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Separation of the Lanthanons at Amalgam Cathodes V.

A Kinetic Study of Lutetium Enrichment in Methanol Electrolytes

MASTER

By

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ABSTRACT

A kinetic study of the electrolytic phase transfer of radioactively tagged Tm in the presence of many-fold excess 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 5-fold 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

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

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 Yb². 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-lanthanone 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 Hg). A modified 300 ml round bottom flask with 5 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 one 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. Lanthanon oxide mixtures were sometimes made by combining 99.9% pure individual oxides purchased from commercial suppliers, but mixtures of known composition were also 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 last traces of the solvent and gave the anhydrous acetate salt, as shown by thermogravimetric measurements of ignited acetates.³

(3) J. R. Witt and E. I. Onstott, J. Inorg. Nucl. Chem., in press.

Analytical Procedures.- Radioactive Tm^{170} was added to lanthanon mixtures so that the Tm could be followed radiochemically. The γ radiation of Tm^{170} was counted in calibrated test tubes with a scintillation counter with a precision of about 1%. $\text{Tm}^{170}_2\text{O}_3$ was made by neutron irradiation of 99.9% pure Tm_2O_3 in the Los Alamos Omega West Reactor.

The lanthanons were extracted from the amalgam with 6 M HCl and hydroxide precipitations were done to insure 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 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.— Fig. 1 shows that Tm electrolysis proceeds nearly linearly with time for electrolysis times less than 100 minutes, 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/cm² to at least 0.02 amp/cm² 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. Data are plotted in Fig. 4. The data 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 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

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

Effect of current density on precipitate formation is shown by 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.

Table I

Effect of C.D. and LiCl Concentration on Yield of Electrolyzed Tm from Tm-Lu Mixtures.

Conditions: electrolyte volume 200 ml except where noted;
electrolysis time 6.3 to 8.0 hr.;
purity of mixtures, 79 to 91% Lu_2O_3 .

<u>Total R</u> <u>Millimolarity</u>	<u>LiCl Molarity</u>	<u>C. D.</u> <u>amp. cm.²</u>	<u>Yield of Tm -</u> <u>% of starting amount</u>
9.5	0.1	0.02	73
9.9 ^a	0.1	0.02	71
12.5 ^a	0.2	0.02	76
15.2	0.2	0.04	63
12.8	1.0	0.02	19.3
12.8	1.0	0.04	0.25
15.2	1.0	0.08	0.006

^aElectrolyte volume 100 ml.

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

Table II

Effect of Lanthanum Concentration on Yield of Electrolyzed Tm

Conditions: C.D., 0.02 amp/cm²; electrolyte volume, 100 ml;
electrolysis time, 7 to 8 hr.

<u>Total Lanthanons</u> <u>Millimolarity</u>	<u>Starting Purity</u> <u>Lu/Tm Ratio</u>	<u>LiCl</u> <u>Molarity</u>	<u>Yield of Tm -</u> <u>% of starting amount</u>
3.5	99	0.2	4.0
5.9	99	0.2	81
7.9	99	0.2	65
9.5	70	0.1	73
10.0 ^a	4.0	0.1	71
10.1	99	0.2	59
12.5	10.7	0.2	76
15.5	99	0.2	40
18.7	99	0.2	29

^aElectrolyte volume 200 ml.

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. 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

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

irrespective of electrolysis conditions, or the presence of other lanthanons.

Optimum conditions for enrichment of Lu can be deduced from data in Fig. 8 in addition to data from Tables I and II. Electrolyte concentration of total lanthanons should be chosen between 6 and about 12 millimolar to avoid excessive degrading precipitation and still allow reasonable electrolysis rates. The optimum yield of electrolyzed Tm should be about 80% at a C.D. 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 reasonable yield of product in a relatively small number of electrolyses. Results of an electrolysis with a mixture of Ho, Er, Tm, 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.

Table III

Electrolysis for Lu Enrichment

Ho, Er, Tm, Lu Mixture

Conditions: Electrolyte, 200 ml 0.2 M LiCl; cathode, 150 ml Hg; C.D., 0.04 amp/cm^2 , electrolysis time, 7.7 hours.

<u>Sample</u>	<u>Wt. R_2O_3, mg.</u>	<u>Composition, % Each Oxide</u>			
		<u>Ho</u>	<u>Er</u>	<u>Tm</u>	<u>Lu</u>
Starting oxide	604	4.5	8.6	25	60
Oxide from Amalgam ^a	251	10.1	17.3	31.4	41
Oxide from residual electrolyte	201	< 0.1	1.1	11.5	87
Oxide from precipitate	152	~ 0.1	2.0	21.7	76

^aYield in amalgam: Ho, 98%; Er, 90%; Tm, 63%; Lu, 28%.

The behavior of Yb is shown by data in Table IV. The appearance of

Table IV

Electrolysis for Lu Enrichment

Tm, Yb, Lu Mixture

Conditions: Electrolyte, 200 ml 0.1 M LiCl; cathode, 150 ml Hg; C.D.,
0.02 amp/cm²; electrolysis time, 16.3 hours.

<u>Sample</u>	<u>Wt. R₂O₃, mg.</u>	<u>Composition, % Each Oxide</u>		
		<u>Tm</u>	<u>Yb</u>	<u>Lu</u>
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 precipitate	224	0.85	74	25

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.

Table V

Lu Enrichments

<u>Mixture</u>	<u>Starting % Purity (oxide)</u>	<u>Product % Purity (oxide)</u>	<u>Phase</u>	<u>Number of Electrolyses</u>	<u>Yield, %</u>
Ho, Er, Tm, Lu	60 Lu	98.9 Lu	Electrolyte	2	10
Ho, Er, Tm, Lu	60 Lu	98.3 Lu	Electrolyte and Precipitate combined	4	34
Tm, Yb, Lu	68 Lu	99.8-99.9 Lu	Electrolyte and Precipitate combined	6	24
Tm, Lu	99 Lu	99.9 Lu	Electrolyte	1	20
		99.7 Lu	Precipitate		50
		97.5 Lu	Amalgam		30

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 6 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 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 (III) lanthanon⁶ are not the same as required for

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- (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.
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large Lu enrichment, since the lightest (III) lanthanon 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

- (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.
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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 5-fold in the

Table VI

Electrolysis for Ho Enrichment

Ho, Er, Tm, Lu Mixture

Conditions: Electrolyte, 400 ml 1 M LiCl; cathode, 100 ml Hg; C.D. 0.05 amp/cm²; electrolysis time ~ 24 hours; starting R₂O₃, 12.20 g; saturated electrolyte plus undissolved lanthanon acetate crystals.

<u>Sample</u>	<u>Composition - % Each Oxide</u>			
	<u>Ho</u>	<u>Er</u>	<u>Tm</u>	<u>Lu</u>
Starting oxide	6.4	11.0	13.1	69.5
Amalgam oxide	34.5	26.5	15.6	23.4

amalgam phase when a large amount of mixed lanthanons is subjected to electrolysis.

This 5-fold enrichment can be compared to the 2-fold 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 5-fold enrichment and 98% for the 2-fold 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 is applicable for determining the order of the reactions.⁸

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

Solvolysis of TmAc₃ on Dissolving. - LiCl dissolves almost instantaneously in methanol, but TmAc₃ requires several hours with agitation at room temperature. If a methanol solution of TmAc₃ 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

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

in the electrolyte as a simple ionic species.

Li Electrolysis. - The Faraday efficiency for lanthanon electrolysis is invariably less than 1%. Undoubtedly the predominant cathode reaction is lithium ion reduction. The electrolysis is driven unidirectionally at constant current density (by choice, to make the mass transport into the mercury linear with time), and Li is continuously electrolyzed into the mercury. Li amalgam is very reactive chemically and almost immediately the Li in the amalgam starts returning to the solvent, evidently by chemical reaction with the solvent. Thus a steady-state cyclic redox reaction of Li should be maintained and reaction products of solvent degradation should be produced linearly with time at the cathode surface. Degradation products expected are, hydrogen atoms, hydrogen gas, hydride ion, methoxide ion, hydroxide ion and possibly methoxide radical and hydroxide radical.

Tm Electrolysis. - Electrolysis of Tm is quite slow compared to what would be expected of Eu, which behaves ideally and is electrolyzed as fast as it diffuses to the cathode.¹⁰ Fig. 8 shows that the electrolysis of Tm

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

is zero order with respect to Tm concentration except at low concentration. Such behavior is typical of a heterogenous reaction taking place on a surface,¹¹ and indicates that the rate limiting step (for conditions for

(11) Sidney W. Benson, *ibid.*, p. 14.

which zero order holds) does not involve the cathode surface concentration of Tm.

If Tm is present in such large concentration that its concentration does not materially affect the rate of electrolysis, then a second reactant present in much smaller concentration at the electrode surface seems to be rate limiting. This second reactant could possibly be electrons with charge transfer limiting the rate, but a more likely reactant is a chemical species generated by a secondary electrode reaction. The rate of electrolysis is first order with respect to current density as shown by Fig. 2, and indicates that a species could be formed at the electrode surface which is proportional to the current passed through the cell.

Thus a chemical exchange reaction with formation of a minority complex ion seems to be necessary for electrolysis to proceed.

We proposed that formation of a hydride complex ion species is necessary for electrolysis to proceed² and pictured the source of hydride ligand from reduction of coordinated water. What seems to be a more probable source of hydride ligand, in view of some recent work on a rhenium hydride complex compound,¹² is the back reaction of lithium amalgam with the solvent.

(12) A. P. Grinsberg, J. M. Miller and E. Konbek, J. Am. Chem. Soc. 83, 4909 (1961).

Recently Ginsberg, Miller and Konbek¹² demonstrated conclusively that dipotassium octahydridorhenate(VI) is formed in aqueous solution by reduction with potassium metal under proper conditions. Thus hydride ligand seems to have a finite lifetime for exchange. Hydride complexes of iridium have been reported recently.¹³

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

Evidence can be cited which indicates that the (III) lanthanons are electrodeposited in mercury as hydride alloys. Warf and co-workers¹⁴ pre-

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

pared rare earth hydride amalgams by combining the rare earth hydride with mercury. By electrolysis of methanol solutions of lanthanon acetates containing predominantly yttrium, we demonstrated that the solid amalgam which

separated on electrolysis contained considerable hydrogen.¹⁵ The hydrogen was

(15) E. I. Onstott and A. N. Syvernd, Division of Inorganic Chemistry, 133rd meeting, ACS, San Francisco, Calif., April, 1958.

identified with a mass spectrometer after placing the amalgam in an evacuated vessel. By reacting similar samples of amalgam with acid and collecting the hydrogen evolved, the average oxidation number of mixed lanthanon amalgams was computed to be 3.2 to 4.0, thus indicating also the presence of hydrogen.¹⁵

In studying the polarography of some (III) lanthanons in lithium halide electrolytes, Triendl¹⁶ observed waves which he attributed to formation of

(16) L. Triendl, Collect. Czechoslov. chem. Commun. 24, 3389 (1959); abstracted in J. Electroanalytical Chem. 1 A50 (1960).

hydrides.

Precipitation Reaction. - The precipitation that takes place (Fig. 4) undoubtedly results from base generation at the cathode. All of the plots extrapolate to approximately the same incubation time and indicate that the time to reach saturation of the electrolyte with precipitate is dependent on the amount of current passed through the cell. Fig. 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 of electrolysis rates on current density has been previously demonstrated.¹⁰ 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.

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

Effect of Water. - Water added to the electrolyte greatly diminishes the rate of electrolysis of Tm (Fig. 3) and at the same time increases the rate of precipitate formation (Fig. 5). The effect on Tm electrolysis can be attributed either to diminished reactivity due to polymer chain lengthening or to a dynamic effect on some exchange reaction at the cathode surface.

The effect on precipitation undoubtedly is increased polymerization due to water acting as a base. A plot of the rate of precipitate formation as estimated from Fig. 5 vs. the added water (this plot not illustrated) shows approximate first order dependence. This dependence seems to verify the stoichiometry depicted above for precipitate formation with water acting as a source for base formation at the cathode surface.

Fig. 5 shows a shorter incubation time with higher water content. Possibly polymer chain lengthening takes place by solvolysis prior to electrolysis.

Effect of Low Tm Concentration. - Fig. 1 shows a striking effect of a Tm concentration allowing a very low electrolysis rate compared to larger concentrations. Such an effect could be due to a large fraction of the Tm being rendered essentially non-reducible by solvolytic polymer formation with residual water in the methanol on dissolving. Such a reaction would inactivate a fixed amount of Tm as long as the electrolyte volume were kept constant, and for the case of low initial Tm concentration, would leave only

a small concentration of reducible Tm species for electrolysis.

Anode Reactions - Judging from the odor of the spent electrolyte, the primary oxidation product is formaldehyde from methanol oxidation. Some chlorine is produced and undoubtedly carbon dioxide is formed by oxidation of acetate. Oxygen may also be produced. The physical arrangement of anodes is such that gases are swept out by ebullition of the electrolyte, hence the amounts that get to the cathode by convective transfer probably are small. Sufficient formaldehyde may be present to consume a large fraction of the cathodic current. It is convenient to assume that anodic effects can be ignored, but of course no proof that this can be done is given.

Summary of Postulated Chronological Reactions -

1. Solvolysis.

2. Li Redox cycle.

- a. $\text{Li}^+ + \text{e}^- \rightarrow \text{Li}(\text{Hg})$
- b. $\text{Li}(\text{Hg}) + \text{H}_2\text{O} \rightarrow \text{Li}^+ + \text{H} + \text{OH}^-$
- c. $\text{Li}(\text{Hg}) + \text{H} \rightarrow \text{Li}^+ + \text{H}^-$

3. Tm Electrolysis.

- a. $\text{Tm polymer} + \text{H}^- (\text{from 2c}) \rightarrow \text{TmH}^{++}$
- b. $\text{TmH}^{++} + 2\text{e}^- \rightleftharpoons \text{TmH} (\text{Hg})$

4. Precipitation.

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.

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.

Fig. 2. Plot of T_m electrolysis rate vs. current density at constant T_m -lu concentration.

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 HCl.

Fig. 4. Effect of concentration of Tm-In (1% Tm-99% In mixture) on rate of precipitate formation at a current density of 0.02 amp/cm². Electrolyte LiCl concentration was 0.2 M.

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

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

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

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/cm². The slope of the line through the precipitate data is 2.1.