

On the Nature of the Solutions of Metallic Sodium in Liquid Ammonia

Simon Freed and H. G. Thode

Citation: [The Journal of Chemical Physics](#) **7**, 85 (1939); doi: 10.1063/1.1750329

View online: <http://dx.doi.org/10.1063/1.1750329>

View Table of Contents: <http://scitation.aip.org/content/aip/journal/jcp/7/1?ver=pdfcov>

Published by the [AIP Publishing](#)

Articles you may be interested in

[Dielectric Properties of Liquid Ammonia and Sodium–Ammonia Solutions](#)

J. Chem. Phys. **50**, 4116 (1969); 10.1063/1.1671679

[Dynamic Polarization in Solutions of Sodium in Liquid Ammonia](#)

J. Chem. Phys. **48**, 2389 (1968); 10.1063/1.1669456

[Salt Effect in MetalAmmonia Solutions: Sodium Chloride in SodiumAmmonia Solution at \$-33^{\circ}\text{C}\$](#)

J. Chem. Phys. **35**, 1820 (1961); 10.1063/1.1732151

[Solutions of Metals in Amine Solvents. II. A Conductance Function for Dilute Solutions of Sodium in Liquid Ammonia](#)

J. Chem. Phys. **30**, 61 (1959); 10.1063/1.1729944

[Solutions of Sodium in Liquid Ammonia](#)

J. Chem. Phys. **21**, 52 (1953); 10.1063/1.1698621



On the Nature of the Solutions of Metallic Sodium in Liquid Ammonia*

SIMON FREED, *University of Chicago, Chicago, Illinois*

AND

H. G. THODE, *Columbia University, New York, New York*

(Received November 29, 1938)

THE recent conclusion of F. Krüger¹ that solutions of sodium in liquid ammonia are colloidal and that therefore the interpretations of the magnetic measurements² require revision appears to us as untenable. That the solutions which Krüger prepared were colloidal, for a time, there can be little doubt. One would scarcely expect them to have been other than turbid from the manner he used to prepare them. Dropping a piece of sodium with a pair of pincers into a vessel and pouring in liquid ammonia must certainly lead to the formation of insoluble sodium hydroxide because of the moisture in the atmosphere. Sodium hydroxide admittedly acts as a catalyst for the decomposition of ammonia and the insoluble sodium amide results. The presence of these insoluble substances in fine suspension can account for Krüger's observations in the ultramicroscope.³ However, it would appear unnecessary to speculate at length on what happens when metals are dissolved in liquid ammonia without those precautions which experimentation during the last fifty years has found indispensable.⁴

While we need not appeal to the magnetic behavior of these solutions to dispose of the assumption that they are colloidal (the strong lowering of the vapor pressure produced by dissolving sodium seems sufficient evidence against that assumption), we shall take this occasion to discuss the nature of these solutions in the light of the magnetic data. At 0.47 *N* the atomic susceptibility of sodium is about equal to that of solid sodium. This fact is consistent with the assumption of a colloidal solution. However, it is also consistent with the model of a free electron gas obeying the Fermi-Dirac statistics. On dilution, the atomic susceptibility increases continuously until at 0.0021 *N*, it is about one hundred times as great as at 0.47 *N*, that is, about two-thirds of the magnitude to be expected if the sodium is dispersed into independent "atomic" or "electronic" magnets distributed according to classical statistics. A further dilution did not increase the susceptibility per gram atom given by the 0.0021 *N* solution. This two-third value seems to have theoretical significance because the diamagnetism of free electrons cancels one-third of the paramagnetic susceptibility as Landau⁵ has shown, and there-

* Publication assisted by the Ernest Kempton Adams Fund for Physical Research of Columbia University.

¹ F. Krüger, *Ann. d. Physik* **33**, 265 (1938).

² S. Freed and H. C. Thode, *Nature* **134**, 774 (1934); see also E. Huster and E. Vogt, *Physik. Zeits.* **38**, 1004 (1937).

³ The color of the colloid first observed may have been conditioned by the sodium absorbed, occluded, or dissolved by the solid sodium amide or hydroxide. It is well known that alkali metals dissolve in molten sodium hydroxide and that sodium halides in the crystalline state absorb sodium vapor. The change in color with time may have been caused by the coagulation into bigger particles and also by the reaction of the sodium in the particles with the solvent. The inability of the solution to pass through the ultra-membrane filter as blue may have been due to the reaction of the sodium with the filter during the long time required for passage.

⁴ For example, the solutions employed for our magnetic measurements were made entirely in a vacuum line. The tube in which the solution was to take place was flamed in a high vacuum (from 10^{-8} to 10^{-6} mm Hg). In this tube was condensed liquid ammonia which had been rigorously dried and twice distilled from sodium. The ammonia was then evaporated and the tube was flamed again at the high vacuum. This contact of the tube with liquid am-

monia was to displace moisture in the glass. Connected to the tube was a capillary which was likewise flamed, pumped, etc., and to this capillary was joined another vessel containing sodium. The sodium was melted in a high vacuum to fill part of the capillary and then forced through the capillary to remove the nonmetallic hydroxide, etc., a procedure which is astonishingly efficient in producing bright metallic sodium in a high vacuum. The sodium was sent through the capillary by permitting propane gas (previously dried with sodium) at a pressure of several centimeters mercury to enter the vessels in which the sodium was melted. The capillary was then sealed off and liquid ammonia which had been twice distilled from sodium was condensed on the clean sodium. The solution was stirred with a glass tube in which a small iron rod had been sealed to permit movement by a magnet on the outside.

The solutions thus prepared scarcely changed their composition in metallic sodium in a week. Krüger's solutions seem to have greatly changed in several minutes. His most stable solution was decomposed (entirely?) in about fifteen hours.

⁵ L. Landau, *Zeits. f. Physik* **64**, 629 (1930).

fore the full freedom of the elementary magnets is actually accounted for. The independence of the elementary magnets (and incidentally the noncolloidal nature of the solutions) is confirmed further by the temperature coefficient of the susceptibilities. At the greater concentrations, the susceptibility drops with decreasing temperature but, at the greatest dilution we have measured, the susceptibility increases, its course appearing to conform roughly⁶ with Curie's law and therefore to the independence of the elementary magnets in the classical sense.

To determine how closely the solutions approximate the idealization of a free electron gas Mr. Richard P. Metcalf in collaboration with one of us is re-investigating the solutions with apparatus of greater refinement. To him we are also indebted for suggestions in connection with this note.

⁶ Perhaps because the deviation of the measurements from the mean is high in the temperature coefficients of these exceedingly dilute solutions.

ADDENDUM

(December 16, 1938)

Our library has just received (December 13) a number of the *Annalen der Physik*⁷ in which E. Huster reports the data which formed the basis of a previous paper by E. Huster and E. Vogt.⁸ This we have referred to in the preceding note.

E. Huster also rejects the supposition of F. Krüger concerning the colloidal nature of the solutions which were measured magnetically. As remarked by E. Huster and E. Vogt, their data confirm in a general way the measurements of S. Freed and H. G. Thode but their data on the very dilute solutions are so scattered as to be inconclusive.

We shall refrain comment on these until more accurate data are available from this laboratory.

⁷ E. Huster, *Ann. d. Physik* **33**, 477 (1938).

⁸ E. Huster and E. Vogt, *Physik. Zeits.* **38**, 1004 (1937).