Volume Changes for Metal Solutions in Liquid Ammonia

BY PHILIP MARSHALL[1] AND HERSCHEL HUNT

RECEIVED MARCH 30, 1955

In the course of recent research it was necessary to obtain the volume change associated with the solution of lithium, sodium and potassium in liquid ammonia. That the solution of these metals in liquid ammonia is accompanied by a relatively large increase in volume has long been known. From the densities of sodium and potassium solutions it has been shown that these volume changes pass through a maximum at about 3 N.[2]

However, the more recent publication of the densities of lithium solutions[3] did not include values for the accompanying volume changes. The mole fractions of lithium and the densities of these solutions as given in the above article are shown in Table I along with the volume changes calculated from these data. Since many properties of these solutions have been shown to be the same or at least quite similar it seems significant to note that the lithium solutions, at least according to the available data, do not exhibit a maximum. As is shown in Fig. 1 the volume change increases steadily as the solutions become more dilute.

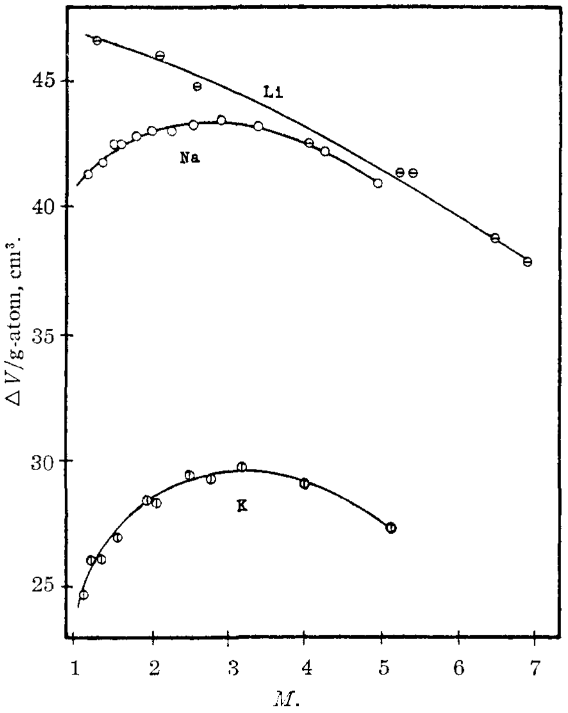

Fig. 1.—Volume changes accompanying the solution of the alkali metals in liquid ammonia, the increase in volume, ΔV/g. atom, as a function of the normality, N.

TABLE I

VOLUME CHANGES FOR LITHIUM SOLUTIONS IN LIQUID AMMONIA[a]

X_2	d, g./cc.	ΔV/g. atom, cc.	X_2	d, g./cc.	ΔV/g. atom, cc.
0.0331	0.639	46.7	0.1557	0.523	41.4
.0571	.611	46.1	.1616	.518	41.4
.0713	.597	44.8	.1958	.498	38.8
.1180	.554	42.5	.2105	.490	37.9

[a] Lithium densities determined at −33.2° by Johnson, Meyer and Martens.[3]

It should be noted, as pointed out by Johnson, *et al.*, that the volume changes in the dilute range are extremely sensitive to errors in the density determinations. Errors of 0.1% in the densities would be sufficient to give a somewhat flat maximum to the curve and errors of the order of 0.5% could give a curve quite similar to those obtained previously for sodium and potassium.

However, at the present time the conclusion that these metal–ammonia solutions are the same or even quite similar in this respect does not seem to be a fair statement. It would seem that further and more precise data, especially in the dilute solutions, is desirable.

DEPARTMENT OF CHEMISTRY
PURDUE UNIVERSITY
LAFAYETTE, INDIANA

---

(1) Department of Chemistry, Albion College, Albion, Michigan.

(2) C. A. Kraus, E. S. Carney and W. C. Johnson, THIS JOURNAL, **49**, 2206 (1927); W. C. Johnson and A. W. Meyer, *ibid.*, **54**, 3621 (1932).

(3) W. C. Johnson, A. W. Meyer and R. D. Martens, *ibid.*, **72**, 1842 (1950).

The Thermal Decomposition of Tri-*n*-butylborane

BY LOUIS ROSENBLUM

RECEIVED JUNE 6, 1955

Sodium,[1] beryllium[2-4] and magnesium[5-7] alkyls thermally decompose under vacuum at 100 to 200°. The main products are a metal hydride or an alkyl metal hydride and an olefin of the same number of carbon atoms as the original alkyl group. Recently, we observed that a boron alkyl, tri-*n*-butylborane, decomposed upon heating under vacuum; the products were dibutyldiborane and butene. The similarity both in the nature of the products and the experimental conditions suggests that the same mechanism is involved in all of these metal alkyl decompositions.

The olefin product formed from the decomposition of $(n\text{-}C_4H_9)_3B$ is found to be either butene-1 or butene-2. This differs somewhat from the decomposition of $(n\text{-}C_4H_9)_2Mg$ where only butene-1 is observed.[6,7] Presumably, butene-1 is produced initially from both the boron and magnesium compounds, but under more vigorous experimental conditions, such as prolonged heating, it can rearrange to give the more stable isomer, butene-2.

The dibutyldiborane isolated probably arises *via* the formation of $(C_4H_9)_2BH$, which then dimerizes and disproportionates. This is comparable to the decomposition of $(i\text{-}C_3H_7)_4Be_2$ to yield $(i\text{-}C_3H_7\text{-}BeH)_n$.[3]

---

(1) W. H. Carothers and D. D. Coffman, THIS JOURNAL, **51**, 588 (1929).

(2) J. Goubeau and B. Rodewald, *Z. anorg. chem.*, **258**, 162 (1949).

(3) G. E. Coates and F. Glockling, *J. Chem. Soc.*, 22 (1954).

(4) G. E. Coates and F. Glockling, *ibid.*, 2526 (1954).

(5) P. Jolibois, *Compt. rend.*, **155**, 353 (1912).

(6) E. Wiberg and R. Bauer, *Z. Naturforsch.*, **5b**, [7] 396 (1950).

(7) E. Wiberg and R. Bauer, *Ber.*, **85**, 593 (1952).