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Ernest O. Lawrence
Radiation Laboratory

THE REVERSIBILITY OF THE REACTION OF POTASSIUM
WITH LIQUID AMMONIA

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Ernest J. Kirschke and William L. Jolly

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Ernest J. Kirschke and William L. Jolly

Inorganic Materials Research Division,
Lawrence Radiation Laboratory and
Department of Chemistry, College of Chemistry
University of California
Berkeley, California

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Abstract. Ammoniated electrons exist in solutions of potassium amide in liquid ammonia that have reached thermodynamic equilibrium with hydrogen gas. By determining electron concentrations by electron spin resonance, an equilibrium constant of 10^5 at room temperature has been obtained for the reaction $e_{am}^- + NH_3 = NH_2^- + 1/2 H_2$.

Indeed, because we believed that the ratio of the activity coefficients for the amide ion and the electron would be relatively independent of ionic strength, we expected the equilibrium quotient to be independent of the potassium amide concentration. Perhaps the esr signals (and hence the calculated electron concentrations) were too low by a factor due to dielectric loss that increased with increasing electrolyte concentration. (As the electrical conductivity of a solution in an esr cavity increases, the dielectric loss increases, and consequently both the cavity Q and the instrument sensitivity decrease.) Our results would be explicable if, as the potassium amide concentration increased, the instrument sensitivity for the ammoniacal electron decreased more rapidly than that for the reference sample of diphenylpicrylhydrazyl (which was located in a different part of the cavity). We hope to investigate this possibility. If the trend in equilibrium quotient is caused by either an unusual activity coefficient trend or a dielectric loss phenomenon, extrapolation of the quotient to zero concentration should yield an approximation to the equilibrium constant. Our data extrapolate to an equilibrium constant of approximately 10^5 , a value in fair agreement with the previously estimated value.

A rough optical absorption spectrum was obtained for a 0.5 M potassium amide solution equilibrated for 45 days with hydrogen at approximately 10 atmospheres pressure in a glass tube of 11 mm. diameter. In the 6000-10,000Å region, the solution showed the gradually increasing absorption characteristic of the short-wavelength tail of the 15,000Å absorption band of the ammoniacal electron. Measurements at longer wavelengths were precluded by strong absorption by the ammonia.

We plan a more extensive study of the equilibrium as a function of temperature, using both electron spin resonance and optical absorption spectroscopy for determining electron concentrations.

Department of Chemistry of the
University of California and
Inorganic Materials Research Division of the
Lawrence Radiation Laboratory,
Berkeley, California, 94720

Ernest J. Kirschke

William L. Jolly

References and Notes

1. W. L. Jolly, J. Chem. Education 33, 512 (1956).
2. C. A. Hutchison, Jr. and R. C. Pastor, J. Chem. Phys. 21, 1959 (1953).
3. These results are consistent with the known exothermicity of the reaction as written above. Thermochemical data of L. V. Coulter, J. R. Sinclair, A. G. Cole and G. C. Roper, J. Am. Chem. Soc. 81, 2986 (1959) and S. R. Gunn and L. G. Green, J. Chem. Phys. 36, 368 (1962) yield $\Delta H^\circ = -12$ kcal./mole.
4. The concentration of amide ion was calculated from the weight of potassium and the volume of the solution. The hydrogen pressure was calculated from the weight of potassium and the volumes of the liquid and gas spaces, taking account of the solubility of hydrogen in liquid ammonia (5). The electron concentration was determined by indirectly comparing the signal with that of a benzene solution of recrystallized vanadium (IV) oxy(acetylacetonate) of known concentration. A sample of solid diphenylpicrylhydrazyl, fixed in the sample cavity, was used as an intermediate standard of comparison.
5. R. Wiebe and T. H. Tremmerne, J. Am. Chem. Soc. 56, 2357 (1934).
6. We wish to thank Professor R. J. Myers, D. W. Pratt and J. B. Spencer for their assistance in obtaining the esr spectra. E. J. K. acknowledges support by the U.S. Naval Postgraduate Educational Program. This research was supported in part by the U.S. Atomic Energy Commission.

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