

Paramagnetic Resonance Absorption in Solutions of K in Liquid NH₃*

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SOLUTIONS OF METALS IN NH₃

THE alkali metals and the alkaline earth metals dissolve readily in liquid NH₃.¹⁻⁵ The solubilities⁴ of Na and K at the boiling point of NH₃, -33.4°C, are about 5.4 and 4.9 mol l⁻¹, respectively, and the solubility changes very little with temperature. The concentrated solutions have the color of bronze and a metallic luster. The more dilute solutions are blue, the absorption spectrum of the dilute solutions of all the alkali metals being identical.⁶ When the solvent is evaporated, the pure alkali metals remain as residues. (Reaction of the metal with the solvent will occur at varying rates depending upon temperature, impurities, etc., but in the absence of impurities the solutions contained in Pyrex glass at room temperature are quite stable enough to make possible a variety of measurements of physical properties.) A study of the vapor pressure⁷ as a function of concentration shows the nonexistence of compounds in the freshly prepared solutions of the alkali metals.

One of the striking properties of such solutions is their electrical conductivity.⁸⁻¹¹ The conductivity is shown in Fig. 1. At all concentrations the equivalent conductivity is greater than that of any known salt in any known solvent. In the most dilute solutions the equivalent conductance reaches a limiting value of approximately 1000 ohm⁻¹ cm² mol⁻¹ which is three times that of the best conducting salts in liquid NH₃. Even more remarkable is the behavior of the conductivity at the higher concentrations. A saturated solution of K in NH₃ has a conductivity of approximately 4500 ohm⁻¹ cm⁻¹. This may be compared with the conductance of Hg at 20°C, which is 10 400, and it is seen that these solutions have a conductivity of the same order as that of metals. The conductances of the

solutions of the various alkali metals in liquid NH₃ agree very closely at all concentrations. Both electromotive force and conductance studies lead to the conclusion that in the most dilute solutions of sodium the speed of the negative charge carrier is about 7 times that of the positive charge carrier. When the concentration is increased, the equivalent conductance decreases, passes through a minimum at about 0.04 M, and then increases to the enormous values already mentioned. In the concentrated solutions the speeds of the negative carriers approach those of the electrons in metals.

One is led to the conclusion that when any of the alkali metals is dissolved in NH₃ there is a dissociation into positive alkali metal ions and electrons. The negative charge carrier is apparently the electron in each case. In the dilute solutions the electrons are evidently bound not too tightly in some way to the solvent molecules. In the concentrated solutions the electrons are much less tightly bound and move in much the same manner as in metals. In such solutions we have the possibility of examining the properties of electrons over a range of concentrations varying by a factor of 10⁴ to 10⁵.

The behavior of the conductivity with concentration was interpreted by Kraus and his co-workers in terms of equilibria between sodium atoms, sodium ions, free electrons, and solvated electrons. Several lines of evidence lead to the discarding of such models. One of the clearest reasons for rejecting models involving the existence of large concentrations of alkali metal atoms or solvated electrons is a consideration of the results of studies of the static magnetic susceptibilities of such

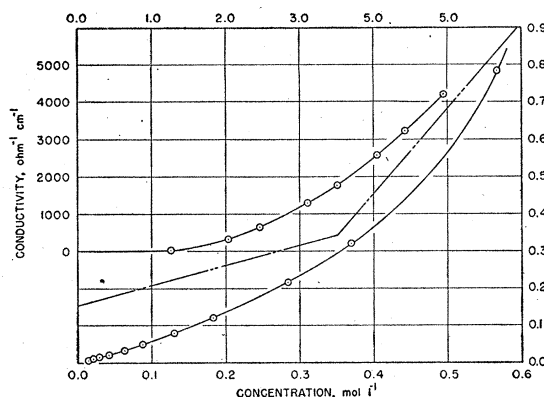


FIG. 1. Conductivity of K in NH₃ at NH₃ B. P. [C. A. Kraus, J. Am. Chem. Soc. 43, 755 (1921)].

* This research was assisted by the U. S. Office of Naval Research.

¹ C. A. Kraus, J. Franklin Inst. 212, 537 (1931).

² C. A. Kraus, *The Properties of Electrically Conducting Systems* (Chemical Catalog Company, New York, 1922.)

³ D. M. Yost and H. Russell, *Systematic Inorganic Chemistry* (Prentice-Hall, Inc., New York, 1944), p. 136.

⁴ W. C. Johnson and A. W. Meyer, Chem. Rev. 8, 273 (1931).

⁵ W. C. Fernelius and G. W. Watt, Chem. Rev. 20, 195 (1931).

⁶ Gibson and Argo, J. Am. Chem. Soc. 40, 1327 (1918).

⁷ Kraus, Carney, and Johnson, J. Am. Chem. Soc. 49, 2206 (1927).

⁸ C. A. Kraus, J. Am. Chem. Soc. 437, 49 (1921).

⁹ C. A. Kraus and W. W. Lucasse, J. Am. Chem. Soc. 43, 2529 (1921).

¹⁰ C. A. Kraus and W. W. Lucasse, J. Am. Chem. Soc. 45, 2551 (1923).

¹¹ G. E. Gibson and T. E. Phipps, J. Am. Chem. Soc. 48, 312 (1926).

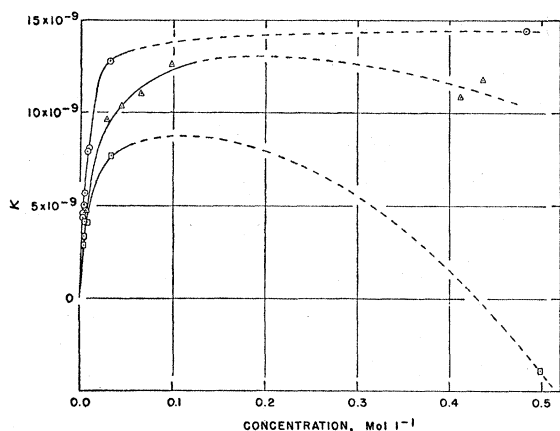


FIG. 2. Magnetic susceptibilities of solutions of alkali metals in liquid NH_3 (see reference 12). \circ K at 240°K. \square K at 220°K (see reference 13). \triangle Na at 238°K.

solutions.^{12,13} If such species existed in large numbers, the solutions would be paramagnetic and their susceptibilities would obey Curie's law with respect to variation of temperature and concentration. This type of behavior is not observed. The experimental measurements of the static susceptibilities are shown in Figs. 2, 3, and 4. In the very concentrated solutions and down to a few tenths normal, the susceptibility is quite small of the order found in the metal and has a very small temperature coefficient. As the concentration is lowered, the molar susceptibility increases rapidly and approaches in the most dilute solutions the value for one mol of spins. This is the general qualitative type of behavior to be expected if the electrons are free or in a periodic potential as in a metal. Under such conditions they would at high concentrations form a degenerate Fermi gas with most of the electrons paired and not contributing to the paramagnetism. At the lower concentrations, however, the degeneracy would be removed and the susceptibility would be of the order of that of a mol of spins. Hence, in this particular respect the solutions behave much as would be expected for a metal in which the concentration of electrons could be varied over a very wide range.

With respect to both conductivity and magnetic susceptibility the behavior is not in detail like that of metals. For example, the temperature coefficient of the conductivity is positive at all concentrations.^{10,11} Also the magnetic susceptibility is considerably lower than that calculated for a free electron gas,^{13a} and at all concentrations investigated the susceptibility increases with increasing temperature.¹² Various attempts have been made to account for this behavior of the susceptibility. Huster¹³ suggested an equilibrium between electrons and Na ions, on the one hand, and diatomic

molecules on the other. The necessary molecular concentrations are, however, in disagreement with the apparent molecular weight measurements of Kraus.¹⁴ Freed and Sugarman¹² have proposed a decrease of density of energy levels near the top of the Fermi distribution because of the binding of the electron in a variety of resonance structures involving NH_3 molecules and solvated metal ions. This would result in a reduction of the magnitude of the susceptibility. They also proposed that there are pairwise interactions between electrons similar to those which lead to the F' centers in crystals in which two electrons are trapped in a single vacancy.¹⁵ These pairs would be expected to be diamagnetic and would thus lead to lowered susceptibilities. In particular they might be responsible for the increase of susceptibility with increasing temperature. Ogg¹⁶⁻¹⁸ has discussed in some detail the formation of F' -like centers. He proposes that individual electrons are trapped in cavities which they create in the solution and are in equilibrium with pairs of electrons similarly trapped. He believes that he can account for the behavior of several physical properties, including the magnetic susceptibility on the basis of such an equilibrium. Moreover, he believes that the cavities are very large, and that as a consequence of this there is an extraordinarily large diamagnetic contribution to the susceptibility.

EXPERIMENTAL METHODS

Some time ago we observed paramagnetic resonance absorption in solutions of K in liquid NH_3 at microwave frequencies.¹⁹ Observations of the resonance have also been made by Garstens and Ryan²⁰ and by Levinthal,

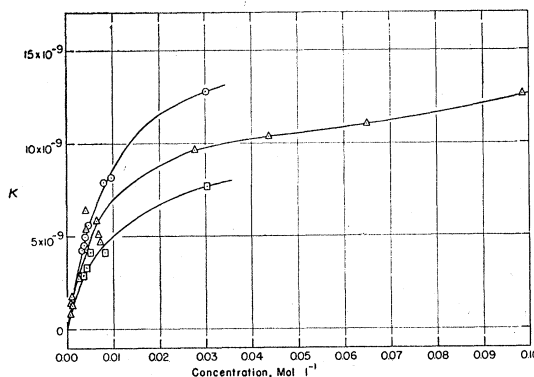


FIG. 3. Magnetic susceptibilities of solutions of alkali metals in liquid NH_3 (see reference 12). \circ K at 240°K. \square K at 220°K (see reference 13). \triangle Na at 238°K.

¹⁴ C. A. Kraus, *J. Am. Chem. Soc.* **30**, 1197 (1908).

¹⁵ F. Seitz, *Revs. Modern Phys.* **18**, 384 (1946).

¹⁶ R. A. Ogg, *J. Chem. Phys.* **14**, 114 (1946).

¹⁷ R. A. Ogg, *J. Chem. Phys.* **14**, 295 (1946).

¹⁸ R. A. Ogg, *J. Am. Chem. Soc.* **68**, 155 (1946).

¹⁹ C. A. Hutchison, Jr., and R. C. Pastor, *Phys. Rev.* **81**, 282 (1951).

²⁰ Martin A. Garstens and Alden H. Ryan, *Phys. Rev.* **81**, 888 (1951).

¹² S. Freed and N. Sugarman, *J. Chem. Phys.* **11**, 354 (1943).

¹³ E. Huster, *Ann. Physik* **33**, 477 (1938).

^{13a} N. F. Mott and H. Jones, *Theory of Properties of Metals and Alloys* (The Clarendon Press, Oxford, 1936), p. 184.

Rogers, and Ogg.²¹ The width of 0.1 gauss, which we initially reported, turned out to be caused largely by magnetic field inhomogeneities. Whereas the resonances in paramagnetic salts are generally several thousands of times this broad and must be studied at microwave frequencies, we have investigated this extremely sharp and consequently enormously intense resonance at low frequencies and field strengths where it was much simpler for us to produce a homogeneous field and measure the actual widths.

We have studied the paramagnetic resonance absorption in solutions of K in liquid NH₃ at frequencies in the range 5.5 to 8.2 mc sec⁻¹ corresponding to field strengths of 2.0 to 2.9 gauss. The static magnetic field was supplied by a solenoid which could be accurately aligned with the earth's field. The sample of K in liquid NH₃ was placed at the center of the solenoid in the coil of a regenerative oscillator-detector circuit. The magnetic field was modulated at 40 cycle sec⁻¹ by means of a small auxiliary coil. A phase sensitive detector was employed and its output was recorded on a recording potentiometer. The modulation amplitude was sufficiently small to insure a signal proportional to the first derivative of the absorption. The static magnetic field was varied linearly with time by means of a motor-driven potentiometer in the current supply circuit. The current through the solenoid was recorded on the same chart as the magnetic signal. A Watkins-Pound calibrator²² circuit was employed for determining signal intensities. With this device one may simulate the change in coil resistance produced by the magnetic signal by means of a changing plate resistance of a thermionic tube. One then employs the regenerative oscillator-detector-amplifier-recorder system to compare the magnetic signal with the calibrator signal produced when a 40 cycle sec⁻¹ signal of known magnitude is placed on the grid of the calibrator tube at known fixed plate current. The recorder chart was

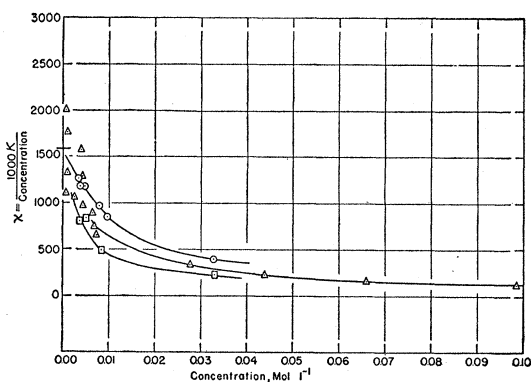


FIG. 4. Magnetic susceptibilities of solutions of alkali metals in liquid NH₃ (see reference 12). ○ K at 240°K. □ K at 220°K (see reference 13). △ Na at 238°K. The bar at 1564×10^{-6} denotes the value of the susceptibility of a mol of electron spins at 240°K.

²¹ Levinthal, Rogers, and Ogg, *Phys. Rev.* **83**, 182 (1951).

²² G. D. Watkins and R. V. Pound, *Phys. Rev.* **82**, 343 (1951).

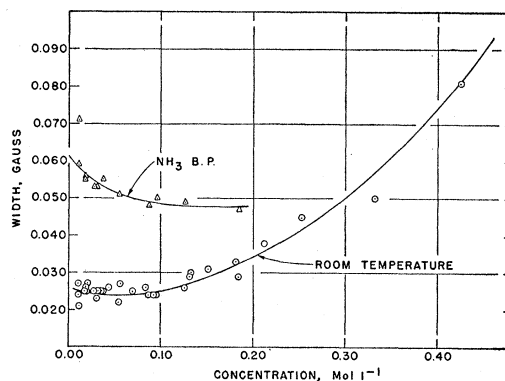


FIG. 5. Width of resonance at maximum slope vs concentration.

calibrated in terms of calibrator grid voltage immediately after each scanning of the magnetic resonance signal.

The samples of K in liquid NH₃ were prepared by distilling K several times in high vacuum and finally distilling it into Pyrex glass capsules. Then NH₃ dried by addition of K and subsequent distillation was added and the capsule sealed. The amount of K in these solutions was determined after completion of magnetic investigation by dissolving in H₂O and boiling to remove the NH₃. The resulting solution was titrated with standard acid. The weight of NH₃+K was determined by weighing the capsule before and after opening it.

Measurements were made at a room temperature of 28°C and at the boiling point of liquid NH₃ which is -33°C. For the low temperature runs the sample was immersed in a Dewar filled with liquid NH₃.

SPECTROSCOPIC SPLITTING FACTOR

The spectroscopic splitting factor for the solutions of K in liquid NH₃ was compared with the factor for 2,2-diphenyl-1-picrylhydrazyl^{19,23} at approximately 8.2 mc sec⁻¹. In the case of the solution of K in NH₃ the rf coil field strength was 0.0023 gauss rms. The shift of the center of the resonance under these conditions due to the Bloch-Siegert²⁴ effect is by the factor

$$1 - [(2H_1)^2 / 16H_0^2] = 1 - 1.6 \times 10^{-7},$$

and is consequently small enough to be neglected. Assuming the splitting factor for 2,2-diphenyl-1-picrylhydrazyl to be 2.0037^{19,23} (the microwave value), we find the factor at room temperature for K in NH₃ to be 2.0010 ± 0.0002 at 0.425 mol l⁻¹, and 2.0011 ± 0.0002 at 0.0365 mol l⁻¹. This is the same as the value 2.0012 ± 0.0002 found at 23 500 mc sec⁻¹.¹⁹ This factor is considerably lower than the value of the *g* factor, 2.0023, for a free electron spin. However, it is not nearly so low as the value 1.995,²⁵ which we have observed for additively colored crystals of KCl.

²³ Holden, Kittel, Merritt, and Yager, *Phys. Rev.* **77**, 147 (1950).

²⁴ F. Bloch and A. Siegert, *Phys. Rev.* **57**, 522 (1940).

²⁵ C. A. Hutchison, Jr., and G. A. Noble, *Phys. Rev.* **87**, 1125 (1952).

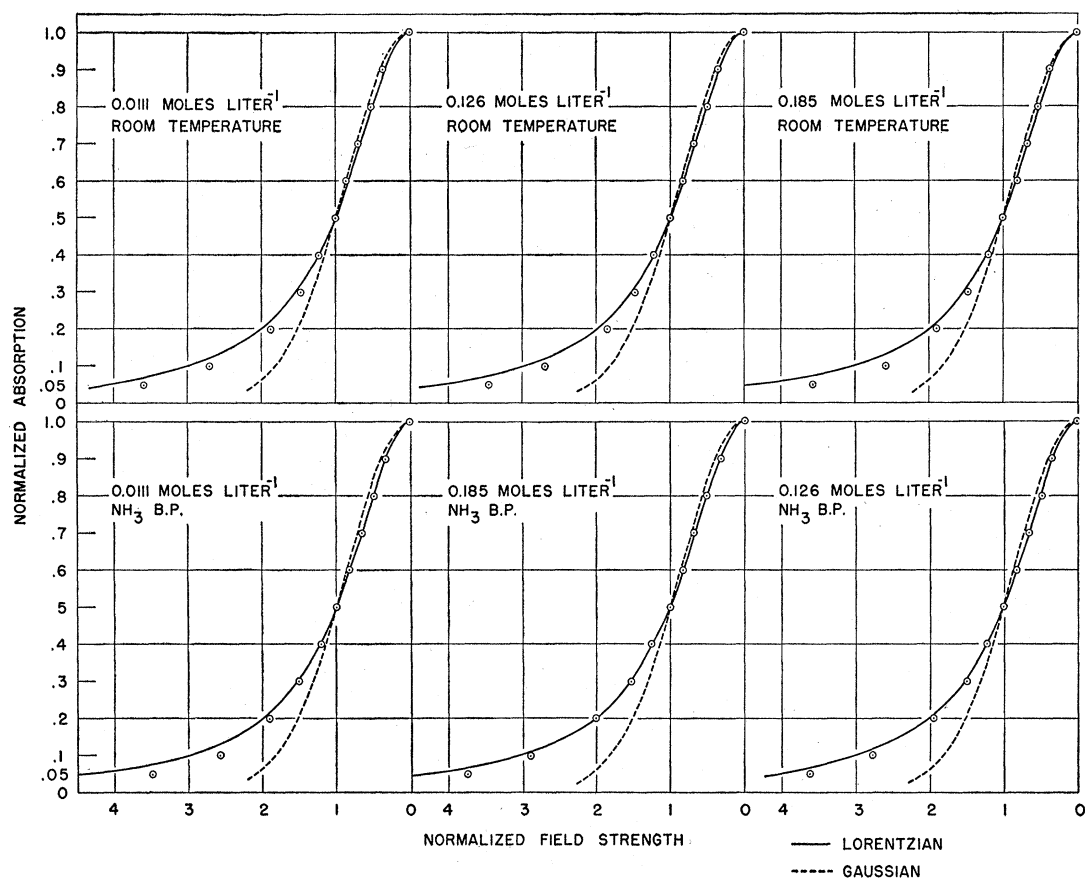


Fig. 6. Line shape.

WIDTH

The width of the resonance between the points of maximum slope was determined by measuring the distance between the maximum and minimum on the recorder chart which, when combined with the current record on the same chart, gave the width. The results are shown in Fig. 5. The width was measured at room temperature from a concentration of 0.425 down to 0.011 mol l⁻¹, and at the boiling point of NH₃ from 0.185 to 0.011 mol l⁻¹. It is clear that this resonance is by far the sharpest electronic resonance so far observed in a condensed phase. In the case of a resonance as sharp as this, one must consider the Rabi²⁶ width associated with the flipping of the spin by the perturbing rf magnetic field. This is approximated by

$$\Delta H/H = 4 \sin(\theta/2),$$

where ΔH is the width at half-height and where θ is given by

$$\theta = \tan^{-1} \frac{\text{rf field strength}}{\sqrt{2}H}. \dagger$$

²⁶ I. I. Rabi, Phys. Rev. **51**, 652 (1937).

† This is the rms field strength.

When θ is very small, as in our case,

$$\Delta H = \sqrt{2} \text{ rf field strength.}$$

For a sample whose concentration was 0.152 mol l⁻¹ the variation of width with rf field strength was investigated with the following results:

$\sqrt{2}$ rf field strength gauss	width at max slope gauss
0.0032	0.0311
0.0081	0.0327
0.0163	0.0335
0.0324	0.0388

It is clear that at the higher coil voltages the Rabi width is seriously interfering with observation of the true width. Consequently, all scannings of the resonance absorption were made at coil voltages corresponding approximately to the smallest rf field listed above, or about 0.05 volt. In the case of an organic free radical which is much wider than the K resonance there is, of course, no observable change of width with coil voltage.

The width of this resonance is several orders of magnitude less than that observed in aqueous solution

of paramagnetic salts of about the same concentrations. There is evidently an extraordinarily large exchange narrowing associated with the great mobility of the electrons in these solutions. The average value of β/r^3 (r is the distance between electrons) ranges from 0.06 to 2.6 gauss. The broadening by magnetic nuclei would be expected to be several gauss. At room temperature there is perhaps a slight increase in the width at the lowest concentrations, and the increase is marked at the lower temperature. This increase becomes pronounced in the vicinity of the region in which the susceptibility begins to rise rapidly with dilution. The room temperature measurements were extended to considerably higher concentrations than at the lower temperature, and there is apparently quite a large increase of width at the higher concentrations.

LINE SHAPES

The areas under the curves drawn by the recording potentiometer were obtained by numerical integration. The scale on the field strength axis was quite linear as determined from the current recording. The scale on the magnetic signal axis was quite linear in calibrator grid voltage. Moreover, it was found that the grid voltage at constant plate current was very close to being proportional to magnetic signal over the range employed in the experiments. This last was determined by comparing calibrator signals with magnetic signals of various sizes produced with an organic free radical by field modulation amplitudes of various sizes. It was consequently a simple matter to obtain the absorption curves with errors not greater than probably 5 percent. Some absorption curves were also determined using the Watkins-Pound RF Spectrometer.²² The results were indistinguishable from those obtained with the regenerative oscillator-detector. The regenerative oscillator-detector was employed in our investigations because of its much more favorable signal-to-noise ratio. The results of the investigation of the line shapes are shown in Fig. 6. The points are taken from the experimental curves. The line shapes of three samples over a range of concentrations and at both room temperature and the boiling point of NH_3 were compared with Gaussians and Lorentzians. It is clear that these absorptions correspond much more closely to the Lorentzian than to the Gaussian over most of the range of the absorption, but drop considerably below the Lorentzian in the wings of the curve.

INTENSITIES

A second numerical integration yielded the areas under the absorption curves. By means of the current and signal calibrations the relative areas under the absorption curves for the various samples could be obtained.

Since the static susceptibilities of the samples are related to the rf susceptibilities by the Kronig-Kramers

relation,

$$\chi = \frac{2}{\pi} \int_0^{\infty} \frac{\chi''(\nu)}{\nu} d\nu,$$

these second integrals afford a means of comparing the static susceptibilities of the spin systems. Our experiments are carried out at constant frequency and varying field strength. We may, however, for a sharp symmetrical absorption make the transformation of the above relation from the one type of experiment to the other and hence obtain static susceptibilities from our measurements of the rf susceptibilities. We must, of course, consider the changes in Q of the coil and the filling factors from sample to sample. We determined Q , ω , and C during each run. Filling factors were determined for each sample. The desired relationship is

$$\chi = \frac{2\beta}{\pi\xi\omega^2Ch} \int_0^{\infty} \frac{\Delta R}{R^2} dH,$$

where χ is the static susceptibility, β is the Bohr magneton, ξ is the filling factor, ω is the angular frequency, C is the capacity across the coil, h is Planck's constant, R is the rf resistance of the coil, and H is the field strength. The grid voltage of the calibrator is proportional to $\Delta R/R^2$. We replaced $\int_0^{\infty} (\Delta R/R^2) dH$ with the second integral of the recorder curves and employed a standard substance to eliminate the proportionality constant. The standard substance employed was tris-*p*-nitrophenylmethyl, a completely dissociated free radical in which resonance was first observed by Pake, Weissman, and Townsend.²⁷ A sample of this material was prepared and later assayed for us by Professor Weissman. We carried out scannings of the resonance of this material. The comparison of the second integrals of the curves so obtained with the similar ones for the K in liquid NH_3 enabled us to

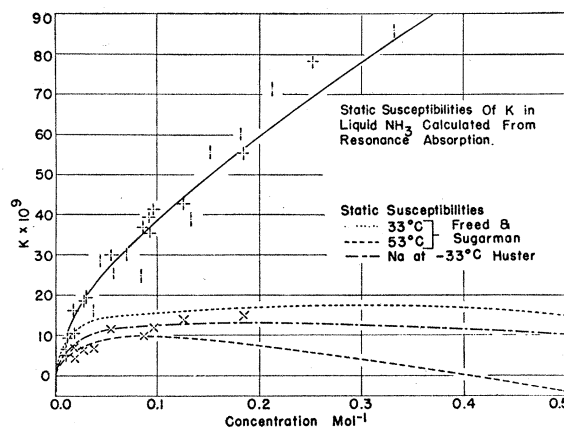


FIG. 7. Static susceptibilities of K in liquid NH_3 calculated from resonance absorption. + Room T. Series I, 28°C; | Room T. Series II, 26°C; x bp of NH_3 -33°C.

²⁷ Pake, Weissman, and Townsend, personal communication.

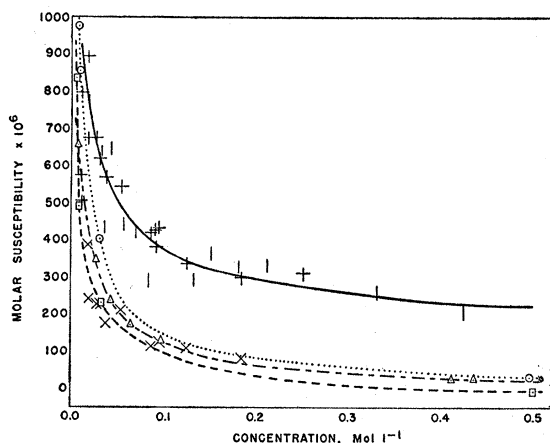


FIG. 8. Static susceptibilities of K in liquid NH_3 calculated from resonance absorption. + Room T. Series I, 28°C . | Room T. Series II, 26°C . X B.P. of $\text{NH}_3 - 33^\circ\text{C}$. $\cdots\cdots$ -33°C .; $-\cdot-\cdot-$ -53°C , Freed and Sugarman; $-\cdot-\cdot-$ Na at -33°C , Huster.

calculate static susceptibilities of the solutions relative to that of the organic compound. The free radical was assumed to have the static susceptibility of 1 mol of spins per mol of free radical at 28°C . The number of mols in the sample of organic free radical was known to approximately 5 percent.

The results of the susceptibility determinations are shown in Figs. 7 and 8. At room temperature the calculated static susceptibility is seen to follow the same sort of pattern as determined in static field experiments at low temperatures. The susceptibilities are considerably higher than those of the static experiments at the boiling point. Like the latter, they rise sharply with dilution at about the same concentration. The low temperature runs were made some time subsequent to the high temperature runs, and two

points have been omitted for the two lowest concentrations where some decomposition is known to have occurred. These two samples also give obviously low results at the higher temperatures. Some of the other points at the lower concentrations are probably suspect for the same reason. The points for the molar susceptibility at the higher concentrations at the lower temperature are in reasonably good agreement with the static field measurements. The resonance phenomenon is peculiar to the paramagnetic spins and is relatively unaffected by the diamagnetism. Consequently, such a comparison of static field measurements with static susceptibilities calculated from rf measurements enables one to detect the presence of any abnormal diamagnetic susceptibilities. It is clear that no abnormally large diamagnetism exists in these solutions at the boiling point of NH_3 at the concentrations investigated by both methods. Such determinations of static susceptibilities from rf measurements afford a powerful tool for a number of problems of chemical and physical interest where large amounts of diamagnetic material or abnormally large diamagnetisms of the paramagnetic species itself may obscure the primary effect. We have discussed this problem recently for the case of the detection of organic free radicals in solution.²⁸

ACKNOWLEDGMENT

We wish to thank Clarence Arnow for the design and construction of the electronic equipment used in these experiments; Jack Boardman for the numerical integrations and other computations; and Edward Bartal for the construction of the solenoid, low temperature apparatus, and other machine work.

²⁸ Hutchison, Kowalsky, Pastor, and Wheland, *J. Chem. Phys.* **20**, 1485 (1952).