| | | | | Table | I | | | | |
|--|---------------------|----------|------------|-------------|-----------|-----------|------------------------|----------|-------|
| | | So | LUBILITIES | IN FLUOROC. | ARBON DEP | RIVATIVES | | | |
| Solubility.Solubility.Solubility.Solubility.g./100.g. solventmole fractiong./100 g. solventmole fractionat 25°at 25°at 35°at 35° | | | | | | | ility. action 5° | | |
| Solute | Solvent | Measured | Average | Measured | Ideal | Measured | Average | Measured | Ideal |
| $C_{10}H_8$ | $(C_4F_9)_2O$ | 0.0726 | 0.0730 | 0.00257 | 0.299 | 0.116 | 0.114 | 0.00402 | 0.384 |
| | | .0733 | | | | .112 | | | |
| $C_{10}H_{8}$ | $(C_{3}F_{7})_{3}N$ | .0774 | .0740 | .00300 | .299 | .115 | .114 | .00461 | .384 |
| | | .0723 | | | | .113 | | | |
| | | .0723 | | | | | | | |
| $C_7H_7NO_2$ | $(C_4F_9)_2O$ | .0818 | .0812 | .00268 | .571 | , 123 | .121 | .00399 | .712 |
| | | ,0806 | | | | .119 | | | |
| $C_7H_7NO_2$ | $(C_{3}F_{7})_{3}N$ | .0850 | .0850 | .00323 | .571 | .134 | .137 | .00517 | .712 |
| | | .0850 | | | | .140 | | | |
| C_2Cl_6 | $(C_4F_9)_2O$ | . 474 | .474 | .00901 | .0526 | .781 | .781 | .0148 | .0709 |
| | | .475 | | | | .780 | | | |
| C_2Cl_6 | $(C_{3}F_{7})_{3}N$ | . 516 | .508 | .0111 | .0526 | .743 | .742 | ,0160 | .0709 |
| | | . 509 | | | | .741 | | | |
| | | .525 | | | | | | | |
| | | .480 | | | | | | | |

fraction and at 35° 0.304. This is much closer to the ideal figure despite the fact that dibutyl ether has a dipole moment whereas neither naphthalene or $(C_4F_9)_2O$ have an appreciable moment. From this, one might expect naphthalene to be more ideally soluble in $(C_4F_9)_2O$ than in $(C_4H_9)_2O$. The reverse is found. This can be explained using the concept of interpenetration.²

The solubility of nitrobenzene falls far below the ideal in both fluorocarbon derivatives. This is due primarily to interpenetration but also to the fact that it is a dipolar material, differing in this respect from the fluorocarbon derivatives.

Hexachloroethane comes much more nearly being ideally soluble in the fluorocarbon derivatives, probably because of the lack of hydrogen atoms in the molecule resulting in little interpenetration between the solute molecules.

From the difference in solubility at two temperatures, the heat of solutions was calculated. For naphthalene in $(C_4F_9)_2O$ this was 8150 cal. per mole and in $(C_8F_7)_8N$ was 7850. This is compared with the ideal value of 4580. For p-nitrotoluene in $(C_4F_9)_2O$ this was 7320 and in $(C_8F_7)_8N$ was 8620. This is compared with the ideal value of 4010. The excess of these values above the ideal gives a rough measure of the heat of interpenetration.

As can be seen from the figures, there appears to be little difference in solubility of these substances in the fluorocarbon oxide or fluorocarbon nitride.

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Conductances, Transference Numbers and Activity Coefficients of Aqueous Solutions of Some Rare Earth Halides at 25^{°1}

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The equivalent conductances, cation transference numbers and activity coefficients at 25° of aqueous solutions of LaBr₃, PrBr₃, NdBr₃, GdBr₃, HoBr₃, ErBr₃ and GdCl₃ have been determined for concentrations up to 0.1 N. Also the equivalent conductances of NdCl₃ have been redetermined. The Onsager law for conductance is obeyed for all halides studied up to a concentration of approximately 0.001 N. The transference numbers, determined by the moving boundary method, were found to be linear functions of the square root of the concentration; the slopes of these functions differed by a factor of approximately one-fifth from those predicted by the Onsager law. The activity coefficients, determined by the use of concentration cells with transference, were found to agree with those predicted by the Debye-Hückel law providing that the experimentally determined å. values were used to calculate the theoretical coefficients. All data reported are correlated with data on the rare earth chlorides previously reported.

Introduction

This paper is the fourth in a series concerning the electrolytic behavior of aqueous solutions of rare earth compounds. The earlier $papers^{3-5}$ have

(1) Work was performed in the Ames Laboratory of the Atomic Energy Commission.

(2) Taken in part from the Ph.D. thesis submitted to the graduate faculty of Iowa State College, 1952.

(3) F. H. Spedding, P. E. Porter and J. M. Wright, THIS JOURNAL, 74, 2055 (1952).

(4) F. H. Spedding, P. E. Porter and J. M. Wright, *ibid.*, **74**, 2778 (1952).

(5) F. H. Spedding, P. E. Porter and J. M. Wright, *ibid.*, 74, 2781 (1952).

presented data on the conductances, transference numbers and activity coefficients of several rare earth chlorides. This paper extends this investigation to other rare earth halides, particularly the bromides, and attempts to correlate the data between the two series of halides. As discussed in the first article of this series,³ such information should be of considerable value in the study of the various factors which enter into the modern theories of electrolytic behavior.

Experimental

Except as specifically discussed below, the experimental

TABLE I

| | Equivalent | CONDUCTANCES OF | AQUEOUS | s Solutions o | f Some Ra | re Earth H | ALIDES AT 25 |) or |
|-----------|------------|-------------------|------------|-------------------------------|-------------------|-------------------|----------------|-------|
| Normality | y LaBra | PrBr ₃ | NdBr₂ | GdBr ₃ | HoBr ₃ | ErBr ₃ | NdCl3 | GdCla |
| | | Equ | uivalent c | ondu <mark>ct</mark> ances, r | nhos cm1 | | | |
| 0.0000 | 147.6 | 147.6 | 147.6 | 145.6 | 144.4 | 144.0 | 145.8 | 143.7 |
| .0002 | 143.6 | 143.6 | 143.6 | 141.7 | 140.5 | 140.1 | 141.8 | 139.8 |
| .0004 | 142.0 | 142.0 | 142.0 | 140.0 | 138.8 | 138.4 | 140.2 | 138.1 |
| .0007 | 140.2 | 140.2 | 140.2 | 138.2 | 137.0 | 136.7 | 138.4 | 136.3 |
| ,0010 | 138.7 | 138.7 | 138.7 | 136.8 | 135.6 | 135.2 | 136.9 | 134.9 |
| .0020 | 137.8 | 137.7 | 137.7 | 133.0 | 132.5 | 132.2 | 133.3 | 131.3 |
| .0040 | 131.8 | 131.7 | 131.6 | 128.8 | 128.4 | 128.2 | 128.7 | 127.1 |
| .0070 | 127.7 | 127.6 | 127.6 | 125.0 | 124.5 | 124.2 | 124.6 | 123.0 |
| .0100 | 124.6 | 124.5 | 124.4 | 122.2 | 121.6 | 121.3 | 121.5 | 120.2 |
| .0200 | 118.5 | 118.4 | 118.3 | 116.1 | 115.8 | 115.6 | 115.0 | 114.0 |
| .0400 | 112.2 | 112.1 | 112.0 | 110.1 | 109.3 | 109.0 | 107.7 | 107.0 |
| .0700 | 109.0 | 108.9 | 108.8 | 105.1 | 104.2 | 103.9 | 101.7 | 101.5 |
| .1000 | 103.8 | 103.6 | 103.4 | 102.0 | 101.0 | 100.7 | 98.6 | 98.4 |
| | | | | | | | | |

^a The data of this table are smoothed values. Anyone desiring the exact data for the experimental points may obtain them from the authors upon request.

procedures and apparatus were the same as those previously reported.³⁻⁵ All measurements were made at $25 \pm 0.02^{\circ}$

The samples of La₂O₃, Pr₆O₁₁ and Nd₂O₃ used for this work had the same analyses as those previously reported.³ The had the same analyses as those previously reported.³ The purities of the other rare earth oxides used were: Gd_2O_3 : $< 0.1\% Sm_2O_3$, $\sim 0.025\% Tb_4O_7$, faint trace of CaO; Ho_2O_3 : $0.05\% Dy_2O_3$, $\sim 0.02\% Y_2O_3$, $\sim 0.01\% Er_2O_3$, faint trace of CaO; and Er_2O_3 : $0.05\% Yb_2O_3$, $0.05\% Tm_2O_3$, $0.05\% Ho_2O_3$, $0.2\% Y_2O_3$, no Dy_2O_3 detected, faint trace of CaO. All analyses were made by spectrographic methods⁶ except that for Tb_4O_7 in Gd_2O_3 which was made by a new fluorescimetric technique.⁷ All oxides were further purified by a minimum of two oxalate precipitations from solutions containing a slight excess of the hydrohalide acid with which they were finally dissolved.

GdCl₃ solutions were prepared from the anhydrous halide.3 Attempts were made to prepare anhydrous rare earth bromides by an analogous method, using purified dry HBr gas. However, although solutions obtained from the dried salts were clear, their pH values ranged from 7.10 to 7.30, and analyses for the rare earth and for the bromide ions indicated that the bromide content in all cases was less than the required stoichiometric amount. Therefore the following method was employed to prepare the rare earth bromide solutions. The purified oxide was dissolved in an insufficient quantity of redistilled hydrobromic acid at room temperature. When the reaction was completed, the undissolved oxide was filtered from the solution, and the filtrate was diluted to a predetermined volume with conductivity water. Analyses of these solutions indicated that the two ionic species were present in the proper stoichiometric ratio to within 0.1%. After filtering the PrBr₃ solution, the filtrate had to be boiled to remove the free Br₂ formed when the higher oxide of this rare earth was dissolved. Dilutions were made from these stock solutions using recalibrated glassware to obtain solutions of the desired concentrations. As a check upon this method of preparation, solutions of NdCl₃ were prepared by this method and were also prepared from the anhydrous chloride. The equivalent conduct-ances of these solutions fell on the same smooth curve and both sets of data extrapolated to the same value at infinite dilution.

LiBr was used as the indicator solution for the determinations of the cation transference numbers of the rare earth bromides and a Ag,AgBr electrode was used as the cathode. The LiBr stock solution was prepared by a method analogous to that used for the preparation of LiCl.⁸ The transference numbers of LiBr were calculated from transference num-ber data on KBr⁹ and LiCl¹⁰ and from the conductance data

(9) L. G. Longsworth, ibid., 57, 1185 (1935).

on KBr¹¹ and on LiCl.¹² As an approximate check upon the calculated transference numbers of LiBr, the transference numbers of KBr were determined at several concentrations, using LiBr as the indicator solution. Within experimental error, the transference numbers of KBr so obtained agreed with those of Longsworth⁹ who used the autogenic boundary technique. Also, in view of the close correlation between experiment and theory for alkali halides, it is believed that the calculated transference numbers of LiBr are in error by no more than 5%. The transference numbers of indicator solutions need not be known to greater accuracy.

Since infrared heating was used for the constant temperature bath (A. H. Thomas Catalog No. 9926-D) in which the concentration cells with the transference were immersed, it was thought expedient to paint the outsides of these cells black to protect the Ag, AgBr electrodes from possible photodecomposition.

Results

A. Conductances.-The equivalent conductances of the eight rare earth halides investigated are listed in Table I. Within experimental error, the conductances of LaBr₃, PrBr₃ and NdBr₃ are identical over the concentration range studied although small differences are observed in the higher concentrations. For the extrapolation to infinite dilution, λ_0 for the chloride ion was taken as 76.34 mhos cm.⁻¹, and that for the bromide ion as 78.15 mhos cm.⁻¹. The latter value was obtained by averaging the values of Λ_0 for KBr obtained by various investigators,^{11,13} and subtracting from that average the accepted value of the limiting conductance of potassium ion, 73.50 mhos cm.⁻¹. The extrapolation curves are illustrated in Fig. 1. The horizontal portion of each curve indicates the concentration range in which the Onsager law is obeyed, up to approximately 0.001 N for each salt. Since the conductances of NdCl₃ previously reported³ were believed to be slightly less accurate than the other salts reported, they were redetermined. The new values are listed in Table I. The equivalent conductances at infinite dilution, Λ_0 , for the rare earth halides reported here and for

(11) G. Jones and C. F. Bickford, ibid., 56, 602 (1934).

(12) T. Shedlovsky, ibid., 54, 1411 (1932); D. A. MacInnes, T. Shedlovsky and L. G. Longsworth, ibid., 54, 2758 (1932).

⁽⁶⁾ V. A. Fassel and H. A. Wilhelm, J. Optical Soc. Am., 38, 518 (1948); V. A. Fassel, ibid., 39, 187 (1949).

⁽⁷⁾ V. A. Fassel, R. H. Heidel and F. Huke. Anal. Chem., 24, 606 (1952).

⁽⁸⁾ G. Scatchard and S. S. Prentiss, THIS JOURNAL, 55, 4355 (1933).

⁽¹⁰⁾ L. G. Longsworth, ibid., 54, 2741 (1:032)

⁽¹³⁾ G. C. Benson and A. R. Gordon, J. Chem. Phys., 13, 473 (1945); H. Zeldes, Dissertation, Yale University, 1947, cited by Harned and Owen, "The Physical Chemistry of Electrolytic Solutions," 2nd Edition, Reinhold Publ. Corp., New York, N. Y., p. 591, 1950



Fig. 1.—Extrapolation of equivalent conductances to infinite dilution of aqueous solutions of some rare earth halides at 25° .

those previously reported^{8,11,14} are plotted in Fig. 2 as a function of the atomic number of the rare earth element. There should be a constant difference between the curves for the two anions of 1.8 mhos; within experimental error, this constant difference is obtained. The only other recent conductance data on rare earth halides¹⁵ appear to differ somewhat from our results. However due to the care taken in our measurements and due to their internal self-consistency, we believe our results are the more nearly correct.

Explanations for the variation of the equivalent conductances of the rare earth halides with atomic number have been previously presented.³ Recent crystallographic data on $Nd_2(SO_4)_8 \cdot 8H_2O^{16}$ confirms the prediction that Nd(III) has only one stable coördination number for oxygen at 25°, namely, nine.

B. Transference Numbers.—The cation transference numbers for LaBr₃, PrBr₃, NdBr₃, GdBr₃, HoBr₃, ErBr₃ and GdCl₃ are listed in Table II. These data were subjected to a least squares analysis and the equations so obtained are tabulated in Table III. The data previously obtained on the transference numbers of the rare earth chlorides⁴ were similarly treated and are listed for comparison. The limiting transference numbers, ob-

(14) L. G. Longsworth and D. A. MacInnes, THIS JOURNAL. 60, 3070 (1938).

(15) G. Jantsch, H. Grabitsch and E. Lischka, Z. Elektrochem., 43, 293 (1937).

(16) R. E. Rundle and D. R. Fitzwater, unpublished work.



Fig. 2.—Equivalent conductances at infinite dilution for aqueous solutions of rare earth halides at 25°.

tained from conductance data, are also listed in this table along with the limiting slopes as predicted from the Onsager limiting law. Although the intercepts of the least squares lines are fairly close to the limiting transference numbers, the slopes of these lines differ from the theoretical slopes by a factor of approximately one-fifth. This discrepancy between theory and experiment has been previously reported,^{4,14} but as yet there is no adequate explanation for this behavior.

The transference numbers of LaBr₃, PrBr₃ and NdBr₃ are quite close to each other, with those of neodymium being slightly higher. In view of the close agreement among the conductances of these three salts, the similarity among their transference numbers was expected. The transference numbers of the heavier rare earth bromides decreased with increasing atomic number as did their conductances. This same general trend has been previously reported for the rare earth chlorides.⁴ From the data in Table III, it can be seen that, except for the higher mobility of the bromide ion over that of the chloride ion, the effect of these anions upon the rare earth cations is relatively the same. Erbium appears to be an exception.

Before experimentally determining the cation transference numbers of HoBr₃, these numbers were estimated from the least squares lines of $ErBr_3$ and of GdBr₃, as listed in Table III, assuming, as a first approximation, that there is a linear variation with atomic number between these two salts. Within experimental error, the transference numbers of HoBr₃ which were experimentally determined agreed with those estimated by this method.

0.

0.

The standard volume and solvent corrections were applied to the observed transference numbers to obtain those listed in Table II. The partial

TABLE II

CATION TRANSFERENCE NUMBERS OF AQUEOUS SOLUTIONS of Some Rare Earth Halides at 25°

| Normality | Clb- served | Average | Volume | Solvent cor- | Cor- rected |
|---------------------------------------|---|---------------------------------------|-----------------|-----------------|----------------|
| sormany | /. | ·+ T1 | n | recton | 1 1 |
| | | 1.21 | BT2 | | |
| 0.1041 | 0.4331 | 0.4327 | ~0.007 | 0.0000 | 0.4320 |
| | . 4326 | | | | |
| | 4323 | | | | |
| 07434 | . 4375 | 4374 | 0005 | .0001 | ,4370 |
| | .4372 | | | | |
| .05947 | . 4407 | . 4408 | 0004 | .0001 | .4405 |
| | . 4408 | _ | _ | | |
| .02974 | . 4481 | . 4481 | 0002 | .0001 | .4480 |
| 01487 | .4535 | . 4536 | 0001 | ,0002 | .4537 |
| | .4536 | | | | |
| .01041 | .4561 | .4561 | 0001 | .0003 | .4563 |
| | | PrI | 3r. | | |
| 0 1057 | 0 4210 | 0 4210 | - 0 0000 | 0.0000 | 0 4210 |
| 0.1007 | 4226 | 1227 | - 0008 | 0.0000 | 1220 |
| . (1.)(1.)() | 4338 | | | .0000 | . 1040 |
| 06039 | 4407 | 4407 | - 0005 | 0001 | 4402 |
| 03020 | 1188 | 4.180 | - 0002 | 0001 | 1188 |
| .04020 | .1.100 | . 4400 | · ,0004 | | . 17()) |
| 01510 | . 1550 | 1550 | - 0001 | 0003 | 4559 |
| 01010 | 1580 | .1586 | 0001 | 0003 | 1588 |
| | 1581 | | | . (70(74) | |
| | די ייידי, | 57.11 | D | | |
| | | ->0 | Br ₂ | | |
| 0.09499 | 0.4344 | 0.4348 | -0.0009 | 0.0000 | 0,4339 |
| | . 4352 | | | | |
| .07124 | .4393 | 4393 | ,0006 | .0001 | .4388 |
| .04750 | . 4450 | . 4450 | 0004 | .0004 | . 4447 |
| | . 1449 | | 0.000 | | |
| .02395 | . 4512 | .4512 | 0002 | .0001 | .4511 |
| 009499 | . 4606 | . 4604 | 0001 | .0003 | .4606 |
| | .4602 | | | | |
| | | Gdl | Bra | | |
| 0.1018 | 0.4273 | 0.4278 | -0.0009 | 0.0000 | 0.4269 |
| | .4283 | | | | |
| ,07633 | . 4336 | . 4333 | 0006 | .0000 | .4327 |
| | .4330 | | | | |
| 05089 | . 4391 | .4391 | 0004 | .0000 | .4387 |
| .02544 | . 4488 | .4485 | 0002 | ,0001 | . 4484 |
| | . 4480 | | | | |
| | . 4486 | | | | |
| .01272 | .4542 | .4542 | 0001 | .0002 | .4543 |
| .01018 | . 4547 | .4551 | 0001 | .0002 | .4552 |
| | .4555 | | | | |
| | | Hol | Bra | | |
| 0.1188 | 0.4138 | 0.4134 | -0.0014 | 0.0000 | 0.4120 |
| | .4130 | | | | |
| .09503 | .4181 | .4181 | 0010 | .0000 | .4171 |
| .07127 | ,4237 | 4239 | 0007 | .0000 | . 4232 |
| | 4241 | | | | |
| .04752 | . 4295 | . 4295 | 0005 | .0001 | . 4291 |
| .02376 | 4365 | . 4369 | - .0002 | .0002 | . 4369 |
| ()1100 | . 4372 | 1490 | 0001 | 0004 | 140- |
| .01188 | . 4429 | ,4462 | 0001 | . 0004 | . 4435 |
| 009502 | . 1 ± 1 ± 0 ± 4.1 50 | 4.150 | - noni | 0005 | 4463 |
| 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 | | · · · · · · · · · · · · · · · · · · · | | | , |

| | | Erl | 3r₃ | | |
|---|--|--|--|--|--|
| 1.104 | 0.4112 | 0.4113 | -0.0010 | 0.0000 | 0.4103 |
| | . 4114 | | | | |
| .08278 | .4163 | .4163 | 0007 | . 0000 | .4156 |
| .05519 | 4238 | .4238 | 0005 | .0001 | .4234 |
| | .4238 | | | | |
| .02759 | .4328 | . 4328 | 0002 | .0001 | .4327 |
| .01380 | .4398 | ,4398 | 0001 | .0003 | .4400 |
| .01104 | . 4405 | .4405 | 0001 | .0003 | .4407 |
| | | Cd | C1. | | |
| | | Cru | C13 | | |
| 0.1051 | 0.4321 | 0.4319 | -0.0004 | 0.0000 | 0,4315 |
| 0.1051 | 0.4321 .4317 | 0.4319 | -0.0004 | 0.0000 | 0,4315 |
| 0.1051 | $^{()}$, 4321 , 4317 , 4369 | 0.4319 .4369 | -0.0004 -0.0003 | 0.0000 | 0,4315 ,4366 |
| 0.1051 0.08174 0.05839 | 0.4321 .4317 .4369 .4412 | 0.4319 .4369 .4416 | -0.0004 -0.0003 -0.0002 | 0.0000 .0000 .0001 | 0,4315 .4366 .4415 |
|), 1051 .08174 .05839 | (), 4321 , 4317 , 4369 , 4412 , 4420 | 0.4319 .4369 .4416 | -0.0004 -0.0003 -0.0002 | 0.0000 .0000 .0001 | 0,4315 .4366 .4415 |
| . 1051 .08174 .05839 .03503 | $\begin{array}{c} 0.4321 \\ .4317 \\ .4369 \\ .4412 \\ .4420 \\ .4488 \end{array}$ | 0.4319 .4369 .4416 .4488 | $\begin{array}{r} -0.0004 \\ -0.0003 \\ -0.0002 \\ -0.0001 \end{array}$ | 0.0000 .0000 .0001 | 0,4315 .4366 .4415 .4488 |
|), 1051 , 08174 , 05839 , 03503 , 02335 | $\begin{array}{c} 0.4321\\ .4317\\ .4369\\ .4412\\ .4420\\ .4488\\ .4532\end{array}$ | 0.4319 .4369 .4416 .4488 .4532 | $\begin{array}{r} -0.0004 \\ -0.0003 \\ -0.0002 \\ -0.0001 \\ -0.0001 \end{array}$ | 0.0000 .0000 .0001 .0001 .0001 | 0,4315 .4366 .4415 .4488 .4532 |

TABLE III

SUMMARY OF DATA ON TRANSFERENCE NUMBERS OF RARE Earth Halides

| | Least-squares equation | | A 4 4 4 4 4 4 |
|----------------------------|--------------------------|-------------|---------------|
| Salt ^a | $T_{-} =$ | T_{+}^{0} | $S(T+0)^{b}$ |
| $LaBr_3$ | $0.4672 - 0.110 N^{1/s}$ | 0.4707 | -0.558 |
| PrBr ₃ | $.4697 120 N^{1/2}$ | . 4707 | 558 |
| NdBr₃ | $.4689113 N^{1/2}$ | . 4707 | 558 |
| $GdBr_3$ | $.4689132 N^{1/2}$ | .4632 | 581 |
| HoBr₃ | $.4586135 N^{1/2}$ | .4591 | 594 |
| $\mathrm{Er}\mathrm{Br}_3$ | $.4555137 N^{1/4}$ | 4573 | 599 |
| LaCl | $.4730108 N^{1/4}$ | . 4775 | 550 |
| CeCl ₂ | $.4746113 N^{1/2}$ | .4778 | 549 |
| PrCl _o | $.4753114 N^{1/2}$ | .4772 | 551 |
| NdCl _a | $.4744112 N^{1/2}$ | 4767 | 553 |
| ${\rm SmCl}_{\rm s}$ | $.4745112 N^{1/2}$ | .4732 | 563 |
| EuCl: | $.4726116 N^{1/2}$ | .4706 | 571 |
| GdCl | $4737 - 131 N^{1/2}$ | .4687 | 577 |
| ErCl ₃ | $.4600118 N^{1/i}$ | .4638 | 591 |
| ${ m Yb} Cl_3$ | $.4629125 N^{1/2}$ | .4605 | 603 |
| | | | |

^a With the exception of the chloride data reported in this paper, all of the chlorides listed are from the data of Spedding, Porter and Wright.⁴ ${}^{b}S(T_{+}^{0}) =$ theoretical limiting slope as calculated from the Onsager equation for transference numbers.

molal volumes of the rare earth halides required for the volume corrections were calculated from density measurements made with a 50-ml. pycnometer. In the concentration range studied, the densities were found to be linear functions of the concentration. These equations are listed in Table IV, along with the partial molal volumes calculated from these equations. The anticipated variation of ρ and \bar{V} with atomic number was obtained.

TABLE IV

DENSITIES AND PARTIAL MOLAL VOLUMES OF SOME RARE Earth Halides at 25°

| Salt | Density equation" $\rho =$ | Partial molal volume, ml |
|-------------------|----------------------------|-----------------------------|
| $LaBr_3$ | 0.99707 + 0.3471C | 31.60 |
| $PrBr_3$ | .99707 + .3525C | 28.25 |
| $NdBr_3$ | .99707 + .3572C | 26.95 |
| GdBr₃ | .99707 + .3723C | 24.42 |
| HoBr ₃ | .99707 + .3813C | 23.47 |
| ErBr_3 | .99707 + .3845C | 22.52 |
| GdCl ₈ | .99707 + .2494C | 13.90 |

^a C = molarity.

C. Activity Coefficients.—Concentration cells with transference of the type

Ag, AgBr, HoBr₃ (m_1) : HoBr₃ (m_2) , AgBr, Ag

were used to determine the activity coefficients. Ag,AgCl electrodes were used for all chloride solutions; the method of preparation has been previously described.⁵ Ag,AgBr electrodes, used for all bromide solutions, were prepared by the above

TABLE V

MEAN MOLAL ACTIVITY COEFFICIENTS OF RARE EARTH HALIDE SOLUTION AT 25°

| Molality | E.m.f., mv. | $\gamma \pm$ | Molality | E.m.f., mv. | $\gamma \pm$ |
|----------|-------------------|--------------|------------------|-------------------|----------------|
| ŕ | LaBr₃ | | | PrBr₃ | |
| 0.03483 | -3.8981 | 0.4340 | 0.03535 | -1.7260 | 0.4293 |
| .02487 | 0.0000 | .4676 | .03030 | 0.0000 | . 4457 |
| .01990 | 2.6452 | .4902 | .02020 | 4.7698 | .4861 |
| .009945 | 11.0389 | .5624 | .01010 | 13.0286 | . 5654 |
| .004971 | 19.854 | . 6389 | .005048 | 21.837 | .6335 |
| .003480 | 24.576 | .6741 | .003533 | 26.613 | . 6667 |
| .002486 | 29.038 | .7097 | .002019 | 33,938 | .7321 |
| .001988 | 32.052 | .7324 | .001010 | 43.754 | .7872 |
| .0009942 | 41.873 | ,7862 | | | |
| | NdBr ₃ | | | GdBr₃ | |
| 0.03178 | -3.3935 | 0.4403 | 0.03505 | -3.2470 | 0.4229 |
| .02383 | 0.0000 | .4678 | ,02553 | 0.0000 | .45 2 3 |
| .01587 | 4.8482 | . 5095 | .01702 | 4.6552 | .4968 |
| .007941 | 13.4223 | . 5833 | .008508 | 13.1131 | .5695 |
| .003175 | 25.254 | .6838 | .004255 | 21.818 | .6483 |
| .002382 | 29.105 | .7142 | .003403 | 24.636 | .6759 |
| .001588 | 34.744 | ,7502 | .002552 | 28.535 | .7027 |
| .0007939 | 44.569 | .8087 | .001701 | 34.073 | .7408 |
| | | | .0008507 | 43.752 | .8022 |
| | $HoBr_3$ | | | ErBr ₃ | |
| 0.03975 | -5.8327 | 0.4291 | 0.03693 | -3.1028 | 0.4204 |
| .03179 | -3.3429 | .4496 | .02769 | 0.000 | .4500 |
| .02384 | 0.0000 | . 4758 | .01846 | 4.6205 | .4894 |
| .01589 | 4.6815 | .5183 | - .009229 | 12.6457 | .5665 |
| .007944 | 12.8016 | .5907 | .004613 | 21.173 | . 6400 |
| .003972 | 21.705 | .6644 | .002768 | 27.538 | .7002 |
| .002383 | 28.403 | . 7133 | .001845 | 32.970 | . 7349 |
| .001588 | 33.805 | .7531 | .0009225 | 42.356 | . 7949 |
| .0007943 | 43.385 | .8105 | | | |
| | GdCl_3 | | | | |
| 0.03515 | -6.7271 | 0.4172 | | | |
| .02734 | -3.8901 | .4429 | | | |
| .01952 | 0.0000 | . 4787 | | | |
| .01171 | 6.1070 | . 5345 | | | |
| .007808 | 11.0586 | . 5816 | | | |
| .003904 | 19.919 | .6572 | | | |
| .002733 | 24.645 | . 6962 | | | |
| .001171 | 36.573 | .7728 | | | |

method and also by the thermal method of Keston.¹⁷ No difference in the behavior of the two types of bromide electrodes was observed, and both types were used interchangeably. The activity coefficients obtained are listed in Table V. The method used for the calculations has been previously described.⁵ For the integration across the concentration gradient, the transference numbers listed in Table III were employed. Table VI lists the experimentally determined å. values and the average absolute difference between the experimentally determined coefficients and those calculated from the Debye-Hückel law using these å. values. Within experimental error, the experimentally determined activity coefficients obeyed the Debye-Hückel law. This same agreement has been previously observed for rare earth chlorides.^{5,18}

TABLE VI

MEAN DISTANCES OF CLOSEST APPROACH FOR RARE EARTH HALIDE SOLUTIONS AND THE AVERAGE DIFFERENCES BE-TWEEN CALCULATED AND OBSERVED ACTIVITY COEFFICIENTS

| Salt | å. | $\Delta\gamma\pm$ |
|---------------------|------|-------------------|
| $LaBr_3$ | 6.20 | 0.0012 |
| $PrBr_3$ | 6.10 | .0026 |
| NdBr₃ | 6.06 | .0011 |
| GdBr₃ | 5.72 | .0012 |
| $HoBr_3$ | 6.42 | .0008 |
| ErBr_{3} | 5.90 | .0015 |
| GdCl₃ | 5.63 | .0010 |

Except that the å. values of the rare earth bromides are larger than those of the corresponding chlorides,⁵ there does not appear to be a regular variation among these values. Unfortunately, the method used to calculate these values is not sufficiently sensitive to determine whether these variations are real. Undoubtedly, these values are also influenced by the approximations inherent in the Debye–Hückel theory which may not be valid for these 3–1 electrolytes. Before more definite conclusions may be made concerning the electrolytic behavior of rare earth solutions, data on the rare earth elements not yet investigated should be obtained and correlated with other physical measurements on these elements.

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(18) T. Shedlovsky, ibid., 72, 3680 (1950).

⁽¹⁷⁾ A. S. Keston, THIS JOURNAL, 57, 1671 (1935).