[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

Observations on the Rare Earths. XXXIX. The Transference Numbers of the Chlorides of Neodymium, Samarium and Gadolinium. Part II. Measurement of the Transference Numbers

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The only important difference in physical properties that has been noted for the rare earth ions is the difference in magnetic susceptibilities. The attempted separation of the rare earths by Kendall and Clarke[1] and the interesting results obtained by Hopkins and Selwood[2] suggest that a difference in ionic mobilities might be found.

The mobility of an ion depends primarily upon its effective diameter although it is probable that the measured value is likely to be affected to a considerable extent by the existence of charged complexes between the cations and anions of the salt. The effective diameter with which we are concerned is that of the solvated ion in solution. The solvation of ions in solution[3] is a "coördination" phenomenon. The coördination forces depend primarily upon the charge and the ionic radius as obtained from crystal densities. The valence is the same for all the rare earth ions and the crystal radii show only small variations.

An additional factor may, however, enter into the binding of solvent molecules by the rare earth ions. The outer group of electrons is the same for each atom but the N shell of electrons varies from element to element and the magnetic susceptibilities vary as a result. It is not likely that the magnetic properties would affect the solvation directly but electrostatic interaction is to be predicted between the electrons of the N shell and the polar water molecules. Such interactions would be slightly different for the different rare earths. Any of the foregoing causes which affect the coördination of solvent molecules will affect the formation of interionic complexes. In the experiments described the transference number is measured rather than the more fundamental ion mobility.

Apparatus

The cell used was similar in principle to the one designed by MacInnes.[4] The glass tube through which the boundary was swept was 3 mm. in diameter. It was etched in intervals of 1 cm. through a 10 cm. length and the volumes calibrated with mercury in a manner similar to that described by Longsworth.[5] The total volume swept through in a measurement was 1.111 cc.

The thermostat was regulated by means of a mercury regulator at 25° within 0.01°. The thermometer used was calibrated against a platinum resistance thermometer.

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(1) Kendall and Clarke, *Proc. Nat. Acad. Sci.*, **11**, 393 (1925).

(2) Selwood and Hopkins, *Trans. Am. Electrochem. Soc.*, **55**, 59 (1929).

(3) Rodebush and Ewart, THIS JOURNAL, **54**, 419 (1932).

(4) MacInnes, Cowperthwaite and Huang, *ibid.*, **49**, 1710 (1927).

(5) Longsworth, *ibid.*, **54**, 2741 (1932).

Materials

All solutions were made up in conductivity water and kept in Pyrex glass-stoppered Erlenmeyer flasks. The solutions of the rare earth chlorides were made up as follows. The calculated volume of redistilled constant boiling hydrochloric acid was added to the pure rare earth oxide suspended in conductivity water. The solution was heated, filtered from the excess oxide and diluted to exactly tenth normal. The normalities were determined by gravimetric chloride analyses. Analyses of the rare earths by the usual method of precipitating the oxalates with oxalic acid and subsequently igniting to the oxide checked satisfactorily with the chloride analyses. The lithium chloride solutions were prepared from Baker and Adamson C. P. lithium carbonate. The carbonate was dissolved in a slight excess of redistilled constant boiling hydrochloric acid. The lithium chloride was recrystallized three times and dried over phosphorus pentoxide in a vacuum desiccator. The solutions were analyzed for chlorides gravimetrically. The lithium was also determined as the sulfate as a check on the neutrality of the salt.

Experimental Procedure

A complete survey of the moving boundary methods has been published recently by MacInnes and Longsworth.[6] There are three types of boundaries that may be used. One is an ascending boundary in which the following solution is formed by the electrolysis of a suitable metal anode. This method is limited in its application and was not found adaptable to the present measurements. The other two types are both formed by shearing two solutions, one in which the following solution is at the bottom and the boundary ascends, and the other where the following solution is at the top and the boundary descends. The latter type of boundary was found most suitable in the present work.

In order to check the apparatus, some preliminary experiments were made on potassium chloride solutions. The transference number of the potassium ion measured was in excellent agreement with the value published by Longsworth.[7]

The measurements were made on 0.1 N solutions of the rare earth chlorides. The chlorides were used in preference to the sulfates, which give some indication of complex ion formation, and in preference to the nitrates, for which there are no conductivity data available. Moreover, the degree of hydrolysis of the rare earth chlorides is inappreciable at a concentration of tenth normal.

Since the transference numbers of the rare earth ions were not even known approximately, it was necessary, first of all, to determine a concentration of lithium chloride which would give reliable results. The concentration of lithium chloride was accordingly varied from 0.05 to 0.1 N. That concentration was chosen as correct for which the data gave the correct transference number of the lithium ion. Since over the above concentration range the transference number of the rare earth ions varied only 0.6% it was not necessary to regulate the concentration of lithium

(6) MacInnes and Longsworth, *Chem. Rev.*, **9**, 171 (1932).

(7) Longsworth, THIS JOURNAL, **52**, 1897 (1930).

chloride exactly, and an approximately 0.07 *N* solution of lithium chloride was found to be a suitable concentration for all three rare earth ions.

The boundaries were found to move independently of potential gradient between 8 and 10 volts per cm.

The transference numbers are calculated from the usual formula, $T = FCV/1000IT$, in which T is the transference number, F is the faraday in coulombs, C the concentration in equivalents per liter of solution, I the current in amperes and V the volume swept through in t seconds. The data were assembled and recorded as shown for a typical run in Table I.

TABLE I

$GdCl_3$, 0.0998 *N*; LiCl, 0.073 *N*; I, 5.594×10^{-3} amperes

X	*V*	*t*	*T*	*X*	*V*	*t*	*T*
0							
1	0.1152	451	0.4397	0–10	1.111	4406	0.4341
2	.2221	877	.4359	0–9	1.002	3976	.4339
3	.3348	1326	.4338	0–8	0.8951	3548	.4343
4	.4495	1778	.4346	1–10	.9970	3955	.4339
5	.5633	2229	.4350	1–9	.8870	3525	.4332
6	.6718	2659	.4349	2–10	.8901	3529	.4334
7	.7767	3078	.4344				
8	.8951	3548	.4343				
9	1.002	3976	.4339				
10	1.111	4406	.4341			Mean	0.4338

The values in the last column are calculated from readings in which the boundary has traveled through eight or more centimeters. Obviously the effect of errors in time and volume measurement is least in these values. The mean of the values in the last column is accepted as the measured transference number. Because the current was maintained constant by hand regulation and the time was measured with a stop watch, the accuracy of MacInnes, whose refinements include automatic constant current regulation and a more accurate device for time measurement, could hardly be expected.

Results

The results of the final measurements with suitable lithium chloride concentrations and at suitable potential gradients are given in Table II.

Transference numbers are subject to two corrections. The volume correction is necessitated from the volume changes occurring at the electrodes during electrolysis. Since in these measurements the cathode chamber was closed and the anode chamber exposed to the atmosphere, only the volume changes occurring at the cathode need be considered in determining the correction factor. Lewis[8] derived the following formula for the correct transference number, T

$$T = T_{\text{meas.}} + C\Delta V/1000$$

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(8) Lewis, THIS JOURNAL, **32**, 862 (1910).

TABLE II

Ion	$I \times 10^3$	Concn. LiCl, N	$T_{\text{meas.}}$	$T_{\text{mean.}}$	Vol.$_{\text{corr.}}$	$T_{\text{corr.}}$
Sm	5.094	0.068	0.4429			
	5.094	.072	.4433			
	5.594	.068	.4430			
	6.094	.068	.4431	0.4431	0.0013	0.442
Nd	5.094	.067	.4432			
	5.594	.067	.4431	.4432	.0013	.442
Gd	5.094	.068	.4344			
	5.094	.073	.4342			
	5.594	.073	.4341			
	6.094	.073	.4346			
	5.594	.073	.4338	.4342	.0013	.433

where C is the concentration and ΔV the volume change expressed in milliliters per faraday equivalent. During the passage of one faraday of electricity one mole of silver chloride is dissolved at the cathode with the formation of one gram atom of silver and one equivalent of the rare earth chloride. Thus

$$\Delta V = V_{\text{Ag}} + T_+ \times {}^1/_3 V_{\text{RCl}_3} - V_{\text{AgCl}}$$

The volume change due to the formation of RCl_3 can only be approximated since a concentration change is occurring during the electrolysis. Since the volume correction is relatively small, however, only an approximation is necessary. The partial molal volumes of the rare earth chlorides in 0.1 N solution were determined from density measurements by Selwood,[9] by a method described by Lewis and Randall.[10] The molal volumes of the three rare earth chlorides are approximated as 18 cc. Silver has an atomic volume of 10.3 cc. and silver chloride of 25.8 cc.

The solvent correction as pointed out by Longsworth[7] is only of importance at concentrations below 0.05 N and need not be considered here.

Discussion of Results

The transference number of gadolinium ion is less by over 2% than that of either the neodymium or samarium ion. Although this is the anticipated result, the degree of difference does not justify the direct conclusion that its mobility is less. When speaking of the mobility of the rare earth ions measured at a finite concentration, one is referring to an apparent mobility which includes the effect of possible intermediate ions. This apparent mobility is represented by T_+. The conductivities of solutions of gadolinium and samarium chlorides have not been measured and the conductivity of $NdCl_3$ has not been measured at exactly 0.1 N. The existing conductivities, however, allow of some interpretation. The conductivities of the chlorides of Pr, Nd, Ce and La show variations within 15% at 0.0625 N. It is probable that the conductivities of Gd and Sm chlorides

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(9) Selwood, Ph.D. Dissertation, Urbana, Illinois.

(10) Lewis and Randall, "Thermodynamics," McGraw-Hill Book Company, Inc., New York, 1923, p. 38.

would fall within this range. If it can be shown that the mobility of the Cl ion is the same in all 0.1 *N* solutions of the rare earth chlorides, the low transference number of gadolinium is indicative of a lower ion mobility. Conductivity measurements are necessary for exact conclusions.

It does not seem possible under any circumstances that the mobility of the gadolinium ion at 0.1 *N* is greater than that of either the samarium or the neodymium ions. These results thus seem to contradict both Kendall and Hopkins, who found gadolinium concentrating at the cathode end of their migration tubes when in a mixture with samarium. They were working with 0.5 *N* solutions, however, and at such widely different concentrations results are hardly comparable. Hopkins could get no evidence of separation of samarium from neodymium, which is as might be expected from the identical values of their transference numbers.

If the relatively small differences in mobility as indicated by the transference numbers of the three rare earth ions investigated is characteristic of all the rare earth ions, it is obvious that material separation of rare earth compounds can hardly be achieved through an ionic migration method.

Summary

The transference numbers of the neodymium, samarium and the gadolinium ions, measured in 0.1 *N* solutions of their chlorides at 25° by the moving boundary method, are 0.442, 0.442 and 0.433, respectively.

The significance of the transference numbers is discussed from the point of view of mobility and ionic hydration.

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Further Studies in the Rare Gases. II. The Diffusion of Helium through Crystalline Substances and the Molecular Flow through Rock Masses[1]

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In the determination of geologic time by the helium–uranium–thorium ratio, it is important to ascertain a factor expressing the possibilities of migration of helium in the substance under investigation. Thus, Paneth and Urry[2] have shown that the loss of helium from the iron meteorites on heating at 1000° for several hours corresponds to the surface helium only. In corroboration of this fact the following experiments on iron and steel

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(1) "Further Studies of the Rare Gases. I. The Permeability of Various Glasses to Helium," appeared in THIS JOURNAL, **54**, 3887 (1932). This second paper presents the negative results obtained with metals and the mechanism and rate of flow through rock masses. A mathematical term is derived expressing the fineness of grain of a rock.

(2) Heliumuntersuchungen IX, *Z. physik. Chem.*, **A152**, 127 (1931).