$$\left[\begin{array}{c} \text{O} \\ \| \\ \overset{\text{C}}{\underset{\text{H}}{\overset{\diagup}{\underset{\diagdown}{}}}} \overset{\text{O}}{\underset{\text{C}}{}} \\ R_3P\!\!=\!\!CH_2 \qquad C< \\ \text{H} \qquad C \\ \diagup\diagdown \end{array} \right]^+ X^-$$

at this temperature until no more olefin distilled (3 hr.). The distillate was fractionated through a semi-micro spinning band column to give 8.3 g. (76%) of mixed octenes, b.p. 46–47° (48 mm.).

(5) National Science Coöperative Graduate Fellow, 1960–1961.

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ON THE VOLUME EXPANSION OF SODIUM-IN-AMMONIA SOLUTIONS

Sir:

We have investigated the expansion accompanying the dissolution of sodium to form dilute solutions in ammonia. The extraordinary results obtained are shown in Fig. 1, where ΔV is defined as, ΔV = (volume of solution — volume of constituents)/g. atoms Na.

We offer a qualitative explanation for the behavior of ΔV. At infinite dilution dissociation of metal is complete into "solvated" or "trapped" electrons and metal ions, and the expansion is large. As the concentration is increased, ions and electrons associate forming "atoms" and "molecules," and ΔV decreases. This would suggest that the latter species may not be the highly expanded types suggested by Becker, Lindquist and Alder.[1] The minimum in ΔV occurs in the concentration range where the conductance also passes through a minimum.[2] This result, together with measurement of transport numbers[3], indicate that incipient metal properties are commencing to show up in this region. In essence, electrons are now being released to solvent, and ΔV increases again.

Prior to this study reliable data for ΔV were not available much below 1 N where ΔV is approximately 42 cc.[4] In making estimates of the size of the trapped electron, it had been assumed that this value of ΔV probably would not be too different from its value at infinite dilution.[3] Judging by our results, the value for infinite dilution appears to be approximately 41.5 cc. It is interesting to note that the two values of ΔV, taken where the states of the system are vastly different, are very nearly the same.

In our study, volume changes were measured directly using a dilatometer technique. We esti-

(1) E. Becker, R. M. Lindquist and B. J. Alder, *J. Chem. Phys.*, **25**, 971 (1956).

(2) C. A. Kraus, *J. Am. Chem. Soc.*, **43**, 749 (1921).

(3) J. L. Dye, G. E. Smith and R. F. Sankuer, *ibid.*, **82**, 4803 (1960).

(4) C. A. Kraus, G. S. Carney and W. C. Johnson, *ibid.*, **49**, 2206 (1927).

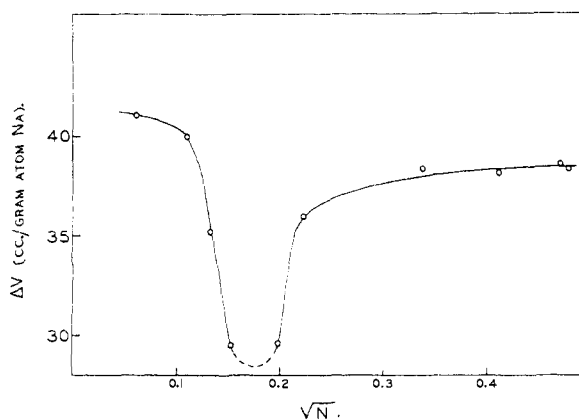(5) W. N. Lipscomb, *J. Chem. Phys.*, **21**, 52 (1953).

Fig. 1.—Expansion *vs.* $\sqrt{N}$ for solutions of sodium in ammonia at −45°.

mate that the maximum error in ΔV in our experiments does not exceed three per cent.; most certainly it is less than this normally. We shall present additional data and describe our experimental method in detail in a paper to be presented soon.

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MECHANISM OF ELECTRICAL CONDUCTIVITY IN FUSED SALTS

Sir:

We wish to make a preliminary report on some recent work pertinent to the mechanism of electrical conductivity in fused salts. The attempts to correlate diffusion, electrical migration and fluidity data, and isotope separations by electrical migration in fused salts may all be affected by these findings.[1]

Mixtures of $LiNO_3$ and KNO_3 were placed in the anode compartment and pure $NaNO_3$ in the cathode compartment of a U-shaped cell,[2] the compartments being separated by ultrafine Pyrex or in some cases quartz porous plate. Electrolysis was allowed to proceed and the total amount of cation and the ratio of Li : K passing from anode to cathode compartment were measured. The results, listed in Table I, show that within experimental error the ions move at the same rate in all mixtures. The transport number of the cation is indicative of which ion the mixture resembles most. The transport numbers of the cations in pure KNO_3 and $LiNO_3$ are 0.60 and 0.84, respectively.[3]

(1) G. J. Janz, C. Solomons and H. J. Gardner, *Chem. Revs.*, **58**, 461 (1958).

(2) F. R. Duke and R. A. Fleming, *J. Electrochem. Soc.*, **106**, 130 (1959).

(3) F. R. Duke and B. B. Owens, *ibid.*, **105**, 548 (1958).