to have a precision corresponding to a probable error of less than 0.1% above 100° K. Additional digits beyond those significant are given in Table II for internal consistency and to permit interpolation and differentiation. The entropies and Gibbs energies have not been adjusted for nuclear spin and isotope mixing contributions and hence are practical values for use in chemical thermodynamic calculations.

DISCUSSION

Assuming the sample to have the proximate composition indicated with impurities of partial molal heat capacities equal to those for the bulk phases tabulated by Kelley and King (5), the heat capacity of pure zirconium carbide corrected for the impurities would have values of 0.62 cal. (g.f.m. °K.)$^{-1}$ at 50° K., 3.01 at 100° K., 5.15 at 150° K., 6.89 at 200° K., and 9.13 at 298.15° K. Corresponding adjustment of the thermodynamic functions at 298.15° K. yields estimates of 7.90 cal. (g.f.m. °K.)$^{-1}$ for the entropy, −3.20 cal. (g.f.m. °K.)$^{-1}$ for the Gibbs energy function, and 1400 cal. (g.f.m.)$^{-1}$ for the enthalpy increment of pure zirconium carbide.

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Dissociation Constant and Limiting Conductance of NaBr in Liquid SO₂ at 0.02°C.

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The dissociation constant, K_d, of NaBr and its limiting conductance, Λ_0, at 0.02° C. are respectively, 4.84 ± 0.05 ×10^{-5} mole per liter and 265 ± 2.8 mhos cm. sq. per mole. The Bjerrum distance of closest approach calculated from K_d is 2.87 ± 0.03A, in excellent agreement with the sum of ionic radii, 2.91 A. The value of Λ_0, although smaller than that calculated from Stokes' law and the ionic radii, indicates a smaller degree of solvation of free Na$^+$ in SO₂ than in several other solvents. The mobility behavior of Na$^-$ in SO₂ resembles that of K$^+$ more than Li$^-$.

WE HAVE previously reported (10, 11, 12) that ionic distances of closest approach calculated with Bjerrum's equation from values of the ion pair dissociation constant, K_d, of KCl, KBr, KI and LiBr in liquid SO₂ all fall within 0.2A of the appropriate crystallographic distances. The experimental limiting equivalent conductances of the potassium salts (10, 11) also fall within 5% of the value calculated from Stokes' equation using Pauling's values of ionic radii. The value of Λ_0, for LiBr (12), however, is less than half that calculated in this way. Thus Li$^+$ appears to be strongly solvated by SO₂ with respect to hydrodynamic transport but not with respect to association with bromide. Sodium bromide provides an additional case of close adherence to Bjerrum's equation in this medium, while

Na$^+$ appears to be intermediate in its mobility behavior between Li$^+$ and K$^-$.

EXPERIMENTAL

The experimental procedures and bridge have been described previously (9, 13). An improved conductance cell, which is described in detail elsewhere (14) was employed. Baker's Analyzed Reagent NaBr was recrystallized three times from freshly boiled distilled water and dried at 135° for 10 days. The compound is considerably less soluble than is reported by Jander (8). Solubility measurements, as such, were not carried out, but observations made in the course of preparing solutions for measurement suggest a value in the vicinity of 0.0003 mole per liter. Because of the low solubility, samples of NaBr (about 1 mg.) were introduced into the conductance cell in the form of weighed aliquots in ethanol solution. The

ethanol was removed under vacuum and the cell pumped at less than 0.001 mm. of Hg over night before admission of SO_2.

RESULTS AND DISCUSSION

Data of a typical conductance run are presented in Table I. It is not necessary to employ Fuoss' procedure, based on the Onsager-Fuoss conductance equation (1), for an ionophore as highly associated as is NaBr in liquid SO_2 at 0° C. Application of Shedlovsky's method (16) to the data provided $K^d = 4.84 \pm 0.05 \times 10^{-5}$ mole per liter and $\Lambda_0 = 265 \pm 2.8$, where the indicated uncertainties were calculated from the square roots of the variances (95% confidence limits, $n = 20$) in the slope and intercept of the linear Shedlovsky plot. Only data at dilutions up to 56,200 liters per mole were employed, so that solvent conductivity was at most 4% of total solution conductivity. The Bjerrum distance of closest approach calculated (2) from K_d is 2.87 ± .03A, while the sum of ionic radii is 2.91A and the interionic distance in the crystal (15) is 2.98A. The limiting conductance calculated from Stokes' equation (4) and Pauling's ionic radii is 316, 19% greater than the experimental value. Thus the mobility of Na^- is not as much greater than that of K^+ as would be anticipated from Stokes' equation. This equation can, of course, not in general be used to calculate ionic conductances accurately and we have, in the past, used it only as a basis for comparison in correlating limiting conductances in liquid SO_2. The limiting conductance of LiBr is actually less than that of tetra-n-propylammonium iodide, so that it is clear that its large deviation from the Stokes value is due to unusual solvation of Li^-. The situation is less clear for NaBr. The limiting conductances of large organic cations (11) decrease with increasing ionic size but they are all considerably larger than would be

expected from ionic dimensions and Stokes' equation, although smaller than the limiting conductances of potassium halides. Thus, Λ_0 for Me_4NBr at 0° C. is 236 (11) while the value calculated from Stokes' Law with the radii of Me_4N^+ and Br^- taken as 3.30 and 1.95A, respectively is 165. A possible interpretation of this is that limiting conductances of normally solvated cations increase less steeply with ion size than would be expected from Stokes' equation but that, accidentally, the conductance of K^+ (as well as that of Cl^-, Br^- or I^-) nearly coincides with the value calculated from the ionic radius and Stokes' equation. On this basis, Λ_0 of Na^+ is not necessarily indicative of solvation which is substantially different in nature from that characteristic of larger ions. In fact, the evidence for enhanced solvation of Na^- by SO_2 is weaker than for its solvation by water (5), methanol (3), pyridine (7), and acetone (7) at 25° C. and by methyl acetamide (6) at 40° C. In all of these solvents the order of limiting ionic conductances is $K^+ > Na^+ > Li^-$ whereas in SO_2 it is $Na^+ > K^+ > Li^+$, e.g. Λ_0 at 0° C. is 265, 249 (10) and 189 for NaBr, KBr and LiBr, respectively.

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Table I.

Volume, Liter/Mole	Λ^a Mhos Cm. Sq./Mole
5779	111.9
8443	131.2
12340	146.4
18020	162.3
26330	177.7
38470	191.4
56200	204.4
82110	217.8

^{a} Corrected for solvent conductivity of 8.4×10^{-8} mho/cm.