

mentally observed values. Standard methods were used to convert molarity to molality.

The activity coefficients for  $\text{LaCl}_3$  have been previously determined by MacInnes and Shedlovsky<sup>5</sup> with precision. The measurements were repeated in this paper as a check upon experimental technique. The agreement, shown in Fig. 1, is well within the experimental error.

Mason<sup>8</sup> has used the isopiestic method to determine the osmotic coefficients of some rare earth chloride solutions. Using the data of Table I, these osmotic data may be used to extend the activity coefficients for these salts up to 2 molal.

The activity coefficients for the rare earth salts studied show very little variation and are plotted in Fig. 2. The data up to 0.1  $N$  agree remarkably well with the Debye-Hückel theory, although evidence that a small deviation is beginning at the higher concentrations is indicated when the data of Mason<sup>8</sup> are combined with our results. The magnitudes of the  $\alpha$  values are quite reasonable for rare earth chlorides. They exceed the sums of the crystallographic ionic radii by an amount approximately equal to the diameter of a water molecule.

**Acknowledgments.**—The authors wish to thank the following members of Dr. Spedding's research group: Mr. Tom A. Butler and Mr. J. E. Powell for the preparation of pure praseodymium, neodymium and samarium oxides, and Mr. Sigmund Jaffe and Mr. I. S. Yaffe for completing the measurements on erbium chloride. They also wish to thank Dr. V. A. Fassel and Mr. Harold Cook for spectrographic analyses of the oxide fractions.

(8) C. M. Mason, *THIS JOURNAL*, **60**, 1638 (1938); *ibid.*, **63**, 220 (1941); R. A. Robinson and R. H. Stokes, *Trans. Faraday Soc.*, **45**, 612 (1949).

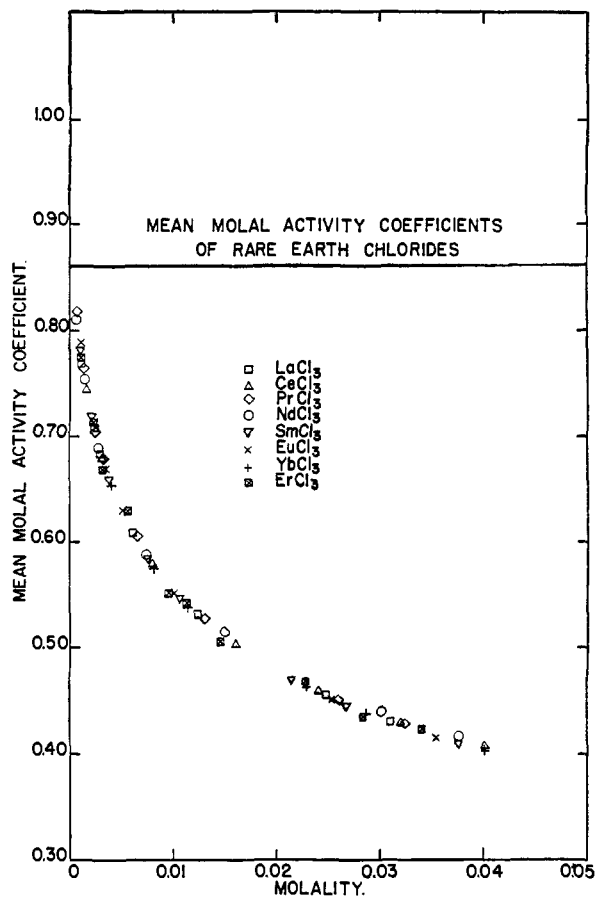


Fig. 2.—Mean molal activity coefficients of the rare earth chlorides.

Finally, we wish to thank Dr. E. I. Fulmer for his interest and helpful advice.

CONTRIBUTION NO. 188 FROM THE INSTITUTE FOR ATOMIC RESEARCH AND DEPARTMENT OF CHEMISTRY, IOWA STATE COLLEGE<sup>1</sup>

## The Preparation of Rare Earth Metals

BY F. H. SPEDDING AND A. H. DAANE

RECEIVED JANUARY 30, 1952

In order to prepare highly pure rare earth metals, a technique was devised whereby rare earth chlorides are reduced by calcium in tantalum crucibles; the resulting rare earth metal is vacuum cast in tantalum containers. Samarium, europium and ytterbium chlorides are reduced only to their stable divalent state and can thus be efficiently removed from rare earth mixtures by such metallurgical processing.

### Introduction

Iowa State College has in progress several researches wherein it is hoped to obtain accurate data on properties of metals such as resistivity, thermal conductivity, magnetic susceptibility, vapor pressures, thermodynamic data, Hall coefficients, etc. It is hoped that the obtaining of such accurate data will prove extremely valuable in arriving at a better understanding of the nature of the metallic state. Due to their unique electronic structures, the rare earth metals seem to offer an ideal group of metals for such an investigation. It

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

has been pointed out elsewhere<sup>2</sup> that with this series, it is possible to get elements which only differ essentially from each other in the radius of the atoms and in their properties which depend on this radius. Therefore, accurate data over this series would permit a simpler theoretical treatment than would be possible for metals in general, since many variables could be held constant which would not be the case in metals from other parts of the periodic table.

(2) (a) F. H. Spedding, P. Porter and J. Wright, *THIS JOURNAL*, **74**, 2781 (1952); (b) F. H. Spedding, H. A. Wilhelm, W. H. Keller, D. H. Ahmann, A. H. Daane, C. C. Back and R. P. Brickson, *Ind. Eng. Chem.*, in press (1952).

This Laboratory has previously reported processes for separating pure rare earth salts, one from the other,<sup>3</sup> and processes for producing relatively pure rare earth metals.<sup>2</sup> Since the metallurgical reactions were carried out in a closed system, the only impurities present in the metal would be those introduced with the raw materials that went into the reaction, and these could be purified to any extent desired. However, in preparing and casting the metals, it was necessary to use ceramic materials which tended to introduce small amounts of nitrogen, oxygen and carbon into the metal as a result of attack on the crucible and degassing of the ceramic materials. It was therefore felt desirable to develop a process capable of producing extremely pure metals, both with regards to metallic, and non-metallic impurities, so that this metal could be used in the study of metallic properties.

The previous history of the preparation of pure rare earth metals was described elsewhere,<sup>2b</sup> and therefore will not be repeated here.

The basis of the method of preparing the metals chosen for this work was the reduction of rare earth halides by an active metal. Of the rare earth compounds which have been employed in such work in the past, the halides were the most promising, since (1) their melting points are low enough to allow complete reaction in a reduction process at relatively low temperatures, (2) the estimated free energies of the reaction of most of the rare earth halides with some active metals were favorable to the formation of the rare earth metals; the calculation of these data from the information recently published by Brewer, *et al.*,<sup>4</sup> permitted confirmation of this; and (3) the active metal halides which would be formed as slag in a reduction would aid in the agglomeration of the product metal by their fluxing action and their low melting points. Because of the ease of their preparation, the chlorides were the halides chosen for this work. Active metals whose heats of reaction with the rare earth chlorides are favorable to formation of rare earth metals include sodium, potassium, calcium and barium. Calcium was the reductant employed in this work since it could be obtained quite pure and was easier to handle than the other metals.

Since the rare earth metals are so electropositive, extremely inert refractories were needed to prepare containers for the metallurgical work. Magnesium oxide, calcium oxide, beryllium oxide, zirconium oxide and dolomitic oxide crucibles were tested for use in this work by holding molten lanthanum or cerium in contact with them for 20 minutes at 1200° in a vacuum. This temperature was chosen for testing, since previous work in this Laboratory<sup>2b</sup> had shown that it was necessary to vacuum melt the metals at this temperature or higher to eliminate volatile impurities from the first metal obtained. In each case there was definite crucible attack by the rare earth metal which introduced oxygen as an impurity in the product metal, and in the case

of beryllium and zirconium oxide crucibles, there was evidence of alloy formation. Some previous workers had prevented such crucible attack by keeping the reaction temperature so low that fusion of the product metal did not occur. However, powdered metal results in such cases and the removal of slag from such metal cannot be done without oxidizing the surface of the metal granules; since the particles are quite small with a large surface area, this represents a serious source of contamination. In a vapor pressure study of cerium metal, Ahmann<sup>5</sup> had shown that cerium did not react with tantalum up to 1700°, and subsequent tests in the course of the present study showed that tantalum does not react with other rare earth metals, rare earth chlorides, calcium or calcium chloride under the conditions of this work. To provide tantalum crucibles, molds, etc., techniques were devised for fabricating such articles from 0.001" tantalum sheet.<sup>6</sup>

### Experimental

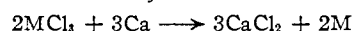
The lanthanum oxalate used in this work was obtained from the Lindsay Light and Chemical Co. and was found to contain between 0.05 and 0.1% each of cerium, neodymium and praseodymium. Cerium ammonium nitrate was purchased from the G. Frederick Smith Chemical Co. and was found to contain less than 0.05% of other rare earths and thorium. The neodymium, praseodymium and gadolinium oxides were purchased in the form of a crude rare earth mixture from the Lindsay Light and Chemical Co. All of these rare earths were purified by another group of this Laboratory by ion-exchange separation techniques, and resulted in lanthanum, cerium, praseodymium and neodymium oxides which were better than 99.9% pure with no other rare earths or thorium detectable; the gadolinium contained 2% samarium and 0.02% europium.

The anhydrous rare earth chlorides were prepared by dissolving the oxides, or in the case of cerium, the cerium ammonium nitrate, in 6 *N* hydrochloric acid, and evaporating the resulting solution to a boiling point of 125–130°. On cooling, the hydrated chlorides crystallized and these were dehydrated by a method similar to that of Kleinheksel and Kremers<sup>7</sup>; this consisted of slowly heating the hydrated chlorides in a stream of dry hydrogen chloride to 400° at a pressure of about 60 mm. A typical analysis of lanthanum prepared by this method is: *Anal.* Calcd. for LaCl<sub>3</sub>: La, 56.64; Cl, 43.36. Found: La, 56.60 ± 0.05; Cl, 43.38 ± 0.04.

Calcium obtained from Dominion Magnesium, Ltd., was reprocessed and ground to size by another group of this Laboratory. The ground material was sieved to remove the undersize particles and loose calcium oxide powder, producing a minus 10 mesh, plus 50 mesh material which had the following analysis, with quantities listed in parts per million: Fe, 40; Mn, 20; N, 50; B, less than 1; Cd, less than 1; Al, 15; Mg, 400; C, 250; Na, less than 50; K, less than 50; Li, less than 20. The freshly ground calcium was stored in an argon atmosphere until used.

The tantalum crucibles were 1<sup>1</sup>/<sub>16</sub>" in diameter and 5" high and were welded from 0.001" sheet, welding in an inert atmosphere by a technique previously reported from this Laboratory.

**Procedure.**—To ensure complete reduction of the rare earth chloride, 10% more calcium was used than was required by the stoichiometry of the reaction



in which M designates a rare earth element. For a typical preparation, 70 g. of the rare earth chloride and 18.5 g. of calcium were thoroughly mixed in an inert atmosphere and either jolt packed in the tantalum crucible or compacted in a

(3) F. H. Spedding, *et al.*, *THIS JOURNAL*, **69**, 2812 (1947).

(4) L. Brewer, L. A. Bromley, P. W. Gilles and N. L. Lofgren, "The Thermodynamic Properties of the Halides." In L. L. Quill, "The Chemistry and Metallurgy of Miscellaneous Materials," McGraw-Hill Book Co., Inc., New York, N. Y., 1950.

(5) D. H. Ahmann, Atomic Energy Commission Declassified Document 3205, Technical Information Service, Oak Ridge, Tenn., 1950.

(6) A. H. Daane, *Rev. Sci. Instruments*, unpublished.

(7) J. H. Kleinheksel and H. C. Kremers, *THIS JOURNAL*, **50**, 959 (1926).

powder press into cylinders which were placed in the tantalum crucible. The loaded outgassed crucible was covered with a tantalum lid, perforated to permit gas to enter and leave the vessel, and was set inside of a covered magnesium oxide crucible 2" in diameter and 7" tall. This was then placed in a 2 1/4" diameter silica tube, one end of which was fused shut, with the other end ground to serve as the inner half of a 55/50 standard taper joint. The silica tube was sealed onto a vacuum system by means of Apiezon "W" sealing wax, evacuated to  $10^{-3}$  mm., and then filled to 1 atmosphere with argon, purified by passing it over hot uranium turnings.<sup>8</sup> The tantalum crucible was heated by means of an Ajax-Northrup 6 KW induction furnace, and at a temperature of about 550 to 600° the exothermic reaction between the calcium and the rare earth chloride took place as evidence by the sudden increase in temperature of the reaction crucible. About 5 minutes was required to reach the final "holding" temperature at which the crucible was held for 13 minutes to permit complete agglomeration of the product metal; this temperature was measured by means of a Leeds and Northrup model 8622-C optical pyrometer, and was 1000° for lanthanum, cerium, praseodymium and neodymium, and 1350° for gadolinium. After cooling to room temperature, the tantalum vessel was soaked in water which removed the calcium chloride slag and most of the excess calcium, leaving a layer of fused rare earth metal in the bottom which contained from 1 to 3% calcium. This impurity was removed by remelting the metal in the same crucible and vacuum apparatus in a vacuum of  $10^{-3}$  mm. or better, heating to 1200° for lanthanum, cerium, praseodymium and neodymium, and 1350° for gadolinium. The thin tantalum skin could be peeled off the resulting rare earth metal cylinder.

### Results

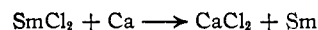
Lanthanum, cerium, praseodymium, neodymium and gadolinium have been prepared by this technique in 40-g. lots with yields consistently greater than 99%. To test the possibility of extending this technique to smaller charges, one reduction of lanthanum chloride was carried out on a 250-milligram scale with a yield of over 90%.

Analyses of the product metals showed them to contain not over 150 p.p.m. calcium, with the amounts of other rare earths the same as in the

(8) A. S. Newton, Atomic Energy Commission Declassified Document 2135, Technical Information Service, Oak Ridge, Tenn., 1948.

original oxide, except in the case of gadolinium, as will be discussed below.

Several attempts were made to prepare samarium metal by this technique on the 40-g. scale, but in each case the reddish-brown  $\text{SmCl}_2$  was the product formed. This is in agreement with the calculated free energy value of 14 kcal. for the reaction



at 1000°K. An interesting consequence of this failure of calcium to reduce samarous chloride was observed when a rare earth chloride mixture containing 98% gadolinium, 2% samarium and 0.02% europium was reduced with calcium. The gadolinium metal was obtained with a yield of better than 99% and contained less than 0.05% Sm (the lower limit of detection); as the samarium:europium ratio in the slag was the same as in the original material, it was apparent that europium chloride also was not reduced by calcium to the metallic state under the conditions of these experiments. A reduction of a sample of gadolinium chloride containing 10% samarium chloride and 0.1% europium chloride also gave gadolinium metal containing no detectable samarium or europium; no reductions have been attempted on mixtures containing more than 10% samarium. An attempt to reduce ytterbium chloride with calcium under the same conditions yielded only ytterbous chloride, and demonstrated that this metallurgical technique is an effective method of separating ytterbium as well as samarium and europium from other rare earths. This separation is particularly valuable in the case of gadolinium and samarium mixtures as the conventional separation methods are quite inefficient in removing small amounts of samarium from gadolinium.

This technique is being extended to the other rare earths as they become available from the separation and purification processes.

AMES, IOWA

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF ROCHESTER]

## Photochemical Investigations. IX. The Photochemistry of Iodine Monochloride and Hydrogen<sup>1</sup>

BY GERALD G. PALMER<sup>2</sup> AND EDWIN O. WIIG

RECEIVED FEBRUARY 28, 1951

The quantum yield for the photochemical reaction between iodine monochloride and hydrogen has been measured with a static system at several different pressure ratios. A value of 9.0 kcal. was found for the energy of activation. The mechanism proposed by Hofer and Wiig has been verified. Agreement between the derived rate equation and the data is quite satisfactory.

In a previous paper<sup>3</sup> the quantum yield of the photochemical reaction between iodine monochloride and hydrogen was determined in a flow system. The observed hydrogen chloride quantum yield of 1.5 suggested a mechanism that included a short chain reaction, thus:

	$\Delta H$ , kcal.	$E_{act.}$ , kcal. (Hirschfelder)
(1) $\text{ICl} + h\nu = \text{I} + \text{Cl}$		
(2) $\text{Cl} + \text{H}_2 = \text{HCl} + \text{H}$	+ 0.9	6.5
(3) $\text{H} + \text{ICl} = \text{HCl} + \text{I}$	-52.2	2.7
(4) $\text{Cl} + \text{ICl} = \text{Cl}_2 + \text{I}$	- 7.5	2.7
(5) $\text{I} + \text{I} + \text{M} = \text{I}_2 + \text{M}$	-35.4	

(1) From a thesis submitted to the Graduate School of the University of Rochester in 1947 in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

(2) Eastman Kodak Fellow in Chemistry 1946-1947.

(3) L. J. E. Hofer and E. O. Wiig, THIS JOURNAL, 67, 1441 (1945).

Without reaction (4) the quantum yield of hydrogen chloride would be exactly two. For a yield of less than two, reactions (2) and (4) must compete for the chlorine atom. The over-all yield