TABLE IX (*Concluded*)

Original complex, wt. %		Saturated solution, wt. %			
KI	$KBrO_3$	KI	$KBrO_3$	Density	Solid phase
15.15	21.95	18.85	2.96	1.182	$KBrO_3$
7.03	23.15	8.77	4.54	1.103	$KBrO_3$
0.00	...	0.00	7.533	1.054	$KBrO_3$

TABLE X

$KBrO_3$–KNO_3–H_2O AT 25°

Original complex, wt. %		Saturated solution, wt. %			
KNO_3	$KBrO_3$	KNO_3	$KBrO_3$	Density	Solid phase
...	0.00	27.71	0.00	1.193	KNO_3
38.10	2.25	27.27	2.64	1.211	KNO_3
35.06	4.48	27.01	3.90	1.228	KNO_3 + $KBrO_3$
29.49	9.57	27.01	3.90	1.225	KNO_3 + $KBrO_3$
23.13	18.04	27.01	3.90	1.223	KNO_3 + $KBrO_3$
Average		27.01	3.90	1.225	KNO_3 + $KBrO_3$
20.05	16.98	23.17	4.00	1.193	$KBrO_3$
14.55	17.99	16.98	4.23	1.148	$KBrO_3$
9.43	19.02	11.10	4.64	1.110	$KBrO_3$
4.29	20.01	5.05	5.61	1.074	$KBrO_3$
0.00	...	0.00	7.533	1.054	$KBrO_3$

TABLE XI

$KBrO_3$–K_2SO_4–H_2O AT 25°

Original complex, wt. %		Saturated solution, wt. %			
K_2SO_4	$KBrO_3$	K_2SO_4	$KBrO_3$	Density	Solid phase
...	0.00	10.76	0.00	1.083	K_2SO_4
20.04	1.51	10.12	1.69	1.094	K_2SO_4
20.01	3.01	9.45	3.40	1.103	K_2SO_4
20.03	5.16	9.34	4.00	1.108	K_2SO_4 + $KBrO_3$
14.06	10.00	9.36	4.00	1.108	K_2SO_4 + $KBrO_3$
9.11	16.01	9.35	4.01	1.108	K_2SO_4 + $KBrO_3$
Average		9.35	4.00	1.108	K_2SO_4 + $KBrO_3$
7.13	16.53	8.20	4.27	1.100	$KBrO_3$
4.73	17.51	5.44	5.02	1.083	$KBrO_3$
2.30	18.97	2.67	6.08	1.066	$KBrO_3$
0.00	...	0.00	7.53	1.054	$KBrO_3$

Summary

1. The three-component systems consisting of water and the following pairs of salts have been studied at 25°: $NaBrO_3$–NaCl (also at 10°); $NaBrO_3$–NaBr (also at 10 and 45°); $NaBrO_3$–NaI; $NaBrO_3$–$NaNO_3$; $NaBrO_3$–Na_2SO_4; $KBrO_3$–KCl; $KBrO_3$–KBr; $KBrO_3$–KI; $KBrO_3$–KNO_3; $KBrO_3$–K_2SO_4. Double salt formation has not been found in any of these cases at the temperatures here reported.

2. These series of systems are briefly compared with the corresponding series involving sodium iodate and potassium iodate.

NEW YORK, N. Y. RECEIVED AUGUST 7, 1933

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

Observations on the Rare Earths. XLI. Electrolytic Preparation of Rare Earth Amalgams. 3. Amalgams of Lanthanum, Neodymium, Cerium, Samarium and Yttrium. Metallic Lanthanum, Neodymium and Cerium by Thermal Decomposition of Their Amalgams

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

Previous investigations[1] have shown that certain rare earth metal amalgams may be prepared readily by the electrolysis of their salts in various non-aqueous solvents using a mercury cathode. Subsequently it was found that lanthanum amalgam could be decomposed thermally to give the metal in a state of high purity.[2]

Since the preparation of the amalgams and their decomposition may be carried out using relatively small quantities of materials—a factor which must be considered in researches dealing with the rare earths—it was deemed advisable to investigate more thoroughly the conditions governing amalgam formation. The present paper gives the results of such a study and includes preliminary observations in the extension of this method to the preparation of the amalgams of samarium and yttrium.

Experimental[3]

Amalgams of lanthanum, neodymium, cerium, samarium and yttrium may be prepared conveniently by electrolysis at room temperatures of concentrated solutions of the anhydrous chlorides in absolute ethyl alcohol as solvent using a mercury cathode. Other solvents, such as glacial acetic acid and the higher alcohols, were found to be too poorly conducting to be of any use. Methyl alcohol was found to be fairly satisfactory. Electrolysis of aqueous solutions resulted in some amalgam formation, but was accompanied in every case by precipitation of considerable quantities of the basic salt.

Attempts were made to use other rare earth salts as electrolytes. Sulfates were too slightly soluble in ethyl alcohol, while nitrates suffered reduction at the cathode. Acetates, both in glacial acetic acid and in alcohol, gave no amal-

---

[1] Audrieth, Jukkola, Meints and Hopkins, THIS JOURNAL, **53**, 1805 (1931).

[2] Meints, Hopkins and Audrieth, *Z. anorg. allgem. Chem.*, **211**, 237 (1933).

[3] See Refs. 1 and 2 for details concerning apparatus and procedure.

gams. Because of the difficulties involved in the preparation of the anhydrous chlorides, the double pyridine hydrochlorides[4] of the rare earths were tried as electrolytes. Dilute amalgams only were obtained.

It was found advisable to keep the current density fairly low (0.05 ampere per sq. cm.) in order to prevent cathodic dispersion of the mercury. The surface of the mercury cathode was also kept agitated to prevent the formation of a layer of solid amalgam.

With the exception of yttrium it was possible to prepare amalgams containing from 1 to 3% of the rare earth metal. In no instance was it possible to prepare yttrium amalgams electrolytically containing more than 0.2%.

Properties of Rare Earth Metal Amalgams.—All of the rare earth amalgams thus far studied are very unstable, decomposing in air to form products consisting largely of the hydroxide with some basic carbonate. The dilute amalgams, prepared directly by electrolysis, are best kept under a concentrated solution of the electrolyte.

All of the amalgams may be concentrated with respect to their rare earth metal content by heating to a temperature of about 235° in an all-glass vacuum distillation apparatus. This procedure results in the elimination of a considerable portion of the mercury and in the eventual formation of solid to powdery masses containing approximately 15% rare earth metal. Using a specially designed vacuum furnace and crucible lined with the respective rare earth oxides these concentrated amalgams may then be decomposed thermally to give the corresponding metals.[5] A temperature of about 1000° must finally be attained in this process in order to eliminate the last traces of mercury and to fuse the metal. Small pellets of lanthanum, neodymium and cerium were prepared in this manner. That the metals obtained contained no mercury is indicated by the fact that they underwent no decomposition in contact with air, whereas the slightest trace of mercury would cause rapid reaction with formation of the oxide. The purity of the metals obtained by this procedure is limited only by the purity of the starting materials.

X-ray diffraction patterns of the metals obtained by the amalgam decomposition method agree with the data required for the hexagonal close-packed structure in the case of neodymium and lanthanum. The cerium samples showed only the face-centered cubic form. These findings check with those reported previously by Quill.[6]

Summary

Dilute amalgams of lanthanum, neodymium, cerium, samarium and yttrium may be prepared by electrolysis of concentrated solutions of the anhydrous chlorides in ethyl alcohol using a mercury cathode.

Lanthanum, neodymium and cerium amalgams have been concentrated by vacuum distillation at temperatures up to 235° to give solid amalgams containing approximately 15% of the rare earth metal.

Metallic lanthanum, neodymium and cerium have been prepared by the complete thermal decomposition of the respective amalgams.

URBANA, ILL. RECEIVED AUGUST 11, 1933

---

[4] These compounds were prepared by dissolving the rare earth oxides in fused pyridine hydrochloride. The excess pyridine hydrochloride was removed by distillation in a vacuum leaving a residue whose composition approximated that required by the formulas $NdCl_3 \cdot C_5H_5N \cdot HCl$ and $YCl_3 \cdot C_5H_5N \cdot HCl$.

[5] For further details see Thesis by E. E. Jukkola, University of Illinois, 1933.

[6] Quill, *Z. anorg. allgem. Chem.*, **208**, 273 (1932).