other atoms combined chemically with it." There seems no reason, then, why the shift of absorption bands should not be produced by the same mechanism. Some information as to the nature of the molecular field could be gained by measurements on the susceptibility of neodymium salts diluted with the isomorphic salts of the diamagnetic rare earth lanthanum.

The author wishes to thank Dr. Charles P. Smyth for his interest and advice in this work. He is also indebted to Dr. B. S. Hopkins, of the University of Illinois, for the use of several hundred grams of pure neodymium oxide.

Summary

The magnetic susceptibility of neodymium nitrate in aqueous solution has been found to decrease with increasing concentration. This behavior is discussed in connection with changes in absorption spectrum and refraction previously reported by the author, and with reference to Fajans' theory of the deformation of electron shells.

PRINCETON, NEW JERSEY

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF ILLINOIS]

OBSERVATIONS ON THE RARE EARTHS. XXXVII. ELECTROLYTIC PREPARATION OF RARE EARTH AMALGAMS. 1. PREPARATION OF AMALGAMS OF LANTHANUM AND NEODYMIUM[1]

BY L. F. AUDRIETH, E. E. JUKKOLA AND R. E. MEINTS, WITH B. S. HOPKINS

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In line with a series of investigations[2] which are being carried out in this Laboratory involving the use of non-aqueous solvents for the electrodeposition of metals, preliminary experiments have been performed in an effort to plate the metals of the rare earth family from solutions of their salts in various organic and inorganic solvents, but with no marked success. That such a suggestion is not new is evident from the researches of Matignon,[3] who prepared anhydrous salts of many of the rare earth elements and investigated their solubilities in various non-aqueous solvents. In connection with these studies he says, "If a solvent could be found in which salts (of the rare earth metals) ionized it would be easy to isolate the metals by simple electrolysis after the manner of Kahlenberg." Matignon had

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[1] This paper was presented before the Division of Physical and Inorganic Chemistry at the Indianapolis meeting of the American Chemical Society, April, 1931.

[2] For earlier papers of this series see Yntema and Audrieth, THIS JOURNAL, **52**, 2693 (1930); Audrieth and Yntema, *J. Phys. Chem.*, **34**, 1903 (1930); Audrieth and Nelson, *Chem. Rev.*, **8**, 335 (1931).

[3] Matignon, *Ann. chim. phys.*, VIII, **8**, 267 (1906).

evidently been much impressed by the researches of Kahlenberg,[4] who succeeded in depositing lithium from solutions of the chloride in pyridine. The preparation of the rare earth metals presents a problem of extraordinary scientific interest, in view of the fact that only six of the sixteen elements of this group have ever been obtained in the free form (Yt, Ce, La, Nd, Sm, Eu) and only two in a high state of purity (Ce, La).

Amalgams of many active metals have been prepared by the electrolysis of concentrated aqueous salt solutions using a mercury cathode. In several instances it has been found that amalgams of higher concentration can be prepared very much more readily and with less attendant decomposition by the use of non-aqueous ionizing media. Thus, Hevesy[5] prepared a 30% barium amalgam by the electrolysis of a concentrated solution of the iodide in pyridine using a mercury cathode. Laszczynski[6] prepared concentrated amalgams of potassium and sodium by electrolysis of the corresponding thiocyanates in acetone under similar conditions. Kettenbeil[7] also studied the preparation of amalgams of various elements, but was not able to prepare those "of the rare earth metals by electrolysis of their salt solutions at a mercury cathode." He reported negative results in his attempts to prepare amalgams of cerium, yttrium, didymium, zirconium and thorium electrolytically, using water, pyridine and alcohol as solvents.

However, amalgams of yttrium, cerium and lanthanum have been prepared by thermal methods and their properties studied. The decomposition of cerium amalgam has been suggested as a method for the purification of the metal.[8] In view of these facts a study of the electrolytic preparation of rare earth amalgams was undertaken in the hope that these would lead indirectly to the isolation of metals of the rare earth family which have not, as yet, been obtained in the free state.

The experimental results outlined below prove conclusively that it is possible to prepare rare earth amalgams electrolytically, not only from aqueous solution, but more conveniently by the use of absolute alcoholic solutions. The present paper concerns itself with the amalgams of lanthanum and neodymium,[9] two of the commoner members of the rare earth family. Subsequent papers will deal with the preparation of other amalgams and their decomposition for the preparation of the free metals.

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[4] Kahlenberg, *J. Phys. Chem.*, **3**, 602 (1899).

[5] Hevesy, *Z. Elektrochem.*, **16**, 672 (1910).

[6] Laszczynski, *ibid.*, **4**, 292 (1897).

[7] Kettenbeil, *Z. anorg. Chem.*, **38**, 213 (1904).

[8] Hirsch, *Trans. Am. Electrochem. Soc.*, **29**, 57 (1911); *Ind. Eng. Chem.*, **3**, 880 (1911).

[9] The authors wish to take this opportunity to acknowledge their indebtedness to Dr. Pierce W. Selwood for his assistance in the preliminary experimental work leading to the preparation of these amalgams.

Experimental

Preparation of Materials.—Anhydrous neodymium chloride was prepared by the dehydration of the hexahydrate in an atmosphere of dry hydrogen chloride in the apparatus designed by Kremers.[10]

Anhydrous lanthanum nitrate can be prepared most advantageously by application of the method employed by Booth[11] in the preparation of anhydrous beryllium nitrate, involving the use of fused ammonium nitrate. In a typical run 20 g. of lanthanum oxide was dissolved slowly in 40 g. of fused ammonium nitrate at a temperature of 170° to yield a clear solution. The temperature was then raised slowly during the course of several hours until most of the ammonium nitrate had been decomposed and the melt had solidified. The material was then ground to a powder and heated for ten hours at a bath temperature of 300° to volatilize completely the remainder of the ammonium nitrate. The resulting product was ignited to the oxide for analysis.

Anal. Subs., 0.3666, 0.3995: La_2O_3, 0.1832, 0.1998. Calcd. for $La(NO_3)_3$: La, 42.77. Found: La, 42.61, 42.65.

The anhydrous nitrate is a white, powdery substance which is extremely hygroscopic. The resulting product is very soluble in water, liquid ammonia, acetone, pyridine and acetonitrile.

Several efforts were made to prepare anhydrous neodymium nitrate by the same method. However, a product was always obtained which contained ammonia and which analyzed for the compound $Nd(NO_3)_3 \cdot NH_4NO_3$. Any attempt to remove the excess of ammonium nitrate by raising the bath temperature above 290° resulted in the formation of the insoluble basic nitrate.

The mono-hydrated halides employed in these experiments were prepared by long continued dehydration of the more highly hydrated salts *in vacuo* at 100°. Their composition was checked by analysis. Dehydration at higher temperatures usually led to the formation of insoluble basic compounds.

Apparatus.—Various types of electrolytic cells were used. The test-tube type (noted as T. T. in the tables) consisted of a large Pyrex test-tube, 200 × 38 mm., to which was sealed a glass-stoppered delivery tube with a small side arm to permit contact with the mercury cathode by means of a platinum wire. A platinum flag was used as the anode and the apparatus fitted with a stirring device. To handle larger quantities of mercury and solution Erlenmeyer flasks of various sizes were used in place of the Pyrex test-tube.

Where aqueous solutions were employed an H-shaped cell was used in order to prevent in so far as possible reaction of the anodic products with

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[10] Kremers, *Ind. Eng. Chem.*, **17**, 298 (1925).

[11] Booth, THIS JOURNAL, **52**, 2581 (1930).

the amalgams. In all cases the electrolytic cells were immersed in running water to keep the solutions at approximately room temperature.

Manipulation.—All solutions were electrolyzed for varying periods of time using a 110 d. c. current. Upon completion of the runs the cathodic materials were separated from the supernatant solutions, washed with either distilled water or absolute alcohol, and then allowed to decompose by contact with air. It was found that hydrochloric acid would not react completely with the amalgams; consequently analyses were carried out by permitting samples to decompose by exposure to the air over a period of ten days, followed by titration with standard acid to determine their rare earth metal content.

Preparation of Neodymium Amalgams.—The results for a number of typical runs are given in Table I. In all experiments involving the use of aqueous solutions an insoluble precipitate of the basic salt was obtained which would settle upon the cathode and render difficult the production of more concentrated amalgams. This did not occur when the anhydrous chloride or the mono-hydrated halides were electrolyzed in alcoholic solution.

Amalgam formation was not observed when the double neodymium ammonium nitrate, $Nd(NO_3)_3 \cdot NH_4NO_3$, was used as the solute. Reduction of the nitrate to the nitrite ion was found to have taken place.

In several experiments a pasty amalgam was obtained, indicating the formation of a Nd–Hg compound only slightly soluble in mercury. This problem is under investigation at the present time.

Neodymium amalgams are readily attacked and decomposed by air with formation of the basic carbonate. Such amalgams also undergo slow reaction with alcohol, acetone and water. They are best preserved in a vacuum or under a saturated alcoholic solution of the electrolyte.

TABLE I

PREPARATION OF NEODYMIUM AMALGAMS

Run	Type of cell	Concn. of soln.	Solvent	Time, hours	Curr. density, amp./sq. cm.	Amalgam, per cent. by weight of N
8[a]	H	15 g. of Nd_2O_3[12] diss. in HCl to 30 cc. of soln.	H_2O	4	0.33	0.2
9[b]	H		H_2O	4	.4	1.75
14[c]	T. T.	6 g. $NdCl_3 \cdot 6H_2O$ in 30 cc.	C_2H_5OH	25	.2	. .
6a[d]	T. T.	25 cc. satd. $NdCl_3$ soln.	C_2H_5OH	10	.06	2.1
19a[e]	T. T.	10 g. $NdCl_3$ in 30 cc.	C_2H_5OH	9	.07	1.6
25[f]	T. T.	8 g. $NdBr_3 \cdot H_2O$ in 20 cc.	C_2H_5OH	37	.15	2.92

[a] Poor amalgam, pptn. of basic chloride. [b] Pellet of solid amalgam formed on the surface which was analyzed. Basic salt precipitated. [c] Some amalgam, ppt. of basic chloride. [d] Good amalgam, soln. clear. [e] Pasty amalgam, clear soln. [f] Very good amalgam, clear soln.

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[12] Aqueous chloride solutions prepared by dissolving the oxide in hydrochloric acid.

Much of the mercury may be removed by distillation *in vacuo*, but not completely even at the temperature at which Pyrex glass begins to melt. The product obtained under these conditions is an extremely pyrophoric, black powder which takes fire in air. This material has been decomposed, with the elimination of the remainder of the mercury to give neodymium metal, in a high vacuum furnace using a tungsten boat, which served as the heating element. This same apparatus has even been used for volatilization of the neodymium metal with the deposition of an extremely reactive film of the element.

Lanthanum Amalgams.—Table II gives some of the experimental data covering the preparation of amalgams of lanthanum. These resemble very closely in reactions and properties the corresponding neodymium amalgams. (Table II.)

TABLE II

PREPARATION OF LANTHANUM AMALGAMS

Expt.	Type of cell	Composition and concn. of soln.	Length of run, hours	Current density, amp./sq. cm.	Atom per cent. of La in amalgam
9a[a]	H	25 g. La_2O_3[12] to give 35 cc. of aqueous chloride soln.	6	0.2–0.1	1.6
1a[b]	T. T.	Satd. soln. of $La(NO_3)_3$ in C_2H_5OH	4	0.3	..
12[c]	T. T.	Satd. soln. of $LaCl_3 \cdot 7H_2O$ in C_2H_5OH	3	.2	..
1[d]	T. T.	10 g. La_2O_3[12] to give 25 cc. of aqueous chloride soln.	0.5	.6	Slight
3b[e]	T. T.	9 g. $LaBr_3 \cdot H_2O$ in 20 cc. C_2H_5OH	20	.35	2.1

[a] Formation of much basic salt causing current to decrease gradually, fair amalgam. [b] Reduction of nitrate to nitrite, no amalgam formed. [c] Basic chloride, LaOCl, precipitated; no amalgam. [d] Basic chloride formed, Hg^{++} ions present in electrolyte. [e] Pasty amalgam formed; solution remained clear; no basic salt precipitated.

Summary

Amalgams of neodymium and lanthanum may be prepared by electrolysis of aqueous and alcoholic solutions of various of their salts using a mercury cathode. Electrolysis of the anhydrous halides, or the monohydrated halides, in alcoholic solution gives better results than the use of water as a solvent. These amalgams are extremely reactive and undergo ready decomposition. The free metals may be obtained from them by heating the amalgams *in vacuo*.

URBANA, ILLINOIS