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

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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RECEIVED JUNE 26. 1961

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, $\Delta V = $ (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-

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(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).

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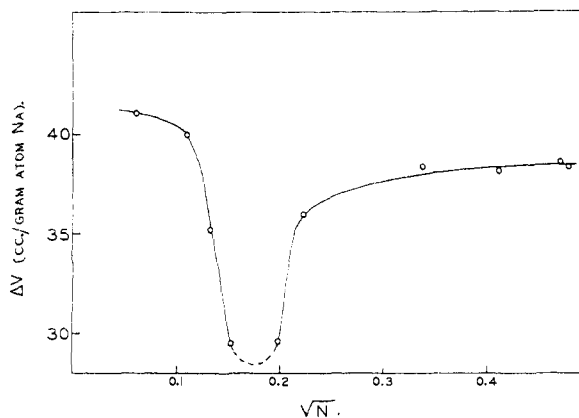(5) W. N. Lipscomb. J. Chem. Phys.. 21. 52 (1953).

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).

The only possible explanation of the observed effects is that ionic conductivity in these fused salts is a polyorder process, the ions moving in groups or by means of some chain mechanism, such as a charged hole moving through many ionic diameters with a single activation step. Other mixtures are currently under investigation.

TABLE I

RELATIVE MOBILITY AND CATION TRANSPORT NUMBER IN KNO₃–LiNO₃ MIXTURES

Total charge passed, ~800 coulombs; $T = 360-370°$

Ratio, K:Li anode, originally	Ratio K:Li, cathode after electrolysis	Transport no of cations
10	10.6	0.61
5	4.95	.60
3	3.06	.60
2	2.11	.64
1	1.06	.74
0.50	0.550	.75
.33	.361	.78
.20	.204	.80
.10	.106	.85

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TROPYLIUM ION-AROMATIC HYDROCARBON CHARGE-TRANSFER COMPLEXES

Sir:

In working with solutions of tropylium[1] perchlorate[2] or tetrafluoroborate[2] in various solvents, we have observed that addition of aromatic hydrocarbons gives rise to new absorption bands in the ultraviolet and visible regions of the spectrum (Table I). It is proposed that the new bands are charge-transfer absorption bands due to charge–transfer complexes[3] of tropylium ion with the various hydrocarbons as donors. The general evidence in favor of this interpretation may be summarized as follows.

(i) A plot of the frequencies of the new absorption bands vs. the frequencies reported for the same aromatic hydrocarbon donors and trinitrobenzene[4] as acceptor leads to a fair straight line with a slope near unity. Similarly, straight lines are obtained when the frequencies observed for tropylium ion are plotted against those observed with iodine[5a] or tetracyanoethylene[6] as acceptors. Since the frequencies of charge-transfer absorption for a series of donors with any one acceptor change nearly linearly with the ionization potential of the donors,[7] straight lines can be expected for

(1) (a) W. E. Doering and L. H. Knox, J. Am. Chem. Soc., 76, 3203 (1954); (b) W. E. Doering and H. Krauch, Angew. Chemie, 68, 661 (1956).

(2) H. J. Dauben, Jr., F. A. Gadecki, K. M. Harmon and D. L. Pearson, J. Am. Chem. Soc., 79, 4557 (1957).

(3) R. S. Mulliken, ibid., 72, 600 (1950).

(4) A. Bier, Rec. Trav. Chim., 75, 866 (1956).

(5) (a) H. A. Benesi and J. H. Hildebrand, J. Am. Chem. Soc., 71, 2703 (1949); (b) R. L. Scott, Rec. Trav. Chim., 75, 787 (1956).

(6) R. E. Merrifield and W. D. Phillips, J. Am. Chem. Soc., 80, 2778 (1958).

(7) (a) R. Foster, Nature, 183, 1253 (1959); (b) G. Briegleb and J. Czekella, Z. Elektrochem., 63, 6 (1959).

the plots of charge-transfer absorption frequencies observed with one acceptor vs. those observed with another.

TABLE I

Donor[a]	ClCH₂CH₂Cl[b] mμ	CH₃CN[b] mμ
Benzene	305(sh)	(c)
Toluene	325	310(sh)
m-Xylene	...	330
p-Xylene	340	323
Mesitylene	365	350[d]
Naphthalene	430	395(sh)
2-Methylnaphthalene	472	...
Phenanthrene	425(sh)	...
Anthracene	530	487
Pyrene	535	...

[a] ca. 0.5 M. [b] Tropylium fluoroborate concentration ca. 10^{-3} M. [c] Under 275 mμ band of tropylium ion. [d] Identical band observed with tropylium perchlorate.

(ii) The wave lengths of the new bands listed in Table I are of the correct order of magnitude for charge-transfer absorptions. Theoretical considerations[3,7b,8] suggest that $h\nu$ for charge-transfer absorption of aromatic hydrocarbon–tropylium ion complexes should be approximated by the difference between the ionization potential of the donor and the electron affinity of the acceptor. This is because classical interactions and wave-mechanical exchange forces in the ground and excited states can be expected[7b] to make only small contributions to $h\nu$. In the LCAOMO first approximation (neglecting overlap) $h\nu$ thus turns out to be 1.445β, 1.063β and 0.859β for benzene, naphthalene and anthracene as donors, respectively.[9] An estimate of an appropriate value for the exchange integral, β, may be obtained from the 275 mμ band of tropylium ion, assuming this transition involves excitation of an electron from the highest energy bonding π-orbital to the lowest-energy anti-bonding one ($h\nu = 1.692\beta$). On this basis, charge-transfer absorption bands for tropylium ion complexes with benzene, naphthalene and anthracene are predicted at 322, 438 and 540 mμ, respectively. These are in very good general agreement with observed bands in ethylene chloride solvent at 305, 430 and 530 mμ, respectively.[10]

(iii) With mesitylene concentrations in the 0.1–0.65 M range and a tropylium tetrafluoroborate concentration of 1.3×10^{-3} M in acetonitrile, a Benesi–Hildebrand plot[5] of the observed absorbances at 350 mμ, assuming 1:1 complex formation as in equation 1, leads to a good straight line. The intercept and slope of the plot lead to an equilibrium constant, K, of 0.67 l. mole⁻¹ at 25.0° and an extinction coefficient for the complex equal to 1850.

(8) S. P. McGlynn, Chem. Reviews, 58, 1113 (1958).

(9) (a) E. Hückel, Z. Physik, 70, 204 (1931); (b) B. Pullman and A. Pullman, "Les Theories Electroniques de la Chimie Organique," Masson et Cie., Paris, France, 1952, pp. 187–199.

(10) The shift to shorter wave lengths accompanying the change from ethylene chloride to acetonitrile as solvent (Table I) seems in line with the general interpretation [see e.g., E. Kosower, J. Am. Chem. Soc., 80, 3523 (1958)]. In ethylene dichloride, ion pairing must be quite important, and it is not yet clear how this affects complexing and the solvent sensitivity of the charge-transfer band.