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PHASE SEPARATION IN METAL AMMONIA SOLUTIONS

Kenneth S. Pitzer

June 1958

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PHASE SEPARATION IN METAL AMMONIA SOLUTIONS¹

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June 1958

(1) This research was performed under the auspices of the U.S. Atomic Energy Commission.

In 1907 Kraus² discovered that solutions of sodium in liquid ammonia

(2) C. A. Kraus, J. Am. Chem. Soc., 29, 1557 (1907).

separate into two liquid solution phases at low temperatures and for a range of composition near 4 mole % sodium. Later Kraus and Lucasse³

(3) C. A. Kraus and W. W. Lucasse, J. Am. Chem. Soc., 44, 1949 (1922).

determined the equilibrium compositions more accurately and measured in addition the electrical conductance of each phase. Some other metal-ammonia solution systems have also been reported to show phase separation. In particular calcium⁴ and lithium⁵ solutions do give phase separation,

(4) C. A. Kraus, J. Am. Chem. Soc., 30, 653 (1908).

(5) O. Ruff and J. Zedner, Ber. 41, 1958 (1908); C. A. Kraus and W. C. Johnson, J. Am. Chem. Soc., 47, 731 (1925).

but cesium⁶ solutions do not. The author is not aware of any published

(6) J. W. Hodgins, Canadian J. Res. 27, 861 (1949).

explanation of this surprising phenomenon.

Solutions of sodium, or similar metals, at high concentration in ammonia show the properties of liquid metals. Indeed many of these systems yield solid ammoniates, such as $\text{Ba}(\text{NH}_3)_6$, which also behave as metals. These systems show specific conductance in the range 10^3 to 10^4 ohm⁻¹ which is similar to the pure metals mercury and bismuth.

McConnell and Holm⁷ extended and modified the model of Huster⁸ and

(7) H. M. McConnell and C. H. Holm, J. Chem. Phys., 26, 1517 (1957).

(8) E. Huster, Ann. Physik, 33, 477 (1938).

of Becker, Lindquist, and Alder.⁹ In the solutions of intermediate

(9) E. Becker, R. H. Lindquist, and B. J. Alder, J. Chem. Phys., 25, 971 (1956).

concentration the dominant species are assumed to be solvated metal atoms and diatomic molecules. The valence electron of the metal atom is assumed to be in a greatly expanded orbital which extends through several layers of the ammonia molecules which surround each positive

metal ion. The analogy was made to the donor state in a semiconductor such as silicon. Similarly expanded diatomic molecules are formed as the concentration increases. This model is in qualitative accord with the magnetic susceptibility data and the Knight shift of the nuclear magnetic resonance.^{7, 10}

(10) K.S. Fitzer, J. Chem. Phys., in press.

I wish to propose that the separation into two liquid phases at low temperatures is a liquid-vapor phase separation of the sodium within the ammonia solvent. The presence of the solvent makes even the dilute solution liquid, of course, but the properties of liquid metals are no longer present. There are just isolated molecules, atoms, and ions of the metallic species. But the concentrated phase shows all the characteristics of a liquid metal.

This picture may be extended somewhat by regarding the ammonia solvent as a dielectric. The solvation effect is dominant in the region near the ion; the ammonia occupies the space but the sodium valence electron can still move through it. The phenomena we are considering depend on the behavior of the valence electron at substantial distances from the ion. In this region it is a reasonable first approximation to take the square of the refractive index as the effective dielectric constant for the fast electron motion. The slow polarization by molecular rotation, etc., is not absent in this region but probably has only second order effects.

The effect of a dielectric constant on an electronic system of this type is to increase all distances by the factor K and to reduce all energies by the factor K^{-2} . At the temperatures of interest $n^2 = K \approx 2.2$ for liquid ammonia.

If the sodium ion kernel with its immediate solvation shell were a negligible portion of the volume through which the valence electron moves, then hydrogen would be the appropriate model for our calculations since we would have just the single positive charge centers. Actually, K is only about 2.2, consequently the effect of the ion kernel and immediate solvation shell is not negligible. The effect of the inner shells of electrons in the sodium ion in this case must be similar to but less than that for a gaseous sodium atom or molecule. Consequently we may expect the properties of sodium in liquid ammonia to be intermediate between those of hydrogen and those of sodium after adjustment for the scale factors arising from the dielectric constant.

The process comparable to the ionization of the gaseous atom is the fast or photo-ionization of the solvated atom to yield a free electron. The observed energy⁹ for this process is about 37 kcal/mole while the calculated values are 66 from hydrogen and 25 from sodium as a model. For the dimerization of the solvated atoms the observed energy⁹ is about 11 kcal/mole of dimer; the calculated values are 21 from hydrogen and 3.6 from sodium.

Hydrogen does not form a metallic liquid, at least not at any pressure so far attained, hence a quantitative comparison of scaled critical properties is not possible from this basis. The critical properties of sodium are not known but may be estimated to be of the order of $T_c = 3300^\circ\text{K}$, $V_c = 80$ cc/mole from comparisons of properties at lower temperatures with those of mercury and other substances. The scaled T_c for the sodium in liquid ammonia is roughly 700°K as compared to the observed value of 230°K . But the more hydrogenlike property of the solvated system means a lower T_c because in hydrogen the diatomic molecule is more stable than metal. The value of V_c scaled from sodium is 800 cc as compared to an observed value of 650 cc.^c The theoretical calculations for a metallic hydrogen¹¹

(11) E. Wigner and H. B. Huntington, J. Chem. Phys., 3, 764 (1935).

indicate volumes smaller than those of sodium. Consequently, we again find that the actual system of sodium in liquid ammonia shows properties intermediate between those scaled from hydrogen and from sodium.

This model is very crude and will undoubtedly fail for other properties. However, the general picture of the metallic solutions in liquid ammonia as metals with reduced energy and increased distance properties appears to be valid. In particular the phase separation at low temperatures is fully understandable on this basis - indeed it is the expected vapor-liquid condensation phenomenon.