Cs		1400			(2)
$1\text{-PrNH}_2 +$ 30% EtNH_2	K		670 870			(9)
BuNH_2	K		660 870			(9)
EDA	Li	23	660 1200	0.9 1.2		(10) (10)
	Na	23	660 1250	2.0 0.03		(10) (10)
	Na	23	670			(1)
	Na		650	1.5	1.0	(12)
	K	23	650 845 1300		0.1	(10)

TABLE XII. Continued.

Solvent	Metal	Temperature °C	Absorption Max. (nm)	Absorbance	Cell Path Length (mm)	Reference
EDA	K		670			(1)
	K		650 800	1.0 0.8	0.1	(12)
	Rb	23	650 890 1280	1.0 0.5		(10)
	Rb		700 900	1.3 1.5	0.1	(12)
	Rb		700 900	0.7 0.6	0.1	(12)
	Cs	23	1030 1250	1.33	0.1	(10)
	Cs	23	1220		0.1	(10)
1,3-PDA	Na	23	600			(11)
	I	23	670 870			(11) (11)

TABLE IX. Continued.

• Strong absorption in IR region.

- | | |
|------|--------------------|
| (1) | Reference 26. |
| (2) | This work. |
| (3) | Reference 116. |
| (4) | Reference 117. |
| (5) | Reference 118. |
| (6) | Reference 36. |
| (7) | Reference 119. |
| (8) | Reference 40. |
| (9) | References 51, 52. |
| (10) | Reference 71. |
| (11) | Reference 30. |
| (12) | Reference 31. |

TABLE XI. Conductance of Sodium in Ethylenediamine.

<u>$C^{\frac{1}{2}} \times 10^2$</u>	<u>Equivalent conductance</u>
4.96	25.5 ^a
4.06	25.5 ^a
3.65	25.8 ^b
3.23	25.9 ^a
1.56	26.3 ^a

^aReference 71.^bThis work.

TABLE XII. Viscosities of Methylamine and Ethylamine.

Temperature °K	Methylamine η centipoise	Ethylamine η centipoise
296.4		0.250
296.4		0.259
289.2		0.276
283.2		0.299
273.2	0.236	0.328
263.2	0.285	0.343
263.2	0.291	0.370
258.8	0.300	
253.2	0.331	0.415
243.2	0.372	0.467
239.7		0.437
238.3	0.400	
233.2	0.422	0.588
223.2	0.480	0.780
223.2		0.671
217.5		0.800
213.5	0.552	
203.5	0.665	
203.2	0.829	

CONCLUSIONS

A. The Assignment of the Optical Absorptions

1. The infrared band. The work of Dalton, Dye, Fielden and Hart (46) leaves little doubt as to the correctness of the assignment by Dye and Dewald (33) of the infrared band to the solvated electron and aggregates.

A comparison of the spin concentration of the EPR singlet attributed to the solvated electron with the absorbance of the infrared band indicates that in many metal-amine solutions the electron exists largely in diamagnetic aggregates.

2. The red band. If we assume that the equilibrium constant for the reaction $2M \rightleftharpoons M_2$ is the same in solution as it is in the gas phase, we can predict the concentration of M_2 from the measured spin concentration of the monomeric species M . The predicted concentration of M_2 is given in Table XXII for a number of metal-amine solutions. The agreement with experiment as can be seen by comparing Tables XXII and XIX is surprisingly good. Indeed it might have been expected that the equilibrium constant would have been significantly shifted as a result of differences of solvation between M and M_2 .

If, as pointed out by workers in this laboratory (42), the red band must be assigned to the ${}^1\Pi_g^+ \leftarrow {}^1\Sigma_g^+$ transition of the dimer an interesting question arises; namely, "where does the ${}^1\Sigma_g^+ \leftarrow {}^1\Sigma_g^+$ transition occur?" By comparison with the higher energy transition it might

TABLE XIII. Concentration of the Solvated Dimer Predicted from Monomer Spin Concentration Measurement by Use of Gas Phase Equilibrium Constant.

Solvent	Dimer Concentration, moles/liter			
	Sodium	Potassium	Rubidium	Cesium
MeNH ₂			6×10^{-3}	2.7×10^{-2}
EtNH ₂		1×10^{-5}	3.6×10^{-4}	1.6×10^{-3}
EtNH ₂ / MeNH ₂	4×10^{-4}			
n-PrNH ₂		9×10^{-6}	4.8×10^{-5}	6.7×10^{-4}
i-PrNH ₂		7×10^{-6}	3×10^{-5}	3.3×10^{-4}
3-XPA		1×10^{-6}	3×10^{-6}	1.6×10^{-5}
1,2-PDA		6×10^{-4}	6×10^{-5}	3.3×10^{-3}
1,3-PDA		9×10^{-4}	2.4×10^{-4}	6.7×10^{-3}

be expected that the ${}^1\Sigma_g^+ \leftarrow {}^1\Sigma_u^+$ transition will be shifted into the infrared region. There now appears to be some experimental evidence to substantiate this. As has been pointed out to the author (105), the normalized infrared absorption tails more when the red band is present than when it is absent. If one argues that this is due merely to overlap with the ${}^1\Pi_g^+ \leftarrow {}^1\Sigma_g^+$ transition it can be pointed out that such overlap would actually result in less tailing of the normalized infrared absorption.

3. The visible band. This work further confirms the argument of Dalton *et al.* (42) that the visible band is not due to the monomeric species responsible for hyperfine splitting. A comparison of Tables XI and XII indicates a complete lack of correlation between the species responsible for these phenomena.

Unfortunately the work reported in this thesis throws little light upon the nature of the visible species. The only thing that is certain is that the species which gives rise to the visible band cannot also give rise to a sharp EPR signal. This does not exclude the possibility that the visible species gives rise to a broad EPR absorption.

If the visible absorption is the $M_2^+ \cdot e^-$ species as postulated by Dye and Dewald (33), two possible paramagnetic absorptions could result. The first of these is a triplet absorption resulting from the interaction of the paramagnetic electron of the M_2^+ cation with the electron trapped in the field of the M_2^+ ion. Kivelson (56) has shown that the line width of a triplet state absorption is given by

$$\tau_2^{-1} = \gamma_e (3/10) \mu^2 (4S^2 + 4S - 3) \left[(3/2) + (5/2)/(1 + \omega_e^2 \tau_c^2) + 1/(1 + 4\omega_e^2 \tau_e^2) \right]$$

where

$$\mu^2 = (1/5) [|D_{zz}|^2 + (16/3) (|D_{++}|^2 + |D_{--}|^2)]$$

and D is the fine structure tensor. To give the reader an idea of the magnitude of triplet state line widths we note that for the case of naphthalene diluted in durene (106) where $D_{zz} = -3 \times 10^9$ cps; $D_{++} = D_{--} = -0.21 \times 10^9$ cps; $g = 2.0133$, and τ_0 is taken to be 10^{-11} sec, T_2^{-1} would be greater than two hundred gauss. It would thus not be a simple matter to see the naphthalene spectrum in solution. Weissman (107) has discussed this problem in some detail.

This seems to rule out the assignment of the EPR absorption in sodium-ethylenediamine solutions to a triplet state $M_2^+e^-$ species. Since the line width at 22°C is only of the order of 0.5 gauss, both the fine structure interaction and the correlation time would have to be extremely small to account for the observed spectra. For example, if a correlation time of 10^{-11} sec is chosen, the fine structure tensor would have to be only 10 G.

A second possibility of an EPR absorption arising from the molecule-ion would be the interaction of the paramagnetic electron of the M_2^+ core with the two equivalent metal nuclei.

Kivelson (108) has shown that such interaction will result in a contribution to the line width given by

$$\tau_2^{-1}(\text{iso. m}) = I(0) [\langle a^2 \rangle - \langle a \rangle^2] m_I^2 / 2$$

where $\langle a \rangle$ is the hyperfine splitting constant, $I(0)$ is the amplitude of the resonance. The secular line widths for Na_2^+ are given in Table XXXIII as a function of m_I . The predicted dependence of T_2^{-1} upon m_I is most interesting. Unfortunately since no hyperfine interaction

TABLE VIII. Calculated Secular Line widths of Na_2^+

N	3	2	2	1	1	1	1	0	0	0
$(m_I)_1$	3/2	3/2	1/2	1/2	3/2	-1/2	1/2	-3/2	3/2	1/2
$(m_I)_2$	3/2	1/2	3/2	-1/2	3/2	1/2	1/2	3/2	-3/2	1/2
$\frac{2T_2^2(1\text{m.m.})^a}{s_I^2(0)}$	1.13	0.50	0.50	0.13	0.13	0.13	0.13	0	0	0
$\frac{2T_2^2(1\text{m.m.})^b}{s_I^2(0)}$	0.60	0.19	0.19	0.05	0.05	0.05	0.05	0	0	0

^aFor this calculation the nuclei are considered to flip abruptly between 0° and 90° .

^bFor this case, the two nuclei carry out a correlated out-of-phase motion in which the instantaneous hyperfine splitting constants a_1 and a_2 vary between 0 and $\pm$ as the nuclei rotate through 90° .

attributable to M_2^+ is observed the above equation is of little use to us directly. We observe, however, that since the absorption in sodium-ethylenediamine solutions displays no hyperfine structure and since in the above relationship T_2^{-1} is proportional to the square of the hyperfine splitting, we must assume that since $T_2(\text{obs}) = 6 \times 10^{-7}$ sec that $\langle a \rangle$ is very small. The argument that this resonance is exchange narrowed is unlikely since the dissociation of M_2^+ would be expected to be slow and all other exchange and chemical processes would lead to broadening rather than narrowing.

On the basis of these two arguments, the author feels that the EPR absorption present in sodium-ethylenediamine solutions cannot be attributed to a triplet $M_2^+ \cdot e^-$ or M_2^+ . It is possible that the valence electron of $M_2^+ \cdot e^-$ experiences very little or no triplet state interaction or nuclear hyperfine interaction and is sufficiently motionally narrowed to account for the observed linewidth.

It may also be noted that $M_2^+ \cdot e^-$ could exist as a singlet in which case it would be expected to be diamagnetic.

There are four characteristics of the visible band which appear to the author to be very difficult to describe on the basis of currently-existing models. These characteristics are (1) the narrowness and high energy at which the band occurs, (2) the independence of the band position on the metal used, (3) the dependence of the absence or presence of the band upon metal, (4) the slow rate of interconversion of the band. No assignment at the present time, including the assignment to M^- , satisfactorily explains all of these characteristics.

B. The Assignment of the EPR Absorptions

1. The hyperfine species. As has already been stated, the nature of the spectrum indicates unambiguously that the species giving rise to hyperfine splitting must involve a single paramagnetic electron interacting with a single alkali metal nucleus.

The magnitude and temperature dependence of the hyperfine splitting precludes assignment of the monomeric species solely to solvated atoms. In order to explain the temperature and solvent dependence of the hyperfine interaction, workers in this field have been forced to resort to either complex stationary state models or multi-state models involving equilibrium between several species.

In this dissertation we shall attempt to discuss g-shifts and the temperature dependence of these shifts in the light of current models.

Let us first review the phenomenological theory for g-shifts. We shall start with the following Hamiltonian for an unpaired electron in an external magnetic field

$$H = 2.0023 \beta \bar{S} \cdot \bar{B} + \left(\frac{e\hbar}{2m} \frac{1}{c} \right) \bar{S} \cdot [\bar{E} \times (\bar{p} + \frac{e}{c} \bar{A})] + \frac{e}{2mc} (\bar{p} \cdot \bar{A} + \bar{A} \cdot \bar{p}) \quad (32)$$

where the second term gives the spin-orbit interaction in which $\bar{A}$ is the vector potential that gives a static magnetic field externally applied, and $\bar{p}$ is the linear momentum operator, $\bar{E}$ is an electric field in which an electron moves. The third term describes the orbital Zeeman interaction. The g shift caused by the combined effect of the spin-orbit and the orbital Zeeman coupling is given by

$$\Delta g_s = 2.0023 - g_{\text{obs.}}$$

$$\Delta g_z = \frac{e}{n^2 c^2} \cdot \frac{1}{B_0} \times \Sigma' \frac{\langle \sigma / (\vec{E} \times \vec{p})_z / n \rangle \langle n / (\vec{p} \cdot \vec{A} + \vec{A} \cdot \vec{p})_z / \sigma \rangle}{E_0 - E_n} \quad (33)$$

where B_0 denotes the magnitude of the external magnetic field.

Regardless of whether we employ a stationary state model or an equilibrium model we must at some point consider a species exhibiting appreciable spin-orbit coupling. Traditionally spin-orbit coupling has been viewed as arising from interaction between the ground and excited orbitals of one paramagnetic electron localized on a central metal atom or ion. In such a situation the ground and excited state energy levels are said to be coupled through spin-orbit coupling. Such coupling gives rise to a negative g-shift, that is, a g-value less than the free electron.

As can be seen from consulting Table IX this is in the right direction for g-values observed in this work. However if one considers Fig. 15 and Table I one sees that the g-values are strongly temperature dependent for rubidium and cesium solutions. This behavior is unexpected in terms of the classical picture.

In further considering g-shifts and the temperature dependence of these shifts it is most convenient to proceed in the context of the several models developed for metal-amine solutions. We shall follow the treatment of Dalton *et al.* (42) and divide the models into two classes. It must be kept in mind that any model proposed to explain g-shifts must also explain the observed hyperfine interactions.

Stationary single-state models

a) The expanding orbital model. As has been previously discussed, this model views the monomeric species as being an alkali metal ion surrounded by several solvation spheres of solvent molecules with the

paramagnetic or valence electron density spread over these layers but with the density maximum localized upon the outer solvation sphere. The solvation binding energy of the secondary solvation spheres is viewed as being on the order of kT so that as the temperature is raised the outer solvation spheres drop off. This is viewed as resulting in the electron density moving closer to the metal nucleus thus increasing the hyperfine interaction. Quantum mechanically this is viewed as an expanding spherically symmetric wavefunction

$$\psi(s) = K \psi_0(s/c)$$

From normalization it is easily shown that $K = c^{-3/2}$. If s is a dimensionless radial variable, c is simply a scaling factor which determines a new variable $s' = s/c$ expressed in units c times as large as those in which s is measured.

Since for such a model $\bar{p} = 0$, the Δg would be predicted to be zero. This result is rigorously true and is completely independent of the nature of the excited state to which the ground state would be expected to be coupled.

Thus we must completely reject the simple (spherically symmetrical) expanding orbital model.

b) The admixture model. The simple admixture model views the wavefunction of the paramagnetic electron of the monomeric species as being an admixture of ground state s and excited state orbitals. For example, the wavefunction for the potassium monomer would be

$$\Psi = \alpha \psi(4s) + \beta \psi(3d) + \gamma \psi(4p) + \epsilon \psi(5s) \quad (34)$$

Since the $4p$ and $3d$ orbitals have nodes at the nucleus and the $5s$ orbital is opposite in sign to the $4s$ orbital at the nucleus, any such admixture would reduce the contact density without requiring

so drastic a change in the mean radius of the electron distribution as required by the simple expanding orbital model. The coefficients of the various orbitals are viewed as being temperature dependent. To explain the observed increase in hyperfine splitting with temperature the ratio of ground state orbital contribution to excited or higher state contribution is viewed as increasing with increasing temperature.

Let us now examine such a model in the light of g-shifts. Although such an admixture does predict the correct sign of the g-shift the magnitude of the g-shift would be expected to decrease with increasing temperature if the admixture of states of non-zero orbital angular momentum is to be viewed as important in determining the observed hyperfine splitting. As has already been noted the magnitude of the negative g-shift is experimentally observed to increase with increasing temperature.

If we are to retain the simple admixture model we must view the decrease in hyperfine splitting with decreasing temperature as entirely due to the mixing of higher s orbitals into the wavefunction. In fact such excited s-state admixture must offset the reverse trend for states of non-zero orbital angular momentum.

c) The expanding admixture model. This model is equivalent to viewing the change in hyperfine splitting as arising from the expansion or contraction of the electron cloud as described for the expanding orbital model and the g-shift as arising from the admixture of states of non-zero p. This is equivalent to the case discussed above of the admixture of ground and excited s-state orbitals accounting for changes in the hyperfine interaction and the admixture of $p \neq 0$ states accounting

for changes in the g-shift with the exception that the expanding admixture model would require greater changes in the mean radius of the electron distribution.

d) The covalent bonding or charge-transfer model. As can be seen from the phenomenological equation for g-shifts, the magnitude and sign of the g-shift will depend upon four properties of the material under investigation. These are (1) the orbital angular momentum of the electron, (2) the nature of the ground state wavefunction, (3) the nature of the excited state wavefunction, and (4) the energy separation of the ground and excited state. It is to be noted that these parameters are not independent.

Traditionally the ground and excited state wavefunctions have been those of the metal atom or central metal ion and the energy separation has been that between the ground and excited electronic energy levels of the metal.

We now wish to consider the case where ligand-metal bonding (particularly covalent) or ligand-electron interaction are sufficiently strong that we can no longer represent the ground and excited wavefunctions to a good approximation in terms of metal orbitals.

The ground state wavefunction which we must consider is now a molecular orbital wavefunction of the type

$$\Psi_0 = N \left\{ \bar{\Phi}_0 - \rho(N)^{-1} \sum_{i=1}^N \sigma_i(s^1) \right\} \quad (35)$$

where $\bar{\Phi}_0$ denotes the s orbital of the alkali metal monomer (or atom) and $\sigma_i(s^1)$ is the σ molecular orbital of the i th solvent molecule directed toward the alkali metal atom or ion. The σ orbital is

assumed to be constructed from the sp^3 hybridized orbitals of carbon and nitrogen and from the atomic s orbitals of the hydrogens. In the above expression, we denote the antibonding orbital by positive ρ .

It is to be noted that this expression will give rise to a g -shift even though a spherically symmetrical s -state of the alkali metal atom is used. In such a case the g -shift is seen to arise from the non-zero orbital angular momenta of the solvent molecule orbitals.

The metal wavefunction Φ of Eq. 35 can also be an admixture of ground state s and higher or excited as in Eq. 34.

A similar expression can be written for the wavefunction of the valence electron interacting directly with the solvent,

$$\Psi'_0 = N \left\{ \phi_0 - \rho(n)^{-1/2} \sum_{i=1}^n \sigma_i(s^1) \right\} \quad (36)$$

where ϕ_0 is the wavefunction of an electron in a spherical square well.

As with the previous expression the spin-orbit coupling arises from the $\bar{p} \neq 0$ character of the solvent σ 's.

If we substitute Eq. 35 into Eq. 33 the following expression for g is obtained

$$\Delta g = \xi(N) \left[\frac{K_1}{\Delta E^b} - \frac{K_2}{\Delta E^a} \right] \quad (37)$$

where ξ is the one-electron spin-orbit interaction parameter for the $2p$ orbital of nitrogen (The nature of the interaction of the amine molecule with the metal ion is such that $\xi(\text{carbon}) \approx 0$).

If the admixture of the ground state s orbital of the metal with higher non-zero orbital angular momentum orbitals of the metal is permitted one obtains the following equation

$$\Delta g = \xi(\text{nitrogen P}) \left[\frac{K_1}{\Delta E^b} - \frac{K_2}{\Delta E^a} \right] + \xi(\text{metal P}) \left[\frac{K_1}{\Delta E^b} - \frac{K_2}{\Delta E^a} \right] \\ + \xi(\text{metal D}) \left[\frac{K_1}{\Delta E^b} - \frac{K_2}{\Delta E^a} \right] + \xi(\text{metal F}) \left[\frac{K_1}{\Delta E^b} - \frac{K_2}{\Delta E^a} \right] \quad (38)$$

As can be seen from Eqs. 37 and 38, charge transfer interaction (ΔE^b = the separation between the ground state and the charge transfer state) results in a positive g-shift.

K_1 and K_2 in Eqs. 37 and 38 relate to the bonding coefficients between the metal atom or ion and the solvent molecules. ΔE^a is the separation between ground and excited molecular orbital energy levels.

An evaluation of the experimental data given in Tables IX and X in terms of equations 37 and 38 is given in Appendix I.

The temperature dependence of the g-shift in the case of Eq. 37 would be viewed as arising from either an increase in metal-solvent bonding or a decrease in charge-transfer interaction with increasing temperature.

Although the "solvent spin-orbit interaction" model, as we shall call the model of Eq. 37, explains the g-shifts and temperature dependence of a given metal-amine system, a look at Table IX causes us to question its applicability. As can be seen from Table IX the g-value is relatively independent of solvent for a given metal but is strongly dependent on metal for a given solvent. This forces us to the conclusion that $\bar{p} \neq 0$ states or orbitals of the metal are important in determining Δg and the temperature dependence of Δg . This does not exclude the possibility of some contribution to Δg from nitrogen 2p orbitals.

Since the observed Δg is large and negative we conclude that probably $K_1 \ll K_2$.

In conclusion we feel that the most appropriate expression for Δg involving a single state model is

$$\Delta g = \left\{ (\beta \xi(\text{MP}) + \gamma \xi(\text{MD}) + \delta \xi(\text{MF}) + \kappa \xi(\text{N2P})) \right\} \left[\frac{K_1}{\Delta E^b} - \frac{K_2}{\Delta E^a} \right]$$

where $K_1 \ll K_2$ and $K_1 \approx 0$.

Multi-State Equilibrium Model

As has been stated in the Historical, Dalton et al. (42) have described the temperature and solvent dependence of the hyperfine splitting and spin concentration in terms of an equilibrium among monomeric species. Because of the large values of the hfs observed at high temperatures they took the solvated atom as the high temperature limit.

The g-shifts of gaseous metal atoms are observed to be very nearly zero as can be seen in Table IX. From Fig. 15 it is obvious that the observed g-shift will be quite large at high temperatures (The curve apparently levels off at zero to a constant value, i.e., $\Delta g (\text{Cs in EtNH}_2) = 0.0075$).

Thus if we take the solvated atom as the high temperature limit we must view the g value of this species as being greatly affected by the solvation process. It must be noted that on the basis of previous arguments this shift must arise largely from the admixture of $p \neq 0$ orbitals of the metal.

In analogy with the treatment of Dalton et al. we assume the low temperature species to be a solvated monomer. The temperature dependence of the g-shift forces us to the conclusion that the g-value is greater in the solvated monomer than in the solvated atom. This

would have to result from an increase in the importance of higher s states relative to $\bar{p} \neq 0$ states in the wavefunction for the monomer. The experimental observed Δg is related to the Δg of the atom and monomer by

$$\Delta g(\text{obs.}) = p_A \Delta g_A + p_B \Delta g_B$$

where p_A and p_B are the concentrations of atoms and monomers respectively. The lack of agreement between the values of p_A/p_B obtained by the two methods forces us to conclude that the equilibrium responsible for the g -shift cannot be the atom-monomer equilibria.

We must now assign the process resulting in the temperature dependence of the g -shift to an equilibrium between solvated monomers and a third species which we shall assume to be an ion pair. Since the square of the wavefunction of the paramagnetic electron in a solvated ion-pair would be expected to have only a very small contact density at the metal nucleus we take a value of $g = 2.0019$ (the value of the solvated electron) for the g -value of the ion pair. The g -shift is now given by

$$\Delta g(\text{obs.}) = p_B \Delta g_B + p_C \Delta g_C$$

where the subscripts B and C refer to the monomer and ion pair respectively. The values of $p_B/(p_B + p_C)$ obtained from analysis of the g -shifts using the monomer-ion pair equilibrium and the values of $p_B/(p_B + p_C)$ obtained from analysis of the hyperfine splitting in terms of an atom, monomer, ion-pair equilibria are compared in Table IXI' and the plot of p_B vs. temperature is shown in Fig. 20. The improvement in agreement provides strong support for the existence of the monomer-ion pair equilibrium.

TABLE XXIV. The ratio $p_B/(p_C + p_B)$ obtained from g-shift analysis and independently from analysis of hyperfine splitting for a solution of cesium in ethylamine.

Temperature °C	$p_B/(p_B + p_C)$ from hf's data	$p_B/(p_B + p_C)$ from g-shift data
-20	0.90	0.86
-30	0.84	0.80
-40	0.78	0.75
-50	0.72	0.70
-60	0.65	0.65
-70	0.60	0.59
-80	0.55	0.55

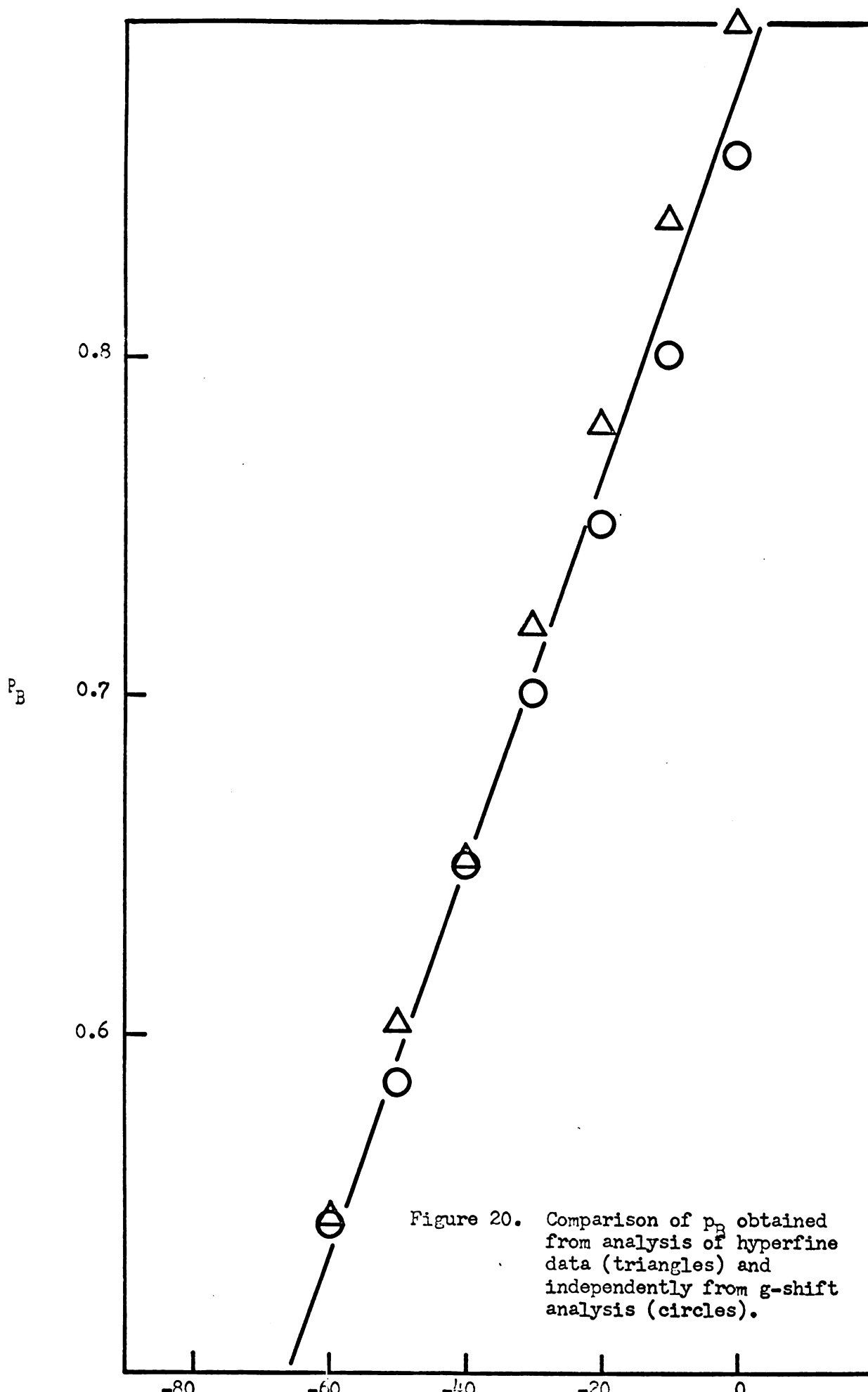


Figure 20. Comparison of p_B obtained from analysis of hyperfine data (triangles) and independently from g-shift analysis (circles).

This being the case we are now faced with the problem of considering the effect of the atom-monomer equilibrium upon the temperature dependence of the g-shifts. Two possible alternatives confront us as we consider the high temperature behavior of the g-shifts. These are summarized schematically in Fig. 21.

- i) Case 1. If we view the observed g-shift as being constant at the higher temperatures then we must see the atom and monomer as having equivalent amounts of $\bar{p} \neq 0$ orbitals of the metal mixed into their wavefunctions. The difference in the magnitude of the hyperfine interaction in the two species would be viewed in this case as arising from the greater extent of admixture of excited s states in the monomer.
- ii) Case 2. Since there is considerable scatter in the data at higher temperature it may be that the g-value increases with increasing temperature. If such a case $\beta \psi(MP) + \gamma \psi(MD) + \delta \psi(MF)$ would be viewed as making only a slight contribution to the total wavefunction.

On the basis of existing experimental evidence Case 1 appears to be the more realistic of the two.

In summary we conclude that the observed hyperfine splitting and g-shifts can be explained on the basis of equilibria between atoms, monomers, and ion pairs. The nature of the g-shifts permits the detailed specification of the wavefunction of these species.

The wavefunction of the ion-pair is viewed as

$$\Psi(\text{ion pair}) = N \left\{ \Phi_0 - \rho(n)^{-\frac{1}{2}} \sum_{i=1}^n \sigma_i(s^i) \right\}$$

where Φ_0 is the wavefunction of an electron in a cavity interacting only weakly with an adjacent metal nucleus. This gives as an expression for the g-shift

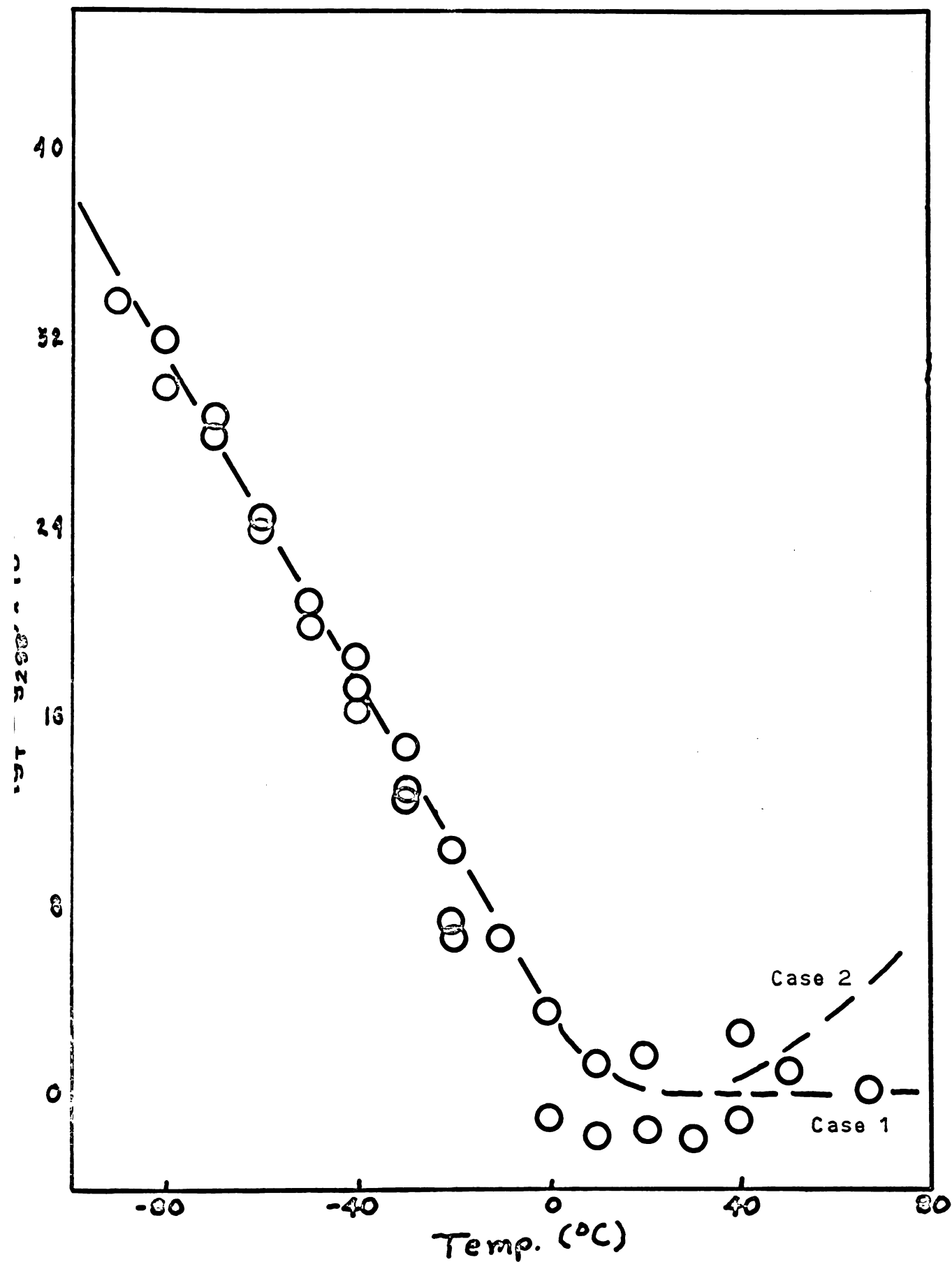


Figure 21. High temperature g-shift behavior in light of models for the solvated atom.

$$\Delta g(\text{ion pair}) = \left(\xi(\text{N2P}) \right) \left[\frac{K_1}{\Delta E^b} - \frac{K_2}{\Delta E^a} \right]$$

or, neglecting charge transfer interaction

$$\Delta g(\text{ion pair}) = - \frac{K_2 \xi(\text{N2P})}{\Delta E^a}$$

Calculations involving the evaluation of this equation in the light of experimental evidence is given in Appendix I.

The wavefunction of the monomer is seen to be

$$\Psi(\text{monomer}) = N \left\{ \alpha \psi(\text{MS}) + \beta \psi(\text{MP}) + \gamma \psi(\text{MD}) + \delta \psi(\text{MF}) + \epsilon \psi(\text{MHS}) \right. \\ \left. - \rho(n)^{-\frac{1}{2}} \sum_{i=1}^n \sigma_i(s^{\frac{1}{2}}) \right\}$$

This gives rise to an expression for the g-shift given by

$$\Delta g(\text{monomer}) = \left\{ a \xi(\text{MP}) + b \xi(\text{MD}) + c \xi(\text{MF}) + d \xi(\text{N2P}) \right\} \left[\frac{K_1}{\Delta E^b} - \frac{K_2}{\Delta E^a} \right]$$

We shall assume that $\frac{K_1}{\Delta E^b} = 0$.

Thus

$$\Delta g(\text{monomer}) = - \left\{ a \xi(\text{MP}) + b \xi(\text{MD}) + c \xi(\text{MF}) + d \xi(\text{N2P}) \right\} \frac{K_2}{\Delta E^a}$$

A consideration of the dependence of spin-orbit coupling on metal in going from sodium to cesium permits us to evaluate the contribution of each of the $\bar{p} \neq 0$ metal and ligand(solvent) orbitals to the total spin-orbit coupling. The details of this treatment are given in Appendix I.

Continuing we view the wavefunction for the atom as

$$\Psi(\text{atom}) = N \left\{ \alpha' \psi(\text{MS}) + \beta' \psi(\text{MP}) + \gamma' \psi(\text{MD}) + \delta' \psi(\text{MF}) \right. \\ \left. - \rho(n)^{-\frac{1}{2}} \sum_{i=1}^n \sigma_i(s^{\frac{1}{2}}) \right\}$$

The difference between the hyperfine splitting in the atom and in the monomer requires that $\alpha' \gg \alpha$.

Neglecting charge transfer we derive for the atom

$$\Delta g(\text{atom}) = - \left\{ a' \xi(\text{MF}) + b' \xi(\text{MD}) + c' \xi(\text{MF}) + d' \xi(\text{N2P}) \right\} \frac{K_2}{\Delta E^2}$$

In Case 1, $b'K_2 = c'K_2 = d'K_2 = 0$ while in Case 2 it is likely that $aK_2 \approx a'K_2$, $bK_2 \approx b'K_2$, $cK_2 \approx c'K_2$, and $dK_2 \approx d'K_2$.

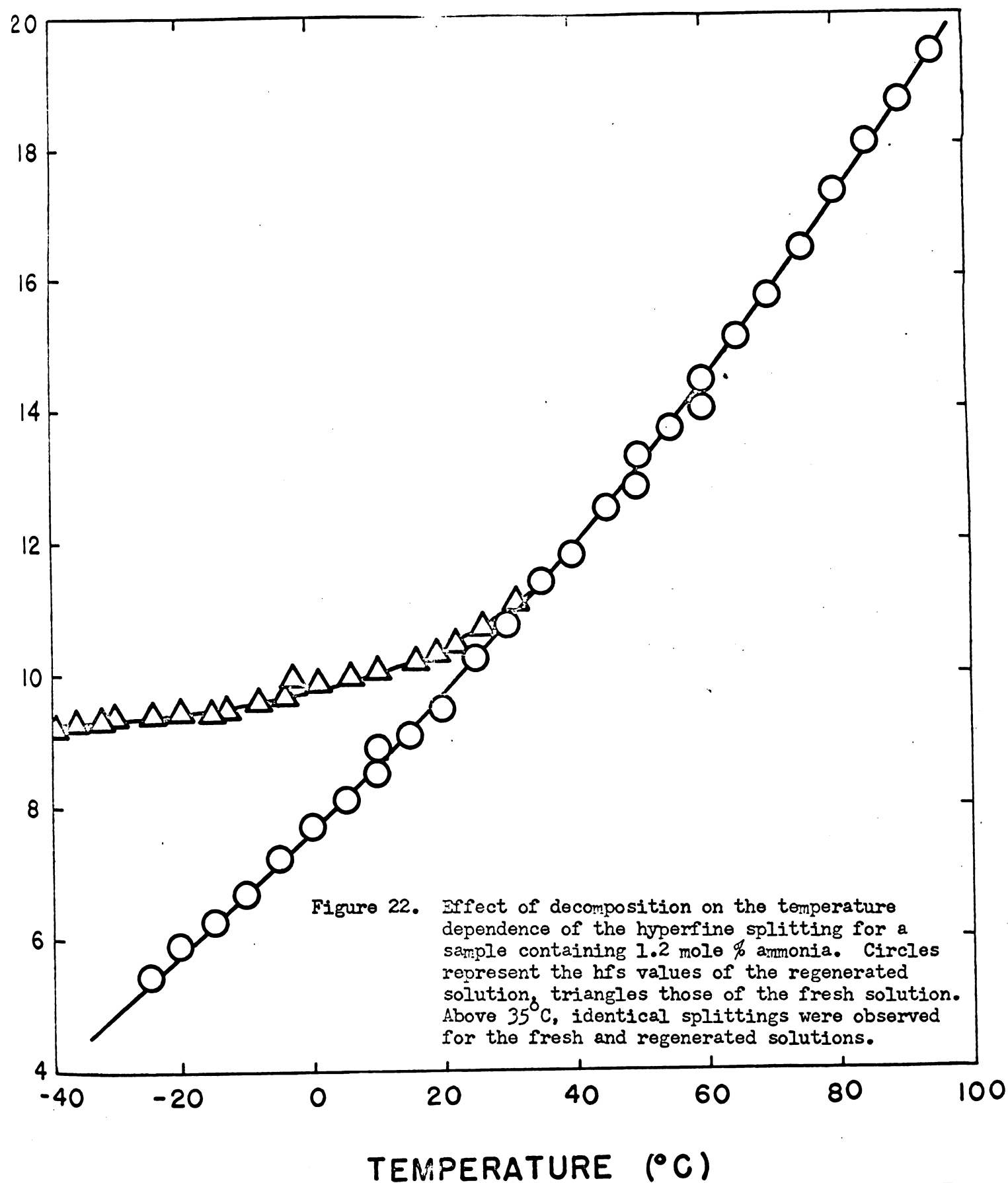
Whether we use a stationary state or equilibrium model, any explanation of the temperature dependence of the g-shifts must also explain the temperature dependence of the hyperfine splitting since both of these physical variables are intimately related to the nature of the wavefunction of the paramagnetic electron. For example

$$\frac{A}{g} = \frac{2 \beta \beta_{\text{N}} \mu_{\text{N}}}{I} \langle r^{-3} \rangle \frac{\langle J | \mathbf{H} | J \rangle}{\langle J | \mathbf{H} | J \rangle}$$

As can be seen from Appendix I the K_2 's calculated from g-shifts explain the correct progression of hyperfine splitting values from metal to metal and from solvent to solvent.

The reader may wonder why only two species (atoms and monomers) were required to explain the temperature dependence of the hyperfine interaction in potassium-ethylamine solutions while three species were required to explain the hyperfine interaction and g-shifts in cesium-amine solutions.

The most reasonable explanation for this is that the concentration of the ion-pair is nearly zero in potassium-ethylamine solutions. In fact this assumption explains the observed temperature independence of the g-shifts. It also serves to explain the unusual change in temperature dependence of a potassium-ethylamine solution after decomposition and regeneration (see Fig. 22 and Ref. 42). The build-up of decomposition



products is viewed as favoring the ion-pair. (It has been pointed out to the author that this can occur only as a result of a change in the activity coefficient.) This concept can also be used to explain the fact that the ion-pair concentration is higher in freshly prepared cesium-amine solutions than in potassium-amine solutions. Cesium solutions are more subject to decomposition than potassium solutions. The favoring of the ion-pair in cesium solutions may also result from the presence of small amounts of ammonia in the amines used. Cesium-amine solutions were invariably the last to be prepared from a given solvent purification. Upon standing over metal the purified amine may have decomposed somewhat, resulting in the build-up of ammonia. The ion-pair appears to be favored by increasing ammonia concentration.

The three-state equilibrium model also serves to explain the temperature dependence of the g-shift and hyperfine interaction observed in rubidium-ethylamine solutions. As has been previously mentioned (42) potassium and rubidium do not appear to be soluble in high purity ethylamine. When samples containing rubidium and ethylamine were allowed to stand at elevated temperatures for extended periods of time blue solutions were formed. The temperature dependence of the hfs and g-shifts suggest that the ion-pair is favored at the expense of the monomer. Indeed if one considers an equilibrium between only ion-pairs and atoms (case 1), one can obtain a reasonable quantitative fit of the data. Such an atom-ion pair equilibrium appears to have been successfully applied by Catterall and Symons (109) to certain potassium-amine solutions.

In fact at this writing there appear to be no results which cannot be at least qualitatively described using the equilibrium model.

Multi-State Distribution Model

The observed temperature dependence of the g-shift can also be explained in terms of a temperature dependent distribution of g-values. The g-value distribution would be viewed as arising from a distribution of the admixture coefficients. The quantitative treatment of such a model involves a knowledge of the distribution of g-shifts as a function of temperature. At this time it is not clear how this distribution should be determined.

Fundamental to the treatment of spin-orbit coupling in the monomer species is the problem of the location of the optical absorption. We would have expected this absorption to occur at lower energies than the atom but at higher energies than the solvated electron. By analogy with the effect of solvent interaction upon the optical transitions in the corresponding alkali metal dimers we have estimated the frequency of the $P \leftarrow S$ (or pseudo $P \leftarrow S$) transition in the monomer.

2. The solvated electron. We assign the EPR singlet observed at $g = 2.0019 \pm 0.0002$ to the solvated electron. The reasons for this assignment are as follows:

a) The observed g-value is close to that of the free electron ($g_0 = 2.0023$). The molecular orbital calculation given in Appendix I supports the contention that the observed g-shift ($\Delta g(\text{obs.}) = 0.0004$) can be viewed as arising from interaction of the paramagnetic electron with the solvent. Moreover, the g-value and hence the g-shift is independent of the metal and solvent used, the metal concentration, and temperature. If the paramagnetic electron were experiencing significant interaction with metal nuclei this independence of experimental

conditions would not be expected. Since the spin-orbit coupling induced by solvent interaction arises from the nitrogens (at least in the simple H.O. approximation) of the solvation structure, the g-shift of the solvated electron would not be expected to change as a result of changing the alkyl group of the amine or diamine.

b) Catterall, Symons, and Tipping (51,52) have shown that the ratio $[\text{singlet}]^2/[\text{hyperfine species}]$ is independent of concentration for dilute solutions of potassium dissolved in the higher alkylamines. In contrast, the ratio of the intensities $[\text{singlet}]/[\text{hyperfine species}]$ is independent of concentration in the presence of an excess of cations (e.g. M^+). These observations are quantitatively in accord with expected concentration ratios for the equilibrium



Although these relationships are not observed in rubidium and cesium solutions this may be due to the interference of additional equilibria.

c) The observed linewidth behavior of these solutions is in accord with processes expected for the solvated electron.

C. Nuclear Spin-Dependent Relaxation

The rationale which we wish to employ in considering nuclear spin-dependent relaxation in metal-amine solutions is to analyze these processes in the light of models developed by analyses of hyperfine interactions and g-shifts. It is to be emphasized that an analysis of relaxation data alone cannot distinguish between the various models. Nevertheless any model capable of explaining hyperfine interactions and g-shifts must also be capable of explaining the nature of paramagnetic relaxation in these solutions. We shall now examine the

various models capable of giving rise to an n_I -dependent paramagnetic relaxation.

The McConnell Mechanism

In an attempt to obtain a more realistic evaluation of the experimental coefficients of Eq. 16 in terms of a McConnell mechanism we have measured the viscosity of ethylamine as a function of temperature. The values of the coefficients plotted versus η/T are shown in Fig. 23.

As can be seen from Fig. 23 and from Fig. 4, the coefficients of the terms in n_I tend to go to zero as the freezing point of the solution is approached. One might reason that this would indicate that a McConnell-type mechanism cannot be operative in these solutions since for this model the coefficients would be expected to increase with decreasing temperature (see References 57 and 59) and the separation into non-symmetrical components (e.g. $A_{||}$, $A_{\perp}$, $g_{||}$, $g_{\perp}$ if the system is axially symmetrical) would be expected upon freezing. While this argument is true to a certain extent and the temperature dependence of the coefficients of the equation in n_I does cause us to doubt the applicability of the McConnell mechanism to these solutions, the experimental behavior does not rule out this possibility. The reason for this is that an increase in the coefficients of the n_I -dependent relaxation equation implies a decrease in the correlation time of the motion averaging the anisotropic hyperfine and g-tensor interactions. In cases where the McConnell mechanism is operative the usual averaging process is the tumbling of the paramagnetic microcrystal (central ion, immediate co-ordinated ligands, and more distant but nevertheless oriented secondary solvation layers). In these cases the coefficients will be proportional to the viscosity of the solution and for normal solvents

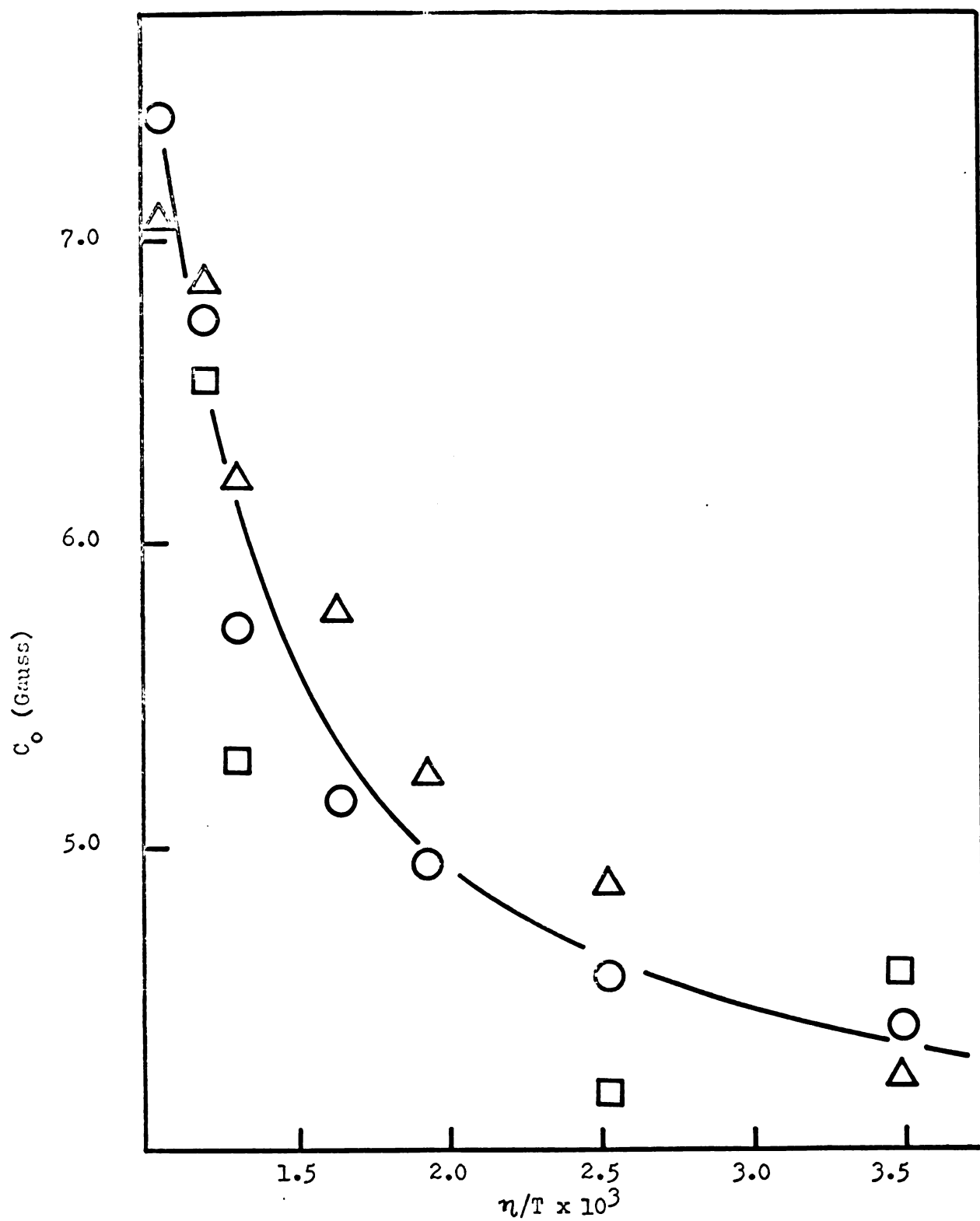


Figure 23a. Variation of the residual linewidth (C_o) with η/T : Cs in EtNH_2 . Results are shown for three different sample preparations.

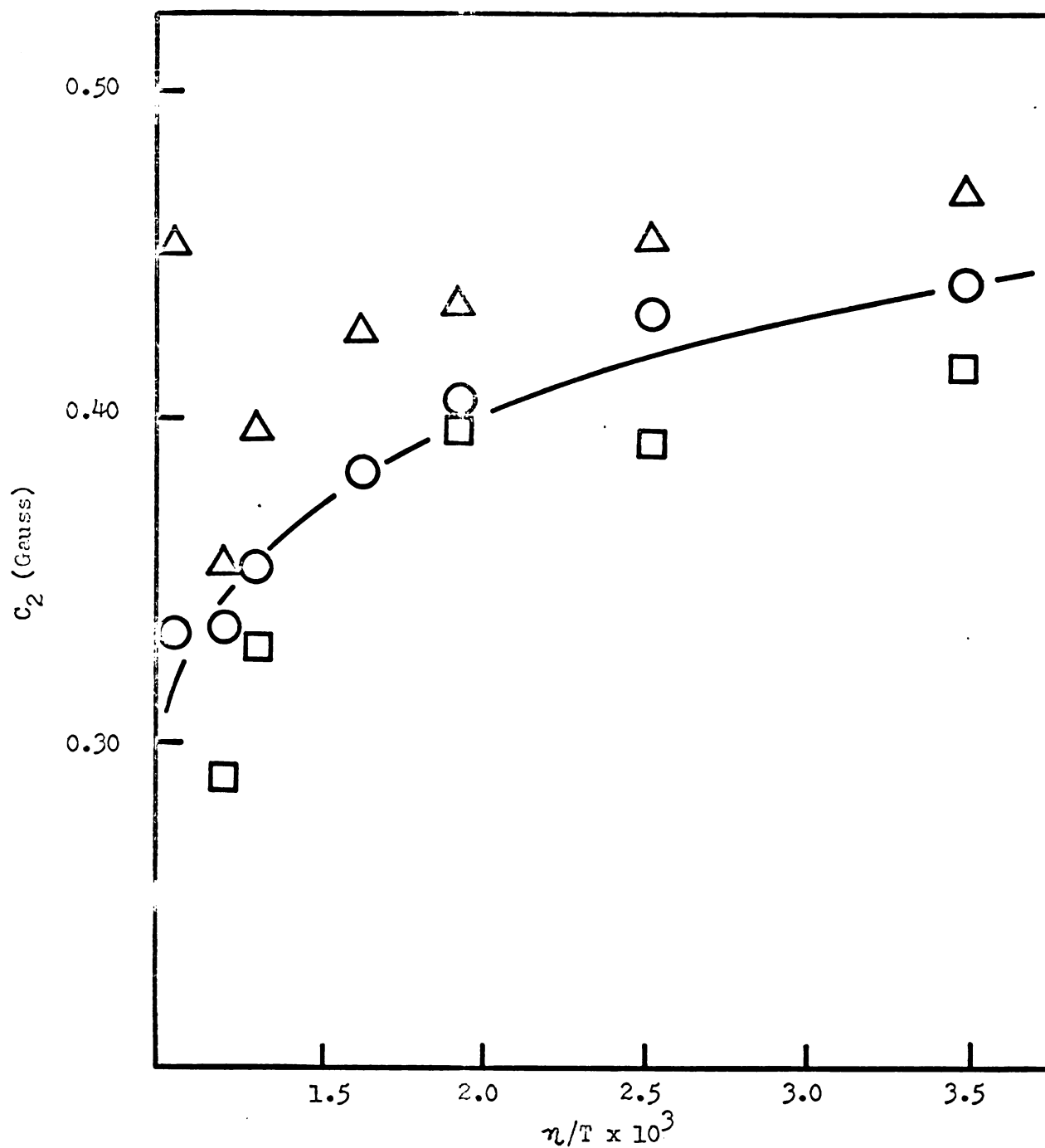


Figure 23c. Variation of the coefficient of m_I^2 (C_2) with n/T : Cs in EtNH_2 . Results are shown for three different sample preparations.

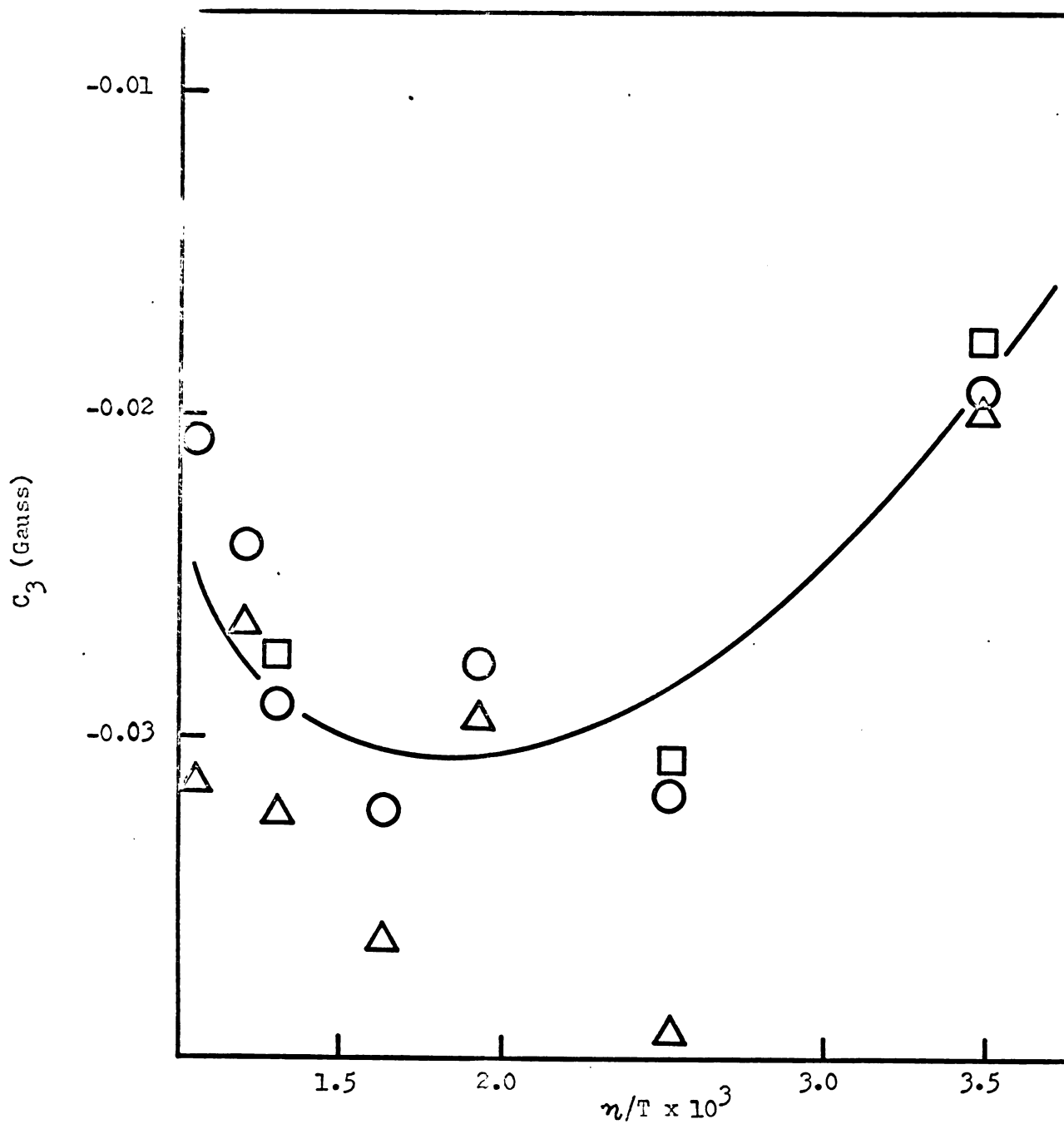


Figure 23d. Variation of the coefficient of m_I^3 (c_3) with n/T : Cs in EtNH₂. Results are shown for three different sample preparations.

would be expected to increase with decreasing temperature. Actually, however, the asymmetric microcrystalline unit can also experience modulation of the A and g tensor asymmetries through lattice vibrations, magnetic interactions (e.g., exchange) with other paramagnetic substances, and through a rotation of the central metal atom or ion with respect to the remainder of the microcrystal.

Thus, although the temperature dependence of the coefficients cannot arise from the tumbling of an asymmetric monomeric species, it is possible that a McConnell mechanism involving some other form of symmetry modulation could result in the observed dependence upon n_1 .

It is highly unlikely, however, that the weak interactions anticipated between an alkali metal monomer and the amine solvent could result in the large asymmetries required by this model.

It may also be observed that the strong temperature dependence of the hyperfine and spin-orbit coupling would not be expected for a single asymmetric species.

In concluding our discussion of the McConnell mechanism it should be noted that for materials in which this mechanism is operative, one cannot use the equation of Bloembergen, Purcell, and Pound (92,109) to relate T_2 to T_1 quantitatively. This is because, although the spin-lattice relaxation effect (T_1) alone would be expected to give the usual Lorentzian curve, the transverse relaxation due to the anisotropies of the hyperfine and Zeeman tensor, T_2' , is expected to give quite unsymmetrical broadening since, in the limiting case of a perfectly rigid glass the resonance would be extremely unsymmetrical. Thus we must relate T_2 and T_1 by the following relationship

$$\frac{1}{T_2} = \frac{1}{T_2'} + \frac{1}{T_1}$$

As this relation indicates the shorter the correlation time of the process modulating the anisotropies the more the observed line shape will approach a Lorentzian curve.

In metal-anion solutions showing n_I -dependent relaxation the resonances were more closely approximated by a Gaussian shape function.

The Equilibrium Model

For concreteness, let us first consider a particularly simple example of the time-dependent variation in hyperfine splitting: suppose that the radical can exist in only two forms, A and B, and that these are in rapid equilibrium with each other. A model such as this is a reasonable representation, for example, of the nitrobenzene anion radical when it is prepared by reduction of nitrobenzene with potassium (76). The ion-pair complex between the radical anion and the alkali-metal cation can be represented by Form A and the uncomplexed radical anion by Form B. If Form A could be isolated and were not undergoing transitions to Form B, a nucleus of spin I with hyperfine splitting A_A would give rise to an EPR spectrum of $2I + 1$ equal-intensity lines with a constant inter-line spacing A_A . Similarly, Form B would give a spectrum of $2I + 1$ lines with spacing A_B . Each line in the two spectra corresponds to a particular value of the quantum number m_I specifying the field-direction component of the nuclear spin angular momentum.

When the two forms are interchanging rapidly, an average of the two spectra is obtained which consists of $2I + 1$ lines with a mean splitting

$$\bar{A} = p_A A_A + p_B A_B$$

where p_A and p_B are the probabilities of finding Forms A and B, respectively.

This result for the mean hyperfine splitting follows from the general relaxation-matrix theory (110) and also from the Bloch equations (93) as modified to include the effects of exchange (111). In the Bloch-equation formulation, lines which appear at (angular) frequencies $\omega_A(m_I)$ and $\omega_B(m_I)$ in the spectra of the two isolated forms coalesce, in the limit of fast exchange, to an average frequency

$$\omega(m_I) = p_A \omega_A(m_I) + p_B \omega_B(m_I) \quad (40)$$

It is important to note that we consider a particular paramagnetic species in Form A with nuclear-spin quantum number m_I in equilibrium with a Form B of the same nuclear spin quantum number m . Effects which cause nuclear-spin transitions can thus not be treated by use of the Bloch formulation.

It can be shown that for rapid interchanges the contribution to the transverse relaxation time, T_2 , from the modulation of the isotropic hyperfine interaction is inversely proportional to the mean-square fluctuation in splitting (80,110),

$$\begin{aligned} \langle (\delta A)^2 \rangle &= \langle [A(t) - \bar{A}]^2 \rangle \\ &= p_A (A_A - \bar{A})^2 + p_B (A_B - \bar{A})^2 \\ &= p_A p_B (A_A - A_B)^2 \end{aligned} \quad (41)$$

The rates of the reactions also affect the widths, and if γ_A and γ_B are the lifetimes of Forms A and B, respectively, the widths are

$$\begin{aligned} T_2^{-1}(m_I) &= p_A T_{2A}^{-1} + p_B T_{2B}^{-1} + \gamma_0^2 \gamma \langle (\delta A)^2 \rangle m_I^2 \\ &= p_A T_{2A}^{-1} + p_B T_{2B}^{-1} + \gamma_0^2 \gamma p_A p_B (A_A - A_B)^2 m_I^2 \end{aligned} \quad (42)$$

where γ_0 = the electron gyromagnetic ratio and

$$\gamma = \gamma_A \gamma_B / (\gamma_A + \gamma_B) \quad \text{and}$$

T_{2A}^{-1} and T_{2B}^{-1} , the contribution to the widths from other line-

-broadening mechanisms, is assumed to be independent of m_I . The quantity $T_2(m_I)$ is the transverse relaxation time for the line corresponding to the nuclear-spin quantum number m_I . The shape of each line is Lorentzian and given by (on an angular frequency basis)

$$I_{m_I}(\omega) = [T_2(m_I)/\pi] \{1 + T_2^2(m_I) [\omega - \bar{\omega}(m_I)]^2\}^{-1} \quad (43)$$

In magnetic field units, the width is

$$[\omega(m_I) - \omega_0(m_I)]_{\frac{1}{2}} = [|\gamma_0| T_2(m_I)]^{-1}.$$

This is the half-width at half-maximum intensity, and is related to the separation of the extrema in the first derivative spectrum by

$$\delta_F = (2/\sqrt{3}) [\omega(m_I) - \omega_0(m_I)]_{\frac{1}{2}}.$$

The above equations result from the Bloch-equation formalism, according to which the widths are

$$T_2^{-1}(m_I) = T_2^{-1}(0) + \gamma \langle [\delta \omega(m_I)]^2 \rangle \quad (44)$$

where for two species undergoing exchange

$$T_2^{-1}(0) = p_A T_{2A}^{-1} + p_B T_{2B}^{-1}$$

and

$$\langle [\delta \omega(m_I)]^2 \rangle = p_A p_B [\omega_A(m_I) - \omega_B(m_I)]^2$$

Fraenkel (80) has shown that the relaxation-matrix gives the same results for this simple two-jump model. Since this is also applicable to much more complicated situations (such as an equilibrium involving many states or a distribution) we shall briefly review this treatment. To understand the method of calculation, several new quantities have to be introduced. The fluctuations in hyperfine splittings enter through a correlation function

$$g(t') = \gamma_0^2 \langle [A(t) - \bar{A}] [A(t + t') - \bar{A}] \rangle \quad (45)$$

which is a time average of the product of deviations in hyperfine splittings at time t , $[A(t) - \bar{A}]$, and at time $t + t'$, $[A(t + t') - \bar{A}]$. The linewidths are related to this correlation function through its Fourier cosine transform,

$$j(\omega) = \int_0^\infty g(t') \cos \omega t' dt', \quad (46)$$

in which, when only secular terms are significant, $\omega = 0$. Finally, the linewidths are given by (110)

$$\tau_2^{-1}(m_I) = j(0)m_I^2 + \tau_2^{-1}(0) \quad (47)$$

As an illustration of the procedure for evaluating the correlation function, we again treat the simple two-jump model considered above. The reaction between Forms A and B is



and the differential equation for the mole fraction of A, X_A , is

$$dX_A/dt = -k_A X_A + k_B X_B$$

The solution of this equation is

$$X_A(t) = p_A + [X_A(0) - p_A] \exp(-t/\tau),$$

where

$$\tau = \tau_A \tau_B / (\tau_A + \tau_B) \quad \text{with } \tau_A = k_A^{-1}, \tau_B = k_B^{-1}, \text{ and}$$

$$p_A = X_A(\infty) = k_B / (k_A + k_B) = \tau_A / (\tau_A + \tau_B).$$

Thus, the probability that Species A at time $t = 0$ will still be in Form A at time $t \geq 0$ is given by

$$P(A/A, t) = p_A + p_B \exp(-t/\tau)$$

while the probability that it will be in Form B at time t is

$$P(A/B, t) = p_B [1 - \exp(-t/\tau)],$$

with similar expressions if the paramagnetic species is initially in Form B.

The correlation function becomes

$$\begin{aligned} \gamma_0^{-2} g(t') &= \sum_{\mu} p_{\mu} [A(\mu) - \bar{A}] \sum_{\nu} P(\mu/\nu, t') [A(\nu) - \bar{A}], \\ &= p_A [p_A + p_B \exp(-t'/\tau)] (A_A - \bar{A})^2 \\ &\quad + p_B [p_B + p_A \exp(-t'/\tau)] (A_B - \bar{A})^2 \\ &\quad + 2p_A p_B [1 - \exp(-t'/\tau)] (A_A - \bar{A})(A_B - \bar{A}) \\ &= p_A p_B (A_A - A_B)^2 \exp(-t'/\tau) \end{aligned}$$

The Fourier transform of $g(t')$ is thus

$$j(\omega) = \gamma_0^2 \tau (1 + \omega^2 \tau^2)^{-1} p_A p_B (A_A - A_B)^2 \quad (49)$$

Substituting this expression into Eq. 47 gives Eq. 42.

The relaxation-matrix procedure is readily extended to quite general types of motion modulation as, for example, complicated jump mechanisms and models in which the hyperfine splitting is a continuously varying function of the time (77,78,79,110). It is also a rigorous theory which is limited only by the requirement that the motion has to be sufficiently rapid when compared to the magnitude of the fluctuations in splittings [$\tau^2 \gamma_0^2 \langle (\delta A)^2 \rangle \ll 1$], and shows that a result of the form of Eq. 47 is valid without recourse to specific models for the calculation of the spectral density $j(0)$.

The Bloch equations can also be employed for simple jump models of the type considered above when the characteristic times are long. In the limit of very long times, the results can be simply expressed, but in the intermediate region, detailed numerical computations of

the spectra are required (111,112,113). For example, at long times the two-jump model reduces to two superimposed spectra each of $2I + 1$ lines. The spectrum with hyperfine splitting A_A has relative intensity p_A , while the one with splitting A_B has relative intensity p_B . The widths in the spectrum from Form A are

$$\tau_{2A}^{-1}(m_I) = \tau_{2A(\infty)}^{-1}(m_I) + \gamma_A^{-1}$$

with a similar expression for the spectrum from B, where $\tau_{2A(\infty)}^{-1}(m_I)$ is the width in the absence of reaction between the two forms. As the rates increase, the lines begin to coalesce as well as to broaden.

The nuclear spin-dependent relaxation observed in metal-amine solutions appears to be characterized by two equilibria involving three species. Above ambient temperatures the linewidth variation appears to be determined by an atom-monomer equilibrium, while at lower temperatures a monomer-ion pair equilibrium is effective in accounting for the nuclear spin-dependent relaxation.

A difficulty in treating the atom-monomer equilibrium arises from the fact that the splittings of potassium atoms, and of rubidium and cesium atoms and monomers are sufficiently large that the high field approximation breaks down. Hence frequencies of the hyperfine lines as obtained from the Breit-Rabi formula (83) or from the expansion of Fessenden and Schuler (84) should be used with Eq. 44.

At low temperatures the coefficient of the m_I^2 is the predominant higher order term in accord with the predictions of Eq. 44 and the monomer-ion pair equilibrium.

D. Nuclear Spin-Independent Relaxation

The effects of metal concentration, salt addition (e.g., KBr or K(EtNH)), and decomposition indicate that spin exchange processes involving M^+ and the species giving rise to the optical absorption at 650 to 725 $\text{m}\mu$ are particularly important in determining the residual or nuclear spin-independent linewidths. Under certain conditions spin exchange processes involving the solvated electron and solvent exchange can result in a slight contribution to linewidths.

APPENDIX I

In order to perform the molecular orbital calculation of metal-solvent bonding coefficients we need to know the energy separation, E^A , between the ground and excited state molecular orbital energy levels and the spin-orbit coupling constants of the orbitals of the ground-state wavefunction which we have constructed. In the simple M.O. treatment the ΔE^A 's must be obtained from experiment. We have obtained approximate values of ΔE^A by comparison of vapor phase and solution spectra of the atomic and dimeric transitions of the alkali metals. This treatment is summarized in Table XIV. The spin-orbit coupling constants of the orbitals used in forming the ground state wavefunction of the solvated species were obtained from Reference 120. These together with the necessary E^A are given in Table XVI. The E 's calculated at 23°C are given in Table XVII.

TABLE XXV. Optical Absorptions of M , M_2 , and e^- in the Vapor Phase and in Solution (in cm^{-1})

$P \leftarrow S$ Transition for M in gas phase

K	Rb	Cs
13,017.5	12,700.2	11,451.7

${}^1\Sigma_\mu^+ \leftarrow {}^1\Sigma_g^+$ Transition for M_2 in gas phase

K_2	Rb_2	Cs_2
11,670.9	11,190	10,100

${}^1\Pi_\mu^+ \leftarrow {}^1\Sigma_g^+$ Transition for M_2 in gas phase

K_2	Rb_2	Cs_2
15,369.2	12,700.2	11,451.7

${}^1\Pi_\mu^+ \leftarrow {}^1\Sigma_g^+$ Transition for M_2 in solution

K_2	Rb_2	Cs_2
11,834	11,236	9709

${}^1\Sigma_\mu^+ \leftarrow {}^1\Sigma_g^+$ Transition for M_2 in solution

K_2	Rb_2	Cs_2
8,340*	7,768*	6,769*

(Pseudo) $P \leftarrow$ (Pseudo) S Transition for M in solution

K	Rb	Cs
9,686*	9,278*	8,120*

*Predicted from analogy with shift of ${}^1\Pi_\mu^+ \leftarrow {}^1\Sigma_g^+$ upon solvation of dimer.

TABLE XVI. Parameters used in Molecular Orbital Calculation.

Solvated Electron

$$\Delta g = -0.0004$$

$$\Delta E^a = 7.813 \text{ cm}^{-1}$$

$$\xi(H)_{\text{solvent}} = 4.57 \text{ cm}^{-1}$$

Ion-Pair

$$\Delta g(\text{assumed}) = -0.0004$$

$$\Delta E^a(\text{assumed}) = 7.813 \text{ cm}^{-1}$$

$$\xi(H)_{\text{solvent}} = 4.57 \text{ cm}^{-1}$$

Lithium

$$\Delta g = -0.0004$$

$$\Delta E^a = 11.169 \text{ cm}^{-1}$$

$$\xi(H)_{\text{solvent}} = 4.57 \text{ cm}^{-1}$$

$$\xi(2p)_{Li} = 0.509 \text{ cm}^{-1}$$

Sodium

$$\Delta g = -0.0008$$

$$\Delta E^a = 9.696 \text{ cm}^{-1}$$

$$\xi(H)_{\text{solvent}} = 4.57 \text{ cm}^{-1}$$

$$\xi(3p)_{Na} = 25.78 \text{ cm}^{-1}$$

Potassium

$$\Delta g = -0.0008$$

$$\Delta E^a = 9.656 \text{ cm}^{-1}$$

$$\xi(H)_{\text{solvent}} = 4.57 \text{ cm}^{-1}$$

$$\xi(4p)_K = 86.54 \text{ cm}^{-1}$$

$$\xi(3d)_K = 1.95 \text{ cm}^{-1}$$

Rubidium

$$\Delta g = -0.0025$$

$$\Delta E^a = 9.278 \text{ cm}^{-1}$$

$$\xi(H)_{\text{solvent}} = 4.57 \text{ cm}^{-1}$$

$$\xi(5p)_{Rb} = 221 \text{ cm}^{-1}$$

$$\xi(4d)_{Rb} = 1 \text{ cm}^{-1}$$

Cesium

$$\Delta g = -0.0075$$

$$\Delta E^a = 8.120 \text{ cm}^{-1}$$

$$\xi(H)_{\text{solvent}} = 4.57 \text{ cm}^{-1}$$

$$\xi(6p)_{Cs} = 637 \text{ cm}^{-1}$$

TABLE XXVII. Calculated Values for $\bar{E}$ at 27°C for Species Present in Metal-amine Solutions.

<u>Species</u>	<u>$\bar{E}$</u>
Solvated electron	0.11
Ion-pair	0.11
Li	0.16
Na	0.15
K	0.07
Rb	0.09
Cs	0.09

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