

CONTRIBUTION FROM THE UNIVERSITY OF CALIFORNIA,
LOS ALAMOS SCIENTIFIC LABORATORY, LOS ALAMOS, NEW MEXICO

Separation of the Lanthanons at Amalgam Cathodes. V. A Kinetic Study of Lutetium Enrichment in Methanol Electrolytes¹

By E. I. ONSTOTT

Received June 26, 1961

A kinetic study of the electrolytic phase transfer of radioactively tagged Tm in the presence of a many-fold excess of Lu at an amalgam cathode was done in boiling, refluxing methanol to demonstrate Lu enrichment in the electrolyte and to show electrode reactions. Under near optimum conditions Lu of 99% purity was enriched to 99.9% purity in one electrolysis in 20% yield. In a different experiment in which a mixture of Ho, Er, Tm, and Lu was electrolyzed, Ho was enriched fivefold in the amalgam phase. The kinetic studies showed that there is a simultaneous electrosolvolytic reaction which generates base (probably hydroxide ion from residual water in the methanol) and precipitates the lanthanons from the electrolyte in a specific region of the system. The parameters of current density, total electrolyte concentration of lanthanons, and water content of the methanol markedly affect certain electrode reactions. Therefore electrolysis conditions must be chosen carefully if a satisfactory yield of purified lutetium is to be achieved.

Introduction

Lutetium should be the most difficult of the lanthanons to electrolyze into a mercury cathode from aqueous and methanol electrolytes if the behavior trend of the lanthanide series can be projected.² Consequently, it would be anticipated that the lighter lanthanons could be preferentially electrolyzed away from Lu, and if the electrolyses were continued long enough, then high purity Lu would be left behind in the electrolyte.

This work was done to show the behavior of Lu and to prove that Lu is rather easily enriched to a high purity. The mechanism by which Lu enrichment occurs was also studied to provide a more fundamental understanding of the discriminatory action of the cathode.

Methanol was chosen as the solvent since previous work showed that it is virtually impossible to obtain a reasonable yield of the heaviest lanthanons by aqueous electrolysis, except for Yb.² Boiling, refluxing conditions were utilized to allow near-isothermal operation and to minimize the effects of concentration gradients both in the electrolyte and in the mercury. Operation at the boiling point of the electrolyte allowed dissipation of Joule heat generated by the passage of current through the cell.

Experimental

Method.—The method developed previously² of electrolyzing the monolithium acetate-lanthanion acetate salt in methanol was tried, but the yield of electrolyzed lanthanons was low. A suitable electrolyte was found to be lithium chloride in methanol with the lanthanons dissolved as the anhydrous acetates.

Electrolyses were done with the electrolyte boiling and refluxing at about 57.5° (barometric pressure at Los Alamos normally is 580–590 mm.). A modified 300-ml. round bottom flask with five standard taper necks was used. Auxiliary heat was applied with a Glascol mantle. Two spectrographic carbon anodes placed in two of the necks at opposite sides of the flask were connected in parallel and placed about 0.5 cm. from the cathode

surface. A platinum wire in polyethylene and glass inner tubes was connected to the cathode mercury. A reflux condenser was placed in the fourth neck, and the fifth neck was used for sampling. No grease was used on the joints. The amount of mercury used was 150 ml. A 1-l. flask was used in experiments for showing the enhanced Ho enrichment in the amalgam phase.

The acetate salt dissolved quite slowly in methanol, and several hours stirring with a magnetic stirrer was necessary for dissolution. The electrolyte was heated to boiling before starting an electrolysis.

Chemicals.—A commercial grade of methanol specified to contain 0.06% water was used without further purification. Reagent grade LiCl was dissolved in methanol to make a stock solution. Lanthanion oxide mixtures were sometimes made by combining 99.9% pure individual oxides purchased from commercial suppliers, but analyzed mixtures also were used.

The heavy lanthanon acetates were prepared by evaporating the acetate salt to dryness on a steam plate after dissolving the oxide in a substantial excess of 50% acetic acid. Heating the evaporated salt at 145–150° for several hours removed the last traces of the solvent and gave the anhydrous acetate salt, as shown by thermogravimetric measurements of ignited acetates.³

Analytical Procedures.—Radioactive Tm¹⁷⁰ was added to lanthanon mixtures so that the Tm could be followed radiochemically. The γ -radiation of Tm¹⁷⁰ was counted in calibrated test tubes with a scintillation counter with a precision of about 1%. Tm¹⁷⁰O₃ was made by neutron irradiation of 99.9% pure Tm₂O₃ in the Los Alamos Omega West Reactor.

The lanthanons were extracted from the amalgam with 6 M HCl and hydroxide precipitations were done to ensure quantitative recovery for the material balances. The electrolyte was evaporated to dryness and treated in a similar procedure. Individual lanthanons were determined spectrophotometrically where feasible and confirmatory spectrographic analyses were sometimes obtained.

The Tm in the mercury phase was found to be homogeneously distributed so that the phase concentration could be measured with an aliquot sample.

Results

Experiments showed that two reactions involving a phase change occur during electrolysis. First, from the start of the electrolysis lanthanons are transported into the amalgam phase. Second, after an incubation period, lanthanons are also precipitated from the electrolyte at the wall of the electrolysis vessel in an annular band at the junction of the electrolyte and the

(1) Work was done under the auspices of the Atomic Energy Commission. Presented in part at the 138th National Meeting of the American Chemical Society, New York, N. Y., September, 1960.

(2) E. I. Onstott, *J. Am. Chem. Soc.*, **81**, 4451 (1959).

(3) J. R. Witt and E. I. Onstott, *J. Inorg. Nucl. Chem.*, **24**, 637 (1962).

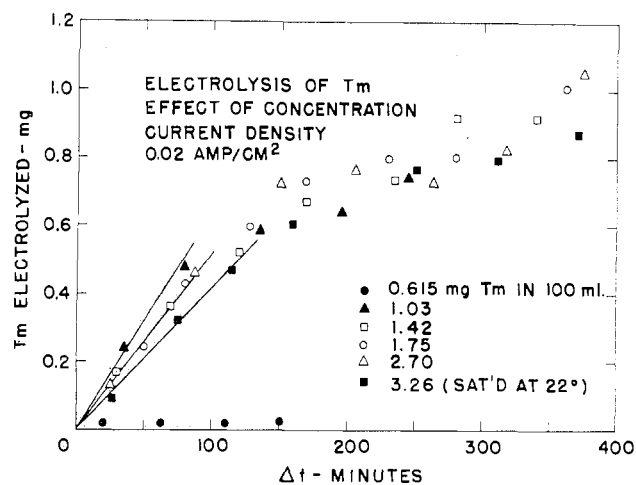


Fig. 1.—Effect of Tm-Lu concentration on electrolysis rate of Tm in 1% Tm-99% Lu mixture with 0.2 M LiCl in electrolyte.

amalgam. This precipitation reaction is localized in the region described and no general precipitation in the bulk electrolyte is observed visually except after severe electrolyte degradation by extended electrolysis.

By chronological measurement of the concentration of Tm in a Tm-Lu mixture in the electrolyte phase and in the amalgam phase it was possible to describe the transport of Tm between phases. Effects of current density and electrolyte composition were studied.

Mass Transfer of Tm to Mercury Phase.—Figure 1 shows that Tm electrolysis proceeds nearly linearly with time for electrolysis times less than 100 min., and mass transfer is almost independent of electrolyte concentration of lanthanons at constant current density, except at low concentration.

In the plateau region shown by Fig. 1 the data represent a changing environment in which a precipitation in the bulk electrolyte generally occurred and thus a homogeneous electrolyte phase was not presented to the cathode. The increase in rate after the plateau region corresponded to redissolving of the precipitate without an imposed alteration of electrolysis conditions. Data given for longer electrolysis times are presented only to show behavior trends and are not used for quantitative interpretation of rates.

The effect of current density on Tm electrolysis is shown in Fig. 2. With a current density of 0.005 amp./cm.² to at least 0.02 amp./cm.² the rate of electrolysis is directly proportional to the current density. The validity of using the origin as a point on the line may be open to question, since a finite threshold current density may be required to effect electrolysis.

Water added to the electrolyte diminishes the rate of electrolysis of Tm as shown by Fig. 3.

Precipitation of Tm-Lu by Electrolytic Base Generation.—After an incubation period, a precipitate containing Tm-Lu appears in an annular band on the vessel wall as described above. The data, plotted in Fig. 4, show a linear region which can be used to interpret rate behavior. Plots of the data for longer electrolysis times show curvature and reciprocal slopes

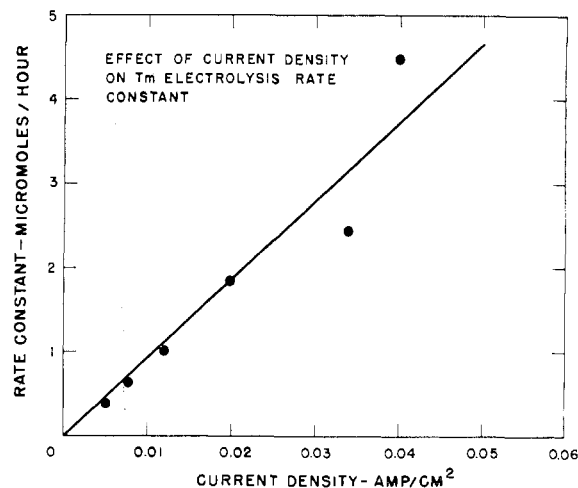


Fig. 2.—Plot of Tm electrolysis rate vs. current density at constant Tm-Lu concentration.

and thus are not usable except for qualitative descriptions of behavior.

Water added to the electrolyte causes an increase in the precipitate formation as shown by Fig. 5. In these experiments the amount of Tm in the precipitate was measured as a function of the elapsed time of electrolysis with the water content of the solvent varied for different electrolyses. Duplicate samples did not give reasonable duplication of data with no water added and indicate a difference in residual water content of the electrolyte.⁴

The effect of current density on precipitate formation is shown by the data in Fig. 6. The rate of precipitate formation, as shown by the increment data, is independent of current density for small electrolysis times. The incubation time interval for the precipitate to appear is variable and inversely dependent on the current density.

Effect of Some Parameters on Electrolysis of Tm-Lu.—In purifying Lu, which is preferentially left behind in the electrolyte, it is desirable to remove as much of the impurity lanthanons as practical. Thus with a mixture of Tm-Lu it is desirable to remove Tm in high yield in one operation. Some experiments were done in which the amount of Tm electrolyzed was measured with respect to that originally present in the electrolyte.

Data in Table I show the effects of current density and the effects of LiCl concentration. A high current density and/or high LiCl concentration degrade the Tm yield very badly.

The effect of total lanthanon concentration on Tm yield is shown by data in Table II. Concentrations between 6 and 12 mM seem to give an optimum yield of Tm in the amalgam phase. The yield is markedly diminished at low concentration. The purity of the starting material (Lu/Tm ratio) does not seem to affect the yield of Tm very much.

Enrichment and Purification of Lu.—In Fig. 7 are plotted data which show enrichment of Tm in the amalgam phase and enrichment of Lu in the electrolyte.

(4) In our experiments the reflux condenser was open to the atmosphere.

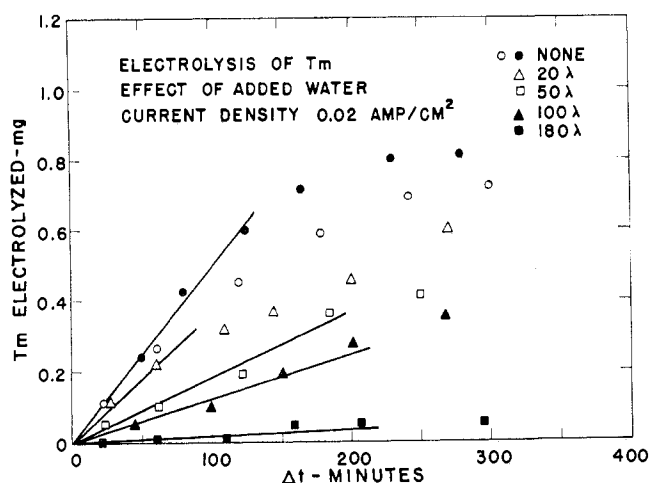


Fig. 3.—Effect of added water on Tm electrolysis rates at constant current density and constant Tm-Lu concentration. Water was added to 100 ml. of electrolyte containing 0.2 M LiCl.

TABLE I
EFFECT OF CURRENT DENSITY AND LiCl CONCENTRATION ON YIELD OF ELECTROLYZED Tm FROM Tm-Lu MIXTURES^a

Total rare earth, mM	LiCl, M	Current density, amp./cm. ²	Yield of Tm, % of starting amt
9.5	0.1	0.02	73
9.9 ^b	.1	.02	71
12.5 ^b	.2	.02	76
15.2	.2	.04	63
12.8	1.0	.02	19.3
12.8	1.0	.04	0.25
15.2	1.0	.08	.006

^a Conditions: electrolyte volume 200 ml. except where noted; electrolysis time 6.3 to 8.0 hr.; purity of mixtures, 79 to 91% Lu₂O₃. ^b Electrolyte volume 100 ml.

TABLE II
EFFECT OF LANTHANON CONCENTRATION ON YIELD OF ELECTROLYZED Tm^a

Total lanthanons, mM	Starting purity, Lu/Tm ratio	LiCl, M	Yield of Tm, % of starting amt.
3.5	99	0.2	4.0
5.9	99	.2	81
7.9	99	.2	65
9.5	70	.1	73
10.0 ^b	4.0	.1	71
10.1	99	.2	59
12.5	10.7	.2	76
15.5	99	.2	40
18.7	99	.2	29

^a Conditions: current density, 0.02 amp./cm.²; electrolyte volume, 100 ml.; electrolysis time, 7 to 8 hr. ^b Electrolyte volume 200 ml.

The data cannot be used to describe the exact behavior of Tm and Lu, since quantitative treatment requires that the changing ratio of Lu/Tm (with respect to elapsed electrolysis time) in the electrolyte be accounted for.⁵ The data show about a 3 to 1 enrichment of Tm in the amalgam irrespective of electrolysis conditions or the presence of other lanthanons.

(5) E. I. Onstott, *Anal. Chem.*, **33**, 1470 (1961).

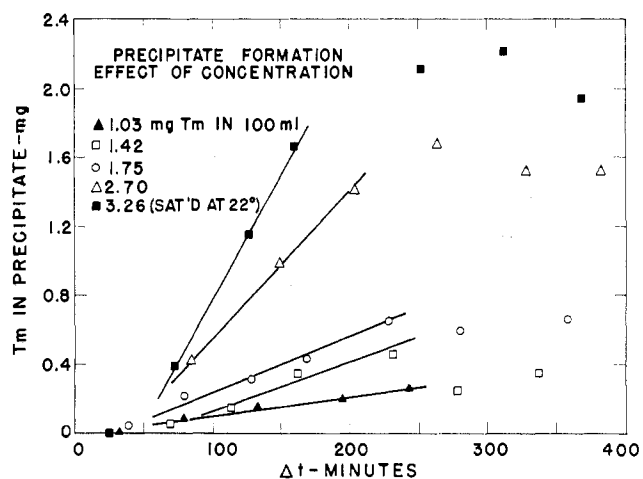


Fig. 4.—Effect of concentration of Tm-Lu (1% Tm-99% Lu mixture) on rate of precipitate formation at a current density of 0.02 amp./cm.². Electrolyte LiCl concentration was 0.2 M.

Optimum conditions for enrichment of Lu can be deduced from data in Fig. 8 in addition to data from Tables I and II. The electrolyte concentration of total lanthanons should be chosen between 6 and about 12 mM to avoid excessive degrading precipitation and still allow reasonable electrolysis rates. The optimum yield of electrolyzed Tm should be about 80% at a current density of 0.02 amp./cm.² since the precipitation reaction will remove about 20% of the available Tm. Higher current densities are not recommended because of the probability of a general precipitation in the bulk electrolyte.

A number of separations were done to demonstrate that Lu can be rapidly and easily purified with a reason-

TABLE III
ELECTROLYSIS FOR Lu ENRICHMENT Ho, Er, Tm, Lu MIXTURE^a

Sample	Wt. of R ₂ O ₃ , mg.	Composition, % each oxide			
		Ho	Er	Tm	Lu
Starting oxide	604	4.5	8.6	25	60
Oxide from amalgam ^b	251	10.1	17.3	31.4	41
Oxide from residual electrolyte	201	<0.1	1.1	11.5	87
Oxide from ppt.	152	~0.1	2.0	21.7	76

^a Conditions: electrolyte, 200 ml. of 0.2 M LiCl; cathode, 150 ml. of Hg; current density, 0.04 amp./cm.²; electrolysis time, 7.7 hr. ^b Yield in amalgam: Ho, 98%; Er, 90%; Tm, 63%; Lu, 28%.

TABLE IV
ELECTROLYSIS FOR Lu ENRICHMENT OF Tm, Yb, Lu MIXTURE^a

Sample	Wt. of R ₂ O ₃ , mg.	Composition, % each oxide		
		Tm	Yb	Lu
Starting oxide	853	3.3	28.6	68
Oxide from amalgam	162	9.0	41	50
Oxide from residual electrolyte	467	3.0	5	92
Oxide from ppt.	224	0.85	74	25

^a Conditions: electrolyte, 200 ml. of 0.1 M LiCl; cathode 150 ml. of Hg; current density, 0.02 amp./cm.²; electrolysis time, 16.3 hr.

TABLE V
Lu ENRICHMENTS

Mixture	Starting % purity (oxide)	Product % purity (oxide)	Phase	No. of electrolyses	Yield, %
Ho, Er, Tm, Lu	60 Lu	98.9 Lu	Electrolyte	2	10
Ho, Er, Tm, Lu	60 Lu	98.3 Lu	Electrolyte and ppt. combined	4	34
Tm, Yb, Lu	68 Lu	99.8-99.9 Lu	Electrolyte and ppt. combined	6	24
Tm, Lu	99 Lu	99.9 Lu	Electrolyte	1	20
		99.7 Lu	Precipitate		50
		97.5 Lu	Amalgam		30

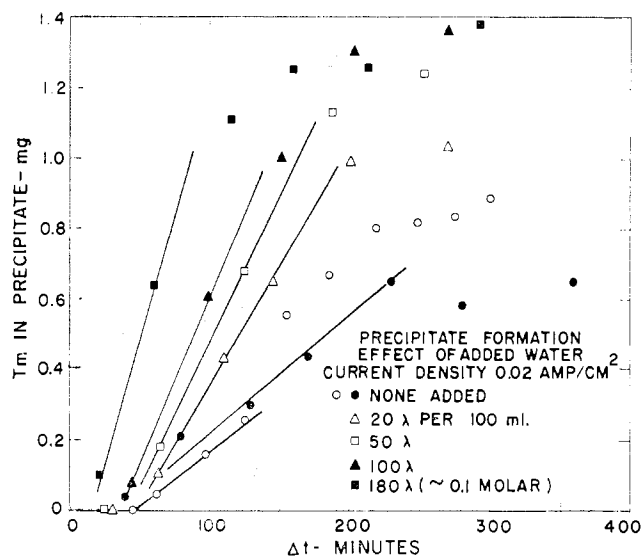


Fig. 5.—Effect of added water on precipitate formation at constant Tm-Lu concentration and constant current density.

able yield of product in a relatively small number of electrolyses. Results of an electrolysis with a mixture of Ho, Er, Tm, and Lu are given in Table III. The enrichment of Lu in the electrolyte was appreciable. A second electrolysis of lanthanons in the residual electrolyte further enriched Lu from 87 to 98.9% purity, as shown by the first entry in Table V.

The behavior of Yb is shown by the data in Table IV. The appearance of enriched Yb in the precipitate phase shows that it must get there by a more selective path than by electrosolvolytic basic precipitation at the cathode. Undoubtedly it is quite rapidly electrolyzed into the cathode and then reacts with solvent trapped underneath the amalgam. Yb amalgam is much more reactive than other heavy lanthanon amalgams.

Lu enrichments obtained in a number of electrolyses are listed in Table V. By combining the electrolyte and precipitate phases from an electrolysis the yield of purified Lu can be increased; however, more electrolyses are required to get the same purity of product. It might be more practical to electrolyze the precipitate mixture separately, since the precipitate always contains lower purity Lu than the residual electrolyte. The preparation of 99.8-99.9% pure Lu from the Tm, Yb, Lu mixture in six electrolyses could have been improved by a better choice of operating conditions, since the yield of electrolyzed Tm was only about 50% for each electrolysis. Enrichment of 99% Lu to 99.9% Lu

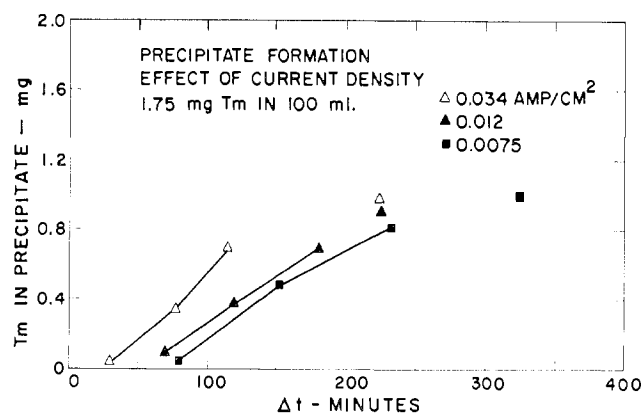


Fig. 6.—Effect of current density on precipitate formation at constant Tm-Lu concentration.

shown in the last entry of Table V was done under nearly optimum conditions.

Enrichment of Light Lanthanons.—The optimum conditions for electrochemically enriching a lighter lanthanon(III)⁶ are not the same as required for large Lu enrichment, since the lightest lanthanon(III) will be preferentially electrolyzed into the cathode phase. A maximum enrichment is desired rather than a maximum yield.⁷ Thus a large quantity of the mixture should be chosen so that the cathode can selectively remove the most easily electrolyzed component under the condition of limited current flow (depolarization). In Table VI are data which show that Ho is enriched about fivefold in the amalgam phase when a large amount of mixed lanthanons is subjected to electrolysis. This fivefold enrichment can be compared to the twofold enrichment obtained when a small amount is electrolyzed for optimum Lu enrichment as shown in Table III. Yields of electrolyzed Ho were 40% for the fivefold enrichment and 98% for the twofold enrichment.

Interpretation of Rate Data and Electrode Reactions

Rate data suitable for analysis were taken with parameters controlled so that mass transport was generally linear with time. Thus the differential treatment of rate data by log-log plotting as in Fig. 8

(6) The term "lanthanon(III)" is used to describe the lanthanon elements, yttrium included, which do not show a stable valence state intermediate between (0) and (III) in methanol electrolytes.

(7) For example, if a mixture of Ho and Lu is electrolyzed so that the yield of both in the cathode phase is quantitative, then the ratio in the mercury phase will be virtually the same as the ratio in the starting electrolyte and no useful Ho enrichment results. However, the trace left in the electrolyte will be very pure Lu.

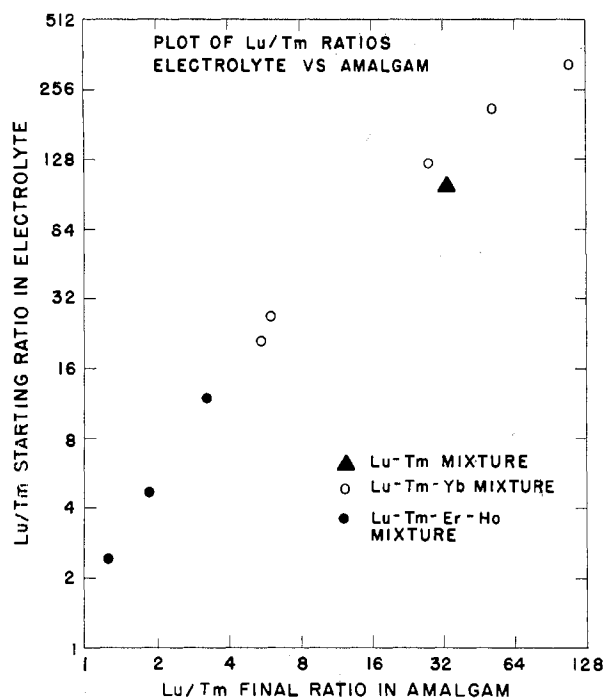


Fig. 7.—Enrichment data for Lu in lanthanon mixtures.

TABLE VI
ELECTROLYSIS FOR HO ENRICHMENT OF Ho, Er, Tm, Lu MIXTURE^a

Sample	Composition, % each oxide			
	Ho	Er	Tm	Lu
Starting oxide	6.4	11.0	13.1	69.5
Amalgam oxide	34.5	26.5	15.6	23.4

^a Conditions: electrolyte, 400 ml. of 1 M LiCl; cathode, 100 ml. of Hg; current density, 0.05 amp./cm.²; electrolysis time ~24 hr.; starting R₂O₃, 12.20 g.; saturated electrolyte plus undissolved lanthanon acetate crystals.

is applicable for determining the order of the reactions.⁸

Solvolysis of Tm(OAc)₃ on Dissolving.—LiCl dissolves almost instantaneously in methanol, but Tm(OAc)₃ requires several hours with agitation at room temperature. If a methanol solution of Tm(OAc)₃ is allowed to stand in a closed vessel for 2 to 3 months, as much as 30% of the Tm may precipitate on the walls of the vessel. These effects indicate that polymer formation takes place as a result of solvolysis with residual water and/or methanol. Rare earth polymers are known,⁹ and it should be recognized that Tm probably is not present in the electrolyte as a simple ionic species.

Tm Electrolysis.—Figure 8 shows that the electrolysis of Tm is zero order with respect to Tm concentration in the range of 0.06 to 0.12 mM Tm (with 99-fold excess Lu also present). Such behavior is typical of a heterogeneous reaction taking place on a surface¹⁰ and indicates that the rate limiting step may involve reduction of Tm and Lu by a chemical species generated by a secondary electrode reaction.

It is proposed that formation of a hydride complex

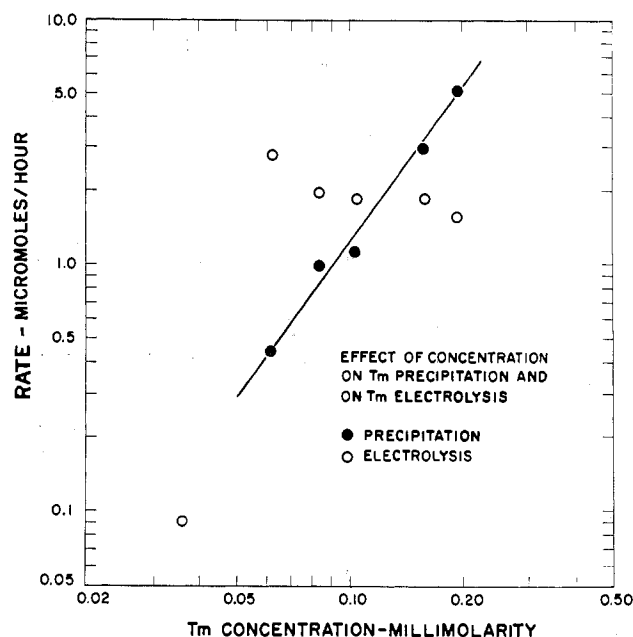


Fig. 8.—Effect of Tm-Lu concentration on Tm electrolysis rates and on Tm precipitation with 1% Tm-99% Lu mixture. Experiments were done at 0.02 amp./cm.². The slope of the line through the precipitate data is 2.1.

ion species such as TmH⁺² is necessary for electrolysis to proceed.² The source of hydride ligand may well be from reduction of coordinated water.

Recently a hydride complex of rhenium was prepared in aqueous solution by reduction of perrhenate with alkali metals.¹¹ Hydride complexes of iridium also are known,¹² and some (III) lanthanons have been deposited in mercury as hydrides. Warf and co-workers¹³ prepared rare earth hydride amalgams by combining directly the rare earth hydride with mercury. In this laboratory evidence for deposition of yttrium-rare earth hydrides of indefinite composition was obtained by electrolysis of yttrium-rare earth mixtures from methanol electrolytes.¹⁴ Hydrogen gas could be liberated from the amalgams under vacuum, and the amalgams (containing no lithium) showed average reducing equivalents of 3.2 to 4.0 per mole of lanthanon metal.

In studying the polarography of some lanthanon-(III) salts in lithium halide electrolytes, Triendl¹⁵ observed waves which he attributed to the formation of hydrides.

Precipitation Reaction.—Figure 6 shows that the rate of precipitate formation is independent of current density and thus is probably governed by the rate at which the soluble polymer reaches the cathode surface by diffusion. Such lack of dependence

(11) A. P. Ginsberg, J. M. Miller, and E. Koubek, *J. Am. Chem. Soc.*, **83**, 4909 (1961).

(12) L. Vaska, *ibid.*, **83**, 753 (1961); R. G. Hayter, *ibid.*, **83**, 1259 (1961).

(13) J. C. Warf and W. L. Korst, Office of Naval Research Report NP-5006 (Nov., 1953); J. C. Warf, J. Donohoe, and K. Hardcastle, *ibid.*, NP-6531 (Oct., 1957).

(14) E. I. Onstott and A. N. Syverud, Division of Inorganic Chemistry, 133rd National Meeting of the American Chemical Society, San Francisco, Calif., April, 1958.

(15) L. Triendl, *Collection Czechoslov. Chem. Commun.*, **24**, 3389 (1959); abstracted in *J. Electroanal. Chem.*, **1**, A50 (1960).

(8) S. W. Benson, "The Foundations of Chemical Kinetics," McGraw-Hill Book Co., Inc., New York, N. Y., 1960, p. 82.

(9) G. W. Pope, J. F. Steinbach, and W. F. Wagner, *J. Inorg. Nucl. Chem.*, **20**, 304 (1961).

(10) S. W. Benson, ref. 8, p. 14.

of electrolysis rates on current density has been demonstrated previously.¹⁶ The incubation period is inversely proportional to the current density as expected if the amount of base generated is proportional to the current-time product.

Figure 8 shows that the precipitation is second order with respect to Tm concentration. This dependence can be pictured as a reaction in which two lanthanon

(16) E. I. Onstott, *J. Am. Chem. Soc.*, **77**, 2129 (1955).

polymer fragments combine with electrosolvolytically-formed base to form a bridged polymer which precipitates.

Acknowledgments.—The spectrographic analyses were done by O. R. Simi. Space in the Omega West Reactor for the Tm_2O_3 irradiation was provided by R. G. Wenzel. The author is indebted to R. J. Bard for help on several revisions of the manuscript.

CONTRIBUTION FROM THE LINCOLN LABORATORY,¹ MASSACHUSETTS INSTITUTE OF TECHNOLOGY, LEXINGTON, MASSACHUSETTS, AND THE SPERRY RAND RESEARCH CENTER, SUDBURY, MASSACHUSETTS

The Reaction of Rare Earth Oxides with a High Temperature Form of Rhodium(III) Oxide

BY AARON WOLD,² RONALD J. ARNOTT, AND WILLIAM J. CROFT

Received May 23, 1963

Lanthanum rhodium oxide and neodymium rhodium oxide, containing rhodium in the trivalent state, have been prepared and possess distorted perovskite structures. They are orthorhombic and probably belong to space group D_{2h} ¹⁶ Pbnm. The lattice constants are $a = 5.524 \text{ \AA}$, $b = 5.679 \text{ \AA}$, $c = 7.900 \text{ \AA}$ for $LaRhO_3$ and $a = 5.402 \text{ \AA}$, $b = 5.772 \text{ \AA}$, $c = 7.816 \text{ \AA}$ for $NdRhO_3$. The distinguishing feature of this distortion is that $a < c/\sqrt{2} < b$, indicating that it is probably due to a size effect only. This is in contrast to the distortion observed for $LaMnO_3$ ($c/\sqrt{2} < a < b$) that is caused by both an electronic ordering (Jahn-Teller) and size effects. Neither samarium oxide nor yttrium oxide form a simple perovskite when allowed to react with rhodium(III) oxide under the same conditions used to prepare neodymium rhodium oxide. This implies that the maximum distortion possible due to size effects is of the type where $a < c/\sqrt{2} < b$ and can be distinguished from the distortion caused by electron ordering. This paper also reports the existence of two forms of rhodium oxide, a hexagonal low temperature form with the corundum structure and a high temperature form apparently related to the perovskites. The low temperature form transforms to the high temperature form above 750°.

Introduction

Lanthanum rhodium oxide, $LaRhO_3$, containing rhodium in the trivalent state, has been prepared and reported³ to have a distorted perovskite structure. It is orthorhombic and belongs to space group D_{2h} ¹⁶ Pbnm with four distorted perovskite units in the true crystallographic cell. The lattice constants are $a = 5.524 \text{ \AA}$, $b = 5.679 \text{ \AA}$, $c = 7.900 \text{ \AA}$. The investigation described in this paper is an attempt to prepare the other rare earth rhodium oxides. Neodymium rhodium oxide possesses a greater distortion than lanthanum rhodium oxide, although for both compounds $a < c/\sqrt{2} < b$. Goodenough⁴ has referred to perovskites with this type of distortion by the symbol O, and these compounds are distinguished from the orthorhombic perovskites labeled O' where $c/\sqrt{2} < a < b$ (e.g., $LaMnO_3$). Samarium and yttrium oxides do not form perovskites of either the O or O' type structure under the same conditions used to prepare neodymium rhodium oxide. Samarium oxide reacts with rhodium oxide to form an unknown phase, and yttrium oxide does not appear to react with rhodium oxide at all.

This paper also reports the existence of two forms of rhodium oxide. A hexagonal low temperature form was prepared by decomposition of hydrated rhodium oxide at 700° and corresponded to the cell dimensions given by Zachariasen.⁵ In addition a high temperature form of rhodium oxide exists when rhodium metal is converted directly to the sesquioxide at 1000°. The hexagonal rhodium oxide transforms to the high temperature form above 750°.

Experimental

Preparation of Hexagonal Rhodium Oxide.—Finely powdered (325 mesh) spectroscopic grade rhodium metal is fused with potassium hydrogen sulfate in a porcelain crucible. After prolonged fusion the contents of the crucible are extracted with boiling water and filtered. A sodium hydroxide solution is added slowly to the filtrate until precipitation of the hydrated rhodium oxide is complete. The precipitate is filtered, carefully washed, and air dried. The oxide is then transferred to a porcelain crucible and heated in air at 700°. The resulting low temperature form of Rh_2O_3 was measured on a Norelco diffractometer using copper $K\alpha$ radiation. The hexagonal values obtained were $a = 5.108 \text{ \AA}$ and $c = 13.81 \text{ \AA}$. The oxide was analyzed for rhodium by reduction in a stream of hydrogen at 800° until constant weight was obtained. The formula corresponded to Rh_2O_3 .

Preparation of High Temperature Rh_2O_3 .—Finely divided

(1) Operated with support from the U. S. Army, Navy, and Air Force.

(2) Brown University, Providence, R. I.

(3) A. Wold, B. Post, and E. Banks, *J. Am. Chem. Soc.*, **79**, 6365 (1957).

(4) J. B. Goodenough, *Landolt-Börnstein Tabellen*, Vol. II/9, Springer-Verlag, Berlin, 1962, pp. 2-187-2-221.

(5) V. M. Goldschmidt, *Skrifter Norske Videnskaps-Akad. Oslo. I. Mat. Naturv. Kl.*, 93 (1926).