The second reaction considered is the hydriding at 850° of the H-richest β-hydride to form the H-poorest γ-hydride

$$4.587\mathrm{ZrH}_{1.021}(\beta) + 1\mathrm{H}_2(g) = 4.587\mathrm{ZrH}_{1.457}(\gamma) \quad (15)$$

For this reaction $\Delta S° = -43.9$ e.u. Proceeding as for the first reaction except assuming that for the γ-phase $Z = 2$ and that the lattice contribution per g.-atom of hydrogen is the same for the two hydrides, it was found that for the β-phase of reaction 15 $Z = 2.9$.

The two values $Z = 4.1$ and 2.9 indicate effectively more hydrogen sites in the β than in the more ordered γ-lattice, for in the latter $Z = 2$. In fact, the β-Zr lattice is isotropic, and if there were two equivalent sites on *each* face, the value of Z would be 3. The estimated vibrational contribution to the entropy is somewhat uncertain, but the assumption of a higher value, *e.g.*, would decrease the first calculated value of Z and increase the second.

The progressive addition of hydrogen to a constant amount of one g.-atom of zirconium at some temperature above the α-phase field such as 900° is revealing. The heat evolved per mole of hydrogen added is smaller in the earlier than in the later stages, averaging only 34 kcal. from Zr to $\mathrm{ZrH}_{0.3}$ but remaining approximately constant at 40 kcal. from $\mathrm{ZrH}_{0.5}$ to ZrH. This difference is qualitatively explained if one assumes that the simultaneous expansion of the metal lattice, which itself is endothermic, occurs more rapidly at first, leading to a highly defect hydride lattice. In addition, the later stages of hydriding may liberate appreciable resonance energy reminiscent of the increasing heats of reaction when many chemical elements are oxidized in successive steps. The initial zirconium has a cohesive energy of approximately 120 kcal., but when the composition ZrH is reached, the cohesive energy of the solid has risen to approximately 190 kcal., and its structure must have become increasingly dependent on satisfying the requirements of the hydrogen for low energies. Further addition of hydrogen causes transition to a new Zr lattice. The new structure (γ) is evidently better adapted than the old (β) to efficient bonding with the now abundant hydrogen, and the large release of energy in the transition (51 kcal. per mole of H_2 absorbed) is great enough to offset the lower entropy of the new, more ordered structure and render it stable.

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Phase Separation in Metal–Ammonia Solutions[1]

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The separation at low temperatures of alkali metal–ammonia solutions of about 4% metal into two liquid phases has seemed surprising. However, if one regards the ammonia as a dielectric medium within which the alkali metal ions and valence electrons move, then the phase separation may be understood as a vapor–liquid condensation. This model is developed semi-quantitatively and is found to be consistent with the experimental properties of the solutions.

In 1907 Kraus[2] discovered that solutions of sodium in liquid ammonia separate into two liquid solution phases at low temperatures and for a range of composition near 4 mole % sodium. Later Kraus and Lucasse[3] 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 calcium[4] and lithium[5] solutions do give phase separation, but cesium[6] solutions do not. The author is not aware of any published 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 $\mathrm{Ba(NH_3)_6}$, which 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 Holm[7] extended and modified the model of Huster[8] and of Becker, Lindquist and Alder.[9] In the solutions of intermediate 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

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[1] This research was performed under the auspices of the U. S. Atomic Energy Commission.

[2] C. A. Kraus, THIS JOURNAL, **29**, 1557 (1907).

[3] C. A. Kraus and W. W. Lucasse, *ibid.*, **44**, 1949 (1922).

[4] C. A. Kraus, *ibid.*, **30**, 653 (1908).

[5] O. Ruff and J. Zedner, *Ber.*, **41**, 1958 (1908); C. A. Kraus and W. C. Johnson, THIS JOURNAL, **47**, 731 (1925).

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

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

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

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

accord with the magnetic susceptibility data and the Knight shift of the nuclear magnetic resonance.[7,10]

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 $n^2 = K \cong 2.2$ 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 energy[9] 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 energy[9] 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 $T_c = 3300°$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 hydrogen-like 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 sealed from sodium is 800 cc. as compared to an observed value of 650 cc. The theoretical calculations for a metallic hydrogen[11] 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.

I wish to thank Dr. W. L. Jolly for discussions of these phenomena.

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(11) E. Wigner and H. B. Huntington, *ibid.*, **3**, 764 (1935).