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GENERAL RESEARCH

DECEMBER 11, 1950 TO APRIL 2, 1951 (DELETED VERSION)

(Actinium Volume)

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SUMMARY

The material presented in this volume concerns the work done on the development of processes for obtaining purified actinium-227 salts from neutron-irradiated radium and for depositing pure actinium metal on various metal surfaces. At the present time a process developed at Argonne National Laboratories is being set up to produce actinium-227 in small quantities and will be used to produce purified actinium for research purposes. Improved methods of separating actinium from radium which are readily adapted to large-scale production will also be investigated.

In order to handle 5-gram batches of radium, a special cave is required for shielding, and specialized equipment is necessary for carrying out the operations by remote control. At the present time the specifications for the building and cave structure are complete. Approximately 75 per cent of the specialized remote-control equipment has been constructed in the shop (p. 6).

A number of research studies are being carried out in conjunction with the process for the separation of actinium from radium.

The original method of separation carried out at Argonne was based entirely upon ion exchange. Because of the difficulty encountered with the formation of the radium precipitates in the effluent from the ion-exchange column, a second method was developed to carry out the separation by liquid-liquid extraction with TTA in benzene. While this method was also successful, it did not eliminate the problem of insoluble radium precipitates being formed. After carefully considering both possible methods, it has been decided that the ion-exchange method can be more readily adapted to the separation on a routine basis than the solvent extraction method. As a result, further research has been done to acquire additional information on the ion-exchange method (p. 7).

The sulfate ion, which causes the precipitates of radium sulfate, undoubtedly is derived from the Dowex-50 resin, a sulfonated hydrocarbon, used in the ion-exchange columns. Preliminary work has been directed toward determining the effect of alpha activity upon this resin. The results which have been obtained indicate the formation of sulfate ion is not related to the alpha activity of the solutions being handled, since sulfate ion is produced in the absence of alpha activity (p. 13).

The procedure which is used for the actinium-radium separation is extremely slow, mainly because of the time required for the evaporation of the various solutions. With the objective of speeding up the evaporation, a number of studies have been made. The rate of evaporation must be sufficiently slow to prevent spattering or entrainment of active materials in the gas stream leaving the evaporators. The spattering may be greatly reduced in returning the condensate to the bottom of the flask by having it run down a glass rod rather than drop back into solution. Special copper bottoms have been added to the evaporation flasks used with active solutions. The copper coat eliminates the use of special catch pans and custom-built heaters formerly used to minimize the danger of contamination from a flask fracture (p. 15).

The radon, which is evolved during the processing of the radium, must be moved before the gases can be sent to the stack. It is to be absorbed on charcoal at low temperatures. A study is being made on the methods and degree of drying required before passing the gases over the charcoal, as well as the efficiency of the traps at various rates of gas flow and temperature (p. 19).

Because of the possible purchases of radium, methods of determining the total quantity and purity of the radium are required. Since barium is likely to be the major impurity, studies are being carried out on methods of determining small amounts of barium in radium. The

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method under consideration employs ion exchange for the separation of the barium which then can be analyzed by standard methods (p. 24).

One of the major needs at the present time is a reliable and rapid method for the determination of actinium-227 in the presence of radium and the combined decay products. At present, work has been directed toward obtaining pure actinium-227, francium-223, and thorium-227 which could be counted after known periods of growth or decay and used to determine the total actinium-227 present, (p. 33).

Because actinium sulfate is highly soluble and radium sulfate insoluble, it was thought that a simple separation might be achieved for extraction of actinium from radium sulfate with dilute mineral acid. However, it was found that, under conditions similar to those which would be obtained with irradiated radium sulfate, only 4 per cent of the actinium could be extracted (p. 43).

In connection with the work on the reduction of actinium to the metal from non-aqueous solutions, work has been done on the polarographic reduction potential of lanthanum in liquid ammonia. An effort was made to study the reduction wave at potentials more negative than 1.6 volts with respect to the mercury pool. In order to prevent interference from the reduction wave of the ammonium ion, the ammonium ion concentration must be kept low. However, under these conditions the solubility of lanthanum is too low to be of practical importance. Since any further work would be of theoretical interest only, this investigation has been concluded at least for the present time (p. 46).

The preparation of lanthanum metal by the thermal decomposition of LaI_3 at a hot filament (DeBoer Process) has been under investigation. Progress has been made in the program by preparing pure LaI_3 in the DeBoer vessel made by heating the filament through inductive coupling to an external source of power (p. 54).

Experiments with a calutron-type mass spectrometer, which is to be used to prepare metal, indicate that larger and more rugged filaments must be designed (p. 61).

An attempt has been made to plate lanthanum metal from fused-salt mixtures. Difficulty has been experienced in removing the salts from the mixture of lanthanum and salts which adhered to the plate. The method does not look promising and has been suspended (p. 63).

Attempts to produce lanthanum metal by the reduction of LaI_3 with sodium metal have failed. The experiments have been performed under various conditions of pressure, temperature, type of container, and type of atmosphere (p. 70).

Lanthanum-mercury amalgams have been prepared by electrolyzing saturated alcoholic solutions of anhydrous LaI_3 with a mercury cathode. The lanthanum metal was separated from the mercury by heating the amalgam in a zirconia crucible under reduced pressure. Production of the metal on a microscale, however, has not been achieved (p. 72).

Research has begun on methods of distilling lanthanum metal from a crucible. Induction heating and resistance heating of the crucible did not sufficiently raise the temperature to volatilize the lanthanum. Distillation was successfully achieved by bombarding the crucible with an intense beam of electrons (p. 80).

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Problem Title -Construction of Facilities for the Actinium Separation Process

Report By -P. M. Engle

Work Done By -W. T. Brown and P. M. Engle

INTRODUCTION

All plans and specifications for the building in which the actinium separation process will be located and for the shielded cave for this work are complete. Design and selection of processing apparatus and auxiliary equipment is estimated to be 75 per cent finished. Most of this equipment has been constructed or purchased and is on hand awaiting installation.

DETAILED REPORT

In cooperation with the Engineering Division, plans and specifications were completed for the architectural, mechanical, and electrical facilities to be installed in that portion of the "GP" Building to be used by the actinium separation project. These plans were employed by the Atomic Energy Commission to negotiate a construction contract for this work. The construction of the building and the cave was provided for in previous contracts and work on these installations is proceeding.

The final choice of an ion-exchange process¹ for the separation of actinium from radium has permitted a layout of the processing apparatus as it will be assembled in the cave. This apparatus is being constructed and will be tested by simulated operations before final designs are selected.

Considerable effort has gone into the design and selection of auxiliary equipment. The special refrigeration system required for chilling the activated-carbon radon traps has been ordered. Fabrication of the liquid-filled, shielded, window frames is proceeding in the machine shop, and the equipment required for handling the zinc bromide solution employed to fill these windows has been designed. A compressed-air-operated press has been purchased for the slug-sealing operation. All the special remote control devices are essentially complete in the shop with the exception of the rectilinear, electrical manipulator. A special, parallel-jaw, hand-operated pair of tongs has been designed and will be constructed in our shop.

REFERENCE

1. Krein, F. P. Jr., This Volume, p. 7.

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Problem Title - The Separation of Actinium from Radium by Ion Exchange

Report By - F. P. Krein, Jr.

Work Done By - F. P. Krein, Jr., and W. S. Stringham

INTRODUCTION

An investigation was made to determine the feasibility of utilizing ion-exchange methods exclusively for separating actinium from irradiated radium. A preliminary separation¹ by Hagemann of Argonne National Laboratory was performed in this manner with good results. However, after this work had been reported, a small amount of radium sulfate was found in the 2 normal nitric acid used for eluting the radium. In an attempt to avoid this difficulty, a liquid-liquid extraction step was substituted by Hagemann in later work.² The greater difficulties produced by the extraction step along with the ease in operating ion-exchange processes by remote control have made the return to an all-ion-exchange process attractive.

A satisfactory actinium product may contain only 0.0003 per cent of the original radium batch. This degree of separation indicates that at least two separation steps will be required.

DETAILED REPORT

The ion-exchange process as developed in this work would consist of an initial separation of radium and actinium, and a further purification of the actinium by another ion-exchange separation.

Because the active materials involved, radium and actinium, were not readily available the following work was done by employing barium as a substitute for radium and lanthanum as a substitute for actinium. The effluent solutions were analyzed for barium colorimetrically and for lanthanum by counting an added lanthanum-140 tracer.

The flow rate of solutions through the column was controlled by a small, adjustable-speed pump; an automatic sampler with an adjustable timer was employed to allow overnight operation.

The resin used throughout this work, Dowex-50, was washed to remove fines, backwashed in the column, and treated with 4 normal nitric acid to convert the resin into the hydrogen form. All experiments were conducted at room temperature.

A preliminary separation (Run 1, Table I), conducted with relatively coarse resin gave incomplete separation.

Run 2 was designed to simulate the conditions of Hagemann,¹ except that the quantities of barium and lanthanum were increased to correspond with the 5 grams of radium and the amount of actinium (approximately 13 milligrams) which will be present in the samples to be processed.

The barium was eluted with 2 normal nitric acid and the lanthanum stripped with 4 normal nitric acid. The separation of lanthanum from barium (Figure 1) is apparently complete, and the elution curves are relatively sharp. It appears that the lanthanum curve tails off to some extent but this is partly due to the low concentration of lanthanum tracer

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employed for this run. After 5 liters of total effluent, most of the samples counted low enough to be considered background variation but because of the small total amount of tracer employed they show quite clearly on the graph. In later runs where much higher concentrations of tracer were used, those counts that approach background variation are hardly detectable (Figure 2).

In Figure 1 a "hump" appears near the end of the lanthanum elution curve. This effect has appeared in all runs that have been conducted so far and is apparently caused by a small amount of an unidentified active impurity in the lanthanum tracer. Recounting these samples after a 2-weeks interval indicates a very slow decay rate when compared to the half life of 40 hours of lanthanum-140.

Run 3 was made duplicating the quantities used in Hagemann's¹ work except that barium and lanthanum were used instead of radium and actinium, and 100 to 150-mesh resin was used instead of 150 to 200 mesh. The purpose of this run was to determine any differences in the behavior of barium and lanthanum from that of radium and actinium. The differences detected could then be applied to the results of other work with barium and lanthanum in predicting the difference to be expected with radium and actinium, respectively.

The results indicate that with 2 normal nitric acid barium is stripped from the resin column at a slightly faster rate than is radium: 400 milliliters of eluate versus 560 milliliters respectively. With 4 normal nitric acid, lanthanum apparently is stripped at a slower rate than actinium: 440 milliliters versus 215 milliliters, respectively. The latter result would not be expected from the relative size of the atoms but it may have resulted from a difference in the care with which the tail of the elution was collected. The separation of lanthanum from barium was sharp as was Hagemann's separation of radium from actinium.

Because of the slow flow rates employed in the second and third runs, approximately 60 hours were needed to complete the elutions. In Run 4, an attempt was made to determine the effect of increasing the flow rate. The conditions were the same as Run 3 except that the flow rate was doubled. The results of this run were nearly identical with those of Run 3; apparently no harm was done by using this faster flow rate, and a great saving of time was achieved.

An attempt was made to separate barium and lanthanum with 4 normal nitric acid used throughout. Conditions were otherwise kept the same as in Run 4. However, the barium was stripped at a sufficient rate to form a precipitate, presumably barium nitrate, in the column. This precipitate plugged the column so that further operation was impossible. This approach has been abandoned, at least temporarily.

If in the initial separation the actinium is stripped with 4 normal nitric acid, a problem arises as to how to absorb the actinium on a second column for further purification. The nitric acid in the solution may be reduced with formic acid but this presents certain practical difficulties in handling the nitrogen dioxide. However if an ammonium citrate solution were used to remove the actinium from the initial column, by reducing the pH of the solution its complexing action can be reduced to allow the actinium to be reabsorbed.

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Runs 5 and 6 of Table I were made to check the use of ammonium citrate as outlined in the preceding paragraph. In Run 5L, the barium was eluted with 2 normal nitric acid and the column rinsed with 100 milliliters of water. The lanthanum was stripped with 7.5 per cent ammonium citrate solution adjusted to a pH of 8.5 with ammonium hydroxide. One tenth of one per cent of phenol was added to all citrate solutions to avoid the growth of mold. The required volume of this solution was the same as the volume of the 4 normal nitric acid solution employed in Run 2. The lanthanum-containing citrate solution was adjusted to pH 2.4 with hydrochloric acid and passed through a smaller column in Run 5S in order to reabsorb the lanthanum. Evidently the pH of the solution was still too high, since an appreciable amount of the lanthanum passed through the column unabsorbed.

Run 6 was made principally to improve the absorption of lanthanum on the purification column. No barium was employed, as the initial separation had been satisfactory in previous experiments. The stripping solution for the lanthanum was a five per cent ammonium citrate solution adjusted by pH 6.4 with ammonium hydroxide. The flow rate was reduced throughout this run in order to limit the volume of solutions required. The results of this elution are shown in Figure 2. The volume of citrate required for complete removal of the lanthanum was the same as that needed in Run 5.

The effluent fractions from this elution which contained the lanthanum were combined and adjusted to pH 1.0 with concentrated hydrochloric acid. When this solution was fed through the smaller purification column, absorption was complete. The lanthanum was then stripped in the normal manner with 4 normal nitric acid.

CONCLUSIONS

On the basis of these results a decision has been reached to substitute an ion-exchange separation for the liquid-liquid extraction employed for the initial separation of actinium from radium at Argonne National Laboratory. The results show that satisfactory separations may be made by ion-exchange, and it is felt that this process will be easier to operate under remote-control conditions.

No final decision has yet been reached on whether nitric acid or ammonium citrate solution will be employed for stripping the actinium from the initial column. Since there are advantages and disadvantages to both methods, further investigation will be required before final selection of this portion of the process can be made.

REFERENCES

1. Hagemann, F. T., and Andrews, H. C., The Separation of Actinium from Radium by Ion Exchange, ANL-4215, p. 15-16, 1948.
2. Engle, P. M., Preliminary Report on the Actinium Separation Project, MLM-454, 1950.
3. Stringham, W. S., Rpt. Gen. Res., MLM-519, p. 7, January 15, 1951.

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TABLE I
SUMMARY OF THE SEPARATION OF LANTHANUM AND BARIUM BY ION EXCHANGE
(DOWEX-50 RESIN AT ROOM TEMPERATURE)

RUN	RESIN MESH	FLOW RATE (ml./min./cm. ²)	COLUMN SIZE (cm.)	FEED SOLUTION			BA STRIPPING SOLN.		LA STRIPPING SOLN.	
				VOLUME (ml.)	M. EQ. BA ⁺⁺	M. EQ. LA ⁺⁺⁺	TYPE SOLN.	VOLUME REQUIRED (ml.)	TYPE SOLN.	VOLUME REQUIRED (ml.)
1	40-70	5.70	1 x 19	1,000	4.9	0.62	2 N HNO ₃	-	4 N HNO ₃	-
2	100-150	0.55	2.3 x 16	750	44.0	0.17	2 N HNO ₃	1,600	4 N HNO ₃	1,200
3	100-150	0.51	1 x 13	150	9.0	0.03	2 N HNO ₃	400	4 N HNO ₃	440
4	100-150	1.02	1 x 13	150	9.0	0.03	2 N HNO ₃	480	4 N HNO ₃	300
5L	100-150	1.00	2.3 x 16	500	44.0	0.30	2 N HNO ₃	1,600	7½% AMMONIUM CITRATE, PH 8.5	1,200
5S	100-150	1.00	1 x 8	1,100	-	RUN 5L LA EFFLUENT	-	-	4 N HNO ₃	-
6L	100-150	0.50	2.3 x 17	150	-	0.30	-	-	5% AMMONIUM CITRATE, PH 6.4	1,200
6S	100-150	0.50	1 x 14	550	-	RUN 6L LA EFFLUENT	-	-	4 N HNO ₃	250

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ION EXCHANGE ELUTION OF Lg FROM A DOWEX 50 RESIN COLUMN BY USE OF 5% AMMONIUM CITRATE SOLUTION OF pH 6.4. RUN 6.

Problem Title - The Effect of Alpha Activity on Dowex-50 Resin

Report By - H. W. Kirby

Work Done By - H. W. Kirby

INTRODUCTION

The proposed separation of actinium from radium by ion exchange presupposes the stability of the resin in the presence of considerable alpha activity.

To determine whether any appreciable destruction of the resin results from alpha bombardment, polonium was used as a convenient source of alpha activity with barium added to simulate the chemical activity of radium. It was assumed that any disintegration of the phenylsulfonic acid polymer would be manifested by the appearance of barium sulfate in the effluent or by the retention of barium in the resin.

DETAILED REPORT

A solution was prepared containing 140 milligrams of inert barium, 100 micro-curies of barium-140 (both as chlorides), one curie of polonium in 6.0 normal nitric acid, and 1.7 grams of 100 to 150-mesh Dowex-50 resin (ammonium form). An identical solution was prepared without polonium to act as a control. Both solutions were made approximately 0.8 normal in nitric acid and 0.2 normal in hydrochloric acid. The total volume in each case was 75 milliliters.

The two solutions were stirred on magnetic stirrers for 28 hours and allowed to settle before being decanted through coarse fritted disks. A distinct turbidity was noted in the filtrate from the control solution which, on settling, had the characteristic appearance of barium sulfate. No precipitate was observed in the polonium-containing filtrate but the much slower rate of filtration indicated that the fritted disk used in this case, while nominally of the same porosity as that used for the control, was actually finer. In that case, any barium sulfate produced might have been retained by the pores of the filter. The barium sulfate found in the control filtrate was estimated to weigh one milligram.

Each resin was transferred to its respective filter and washed repeatedly with 4.0 normal nitric acid until the filtrate gave no further precipitate on addition of sulfuric acid. The resin was air-dried, transferred to a small vial, and gamma-counted.

Immediately after drying, the control resin had 42 gamma counts per minute as compared with 180 counts per minute in the resin exposed to polonium. However, another count, taken seven days later, showed 54 counts per minute in the control and 12 counts per minute in the experimental. In each case, the counts were only slightly higher than background and the differences observed cannot be regarded as significant.

CONCLUSIONS

It has been demonstrated that some free sulfate ion may be extracted from Dowex-50 resin. This confirms information received from Argonne National Laboratory¹ and from Oak Ridge National Laboratory.² No evidence has been found, however, to indicate that a breakdown in the resin molecules has been caused by alpha activity under the conditions investigated.

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Approximately the same amount of barium sulfate was produced whether polonium was present or absent.

Although no resin decomposition caused by polonium activity was detected under the conditions of this experiment, the effects of higher alpha activity and exposure periods have not been determined.

REFERENCES

1. Engle, P. M., Rpt. Gen. Res., MLM-454, p. 7, March 21, 1950.
2. Rupp, A. F., Verbal Communication.

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Problem Title - Evaporation of Highly Active Solutions

Report By - W. S. Stringham

Work Done By - W. S. Stringham

INTRODUCTION

The process for separating actinium from irradiated radium requires, in several steps of the process, the evaporation of small volumes of highly active solutions. In certain cases this evaporation must proceed to dryness. Requirements which must be met during this process are that entrainment of activity and spattering of solid material on the walls of the flask both be avoided. In previous work on this process at Argonne National Laboratory, a very slow evaporation rate was considered necessary to meet these requirements. The work described in this report was done to increase the rate of evaporation without sacrificing the efficiency of separation.

DETAILED REPORT

The evaporator that was used in these studies has been discussed in a previous report.¹ A photograph of the evaporator is shown in Figure 1. The important components of the flask are (1) a copper plate on the bottom half of the flask to act as a self-contained catch pan, (2) various dip lines, (3) an inlet to allow air to sweep over the solution, and (4) a reflux-return rod to return the reflux to the bottom of the flask rather than to allow it to drop from the condenser to the surface of the liquid which would cause spattering. Spattering must be held to a minimum to facilitate the complete removal of radium from the apparatus. The condenser, which is permanently attached to the flask, is constructed so that various entrainment separating devices may be studied in order to determine the most efficient type.

These devices included glass beads, sintered-glass disks, glass wool, and glass, umbrella-type baffles. Results indicated that glass beads were superior to the other materials for efficiency, ease of handling, and resistance to flooding.

In general the air flow was 1 liter per minute. A faster air flow caused flooding of the condenser. With an air flow of 1 liter per minute the evaporation rate is approximately 1 milliliter per minute with bed depths of 1 3/8 and 2 inches of 1/4-inch glass beads in the condenser.

Two radioactive elements were used to simulate radium and actinium during the evaporation studies. The first one to be used was polonium-210. It soon became evident that the high vapor pressure of polonium gave erroneous results. When the volume in the evaporator became low enough that salts began to form on the heated walls of the vessel, local hot spots developed which vaporized the polonium. At this point the decontamination factor (ratio of activity remaining in the still to that in the distillate) dropped very rapidly. This was true regardless of the type of entrainment device used in the condenser.

In order to circumvent the difficulties from the high vapor pressure of polonium, a solution of cobalt-60 was used in the evaporator. The vapor pressure of the cobalt compound is low enough that it caused no problem when the solution was taken to dryness. Beta counts were made in the still and in the receiver in order to obtain the decontamination factor (Table 1).

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It was observed during the preceding run that most of the spattering that occurred could be attributed to the condensed vapors dropping back into the still. Another evaporator was constructed incorporating a condensate-return line from the condenser to the bottom of the still. The results (Table II) showed that this line alleviated the situation and enabled us to obtain an even distribution of solids in the bottom of the still.

CONCLUSIONS

As a result of these and other¹ studies, the following procedure is suggested for the evaporation of small (less than one liter) amounts of radioactive solutions.

1. Use copper plated evaporator containing a condensation-return line and air-sweep inlet.
2. Use Glas-Col heating mantle.
3. Set starting voltage at 65 volts. When approximately 75 per cent of the solution has evaporated, reduce voltage to 50 volts.
4. Set air flow at one liter per minute. This may be increased if flooding does not occur in condenser.
5. Use one to two-inch bed of glass beads in condenser.

REFERENCES

1. Brown, W. T., and Stringham, W. S., Rpt. Gen. Res., MLM-519, p. 10, January 15, 1951.

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TABLE I
DECONTAMINATION FACTOR OF COBALT-60⁺ SOLUTION

SAMPLE No.	VOL. IN STILL (ML.)	ACTIVITY IN STILL (CTS./ML.)	ACTIVITY IN CONDENSATE	
			HT. OF BEADS IN CONDENSER 1 3/8 IN. (CTS./ML.)	2 IN. (CTS./ML.)
ORIGINAL	250	1.1×10^4	-	-
1	225	1.2×10^4	0	-
2	200	1.4×10^4	2	0
3	175	1.6×10^4	0	2
4	150	1.9×10^4	0	2
5	125	2.2×10^4	0	0
6	100	2.8×10^4	0	0
7	75	3.7×10^4	2	0
8	50	5.6×10^4	8	0
9	25	1.1×10^5	SOLIDS DEVELOPED ON METAL SLIDES BECAUSE OF CORRO- SION FROM HCL IN CONDENSATE.	
10	1	2.8×10^6		

EVAPORATION RATE OF 1 ML./MIN. COBALT-60 IN HYDROCHLORIC ACID SOLUTION. COUNTS MADE ON METAL SLIDES.

TABLE II
DECONTAMINATION FACTOR OF COBALT-60 SOLUTION RUN II

SAMPLE No.	VOL. IN STILL (ML.)	ACTIVITY IN STILL (CTS./ML.)	ACTIVITY IN CONDENSATE
			HT. OF BEADS IN CONDENSER 2 IN. (CTS./ML.)
3	150	1.9×10^4	2
5	100	2.8×10^4	0
7	50	5.6×10^4	2
8	25	1.1×10^5	2
9	1	2.8×10^6	1

CONDITIONS SAME AS TABLE I. CONDENSATE-RETURN LINE WAS ADDED, AND MOUNTS WERE MADE ON GLASS SLIDES.

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FIGURE 1

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Problem Title - The Adsorption of Radon

Report By - W. S. Stringham

Work Done By - W. S. Stringham

INTRODUCTION

During the separation of actinium from irradiated radium, large quantities of radon are evolved. Inasmuch as radon and its decay products are health hazards, precautions must be taken to prevent their escape to operating areas and to the atmosphere. The most efficient means of removing radon from an air stream carrier is considered to be by adsorption on activated carbon at low temperatures. Equipment has been assembled to study the practical aspects of this problem particularly in regard to the following variables:

1. Permissible flow rate of the gas per volume of adsorber for complete removal of radon.
2. Degree of refrigeration that is required for the adsorber.
3. Type of adsorber best suited for the removal of radon.
4. Degree to which water vapor must be removed to prevent loss of adsorption efficiency and practical methods for this removal.
5. Tendency for radon to escape from the adsorber at room temperature.
6. Total absorptive capacity of a given amount of adsorber.

DETAILED REPORT

To determine the procedure for an assay of the amount of radon present by gamma counting, a sample of radon freshly adsorbed on charcoal was counted every half hour until a plateau developed, indicating that the growth of RaB , RaC , and RaC' was in equilibrium with the decay of radon. Counting was continued until results showed that the slope of the curve was following the normal radon decay curve. Essentially constant gamma counts were obtained between 3 and 8 hours after the radon had been adsorbed on the charcoal. Therefore all samples were allowed to age for at least 3 hours before counting. The effective half life of the decay products can be assumed to be roughly the sum of the half lives of the chain or about 50 minutes. Equilibrium should be reached (97 per cent) in about 5 half lives or 250 minutes.

The tests at present are being conducted in the following manner. Air, at a predetermined rate, is bubbled through a radium solution into which a known amount of radon has grown. Heat is applied for 60 minutes. The air stream containing the evolved radon passes through a vertical water condenser then through two traps chilled in a dry ice-trichloroethylene mixture in order to remove as much of the water vapor as possible. If adsorption at room temperature is desired the gas stream is warmed to room temperature by passing it through a U-tube approximately 20 inches long before it enters the charcoal trap being tested. The remaining radon is adsorbed in a trap containing reactivated charcoal chilled in a dry ice-trichloroethylene mixture. It is assumed that the latter trap is at optimum adsorbing conditions. The charcoal was reactivated by heating the charcoal to red heat while under vacuum. A safety trap containing 150 grams of activated charcoal is the final unit in the system. Each trap is equipped with stopcocks in order to prevent escape of radon during the counting time. After a growth period of 3 hours the charcoal traps are counted for gamma activity.

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To date only the permissible flow rate and the degree of refrigeration required have been investigated. The degree to which the gas stream is dried has been temporarily fixed by repeatedly freezing out at -75°C . as much of the water vapor as possible in order that the adsorption efficiency of the charcoal may be obtained under ideal conditions. As soon as the absorption efficiency of the charcoal on a dry gas stream has been determined, experiments will be run to determine the amount of water vapor which may remain in the radon-bearing air stream without materially affecting the efficiency of the charcoal.

We are considering the use of silica gel traps to remove the water vapor during actual operation in the cave. Run 1 in Table I shows that large amounts of silica gel adsorb radon to a considerable extent.¹ Run 2 was made to determine the adsorption efficiency of small amounts of silica gel. It was found that this efficiency is very much lower than that of an equal amount of activated charcoal. Runs 3, 4, and 5 were made to compare the efficiency of activated and reactivated charcoal, but because of the conditions chosen, no definite conclusions can be reached. In an attempt to determine the minimum amount of charcoal necessary for removal of the radon, the amount of charcoal was reduced 50 per cent in Run 6 and the flow was doubled in Run 7. The temperature was lowered from 20°C . to -20°C . in Run 8, with other conditions the same. The amount of charcoal was reduced again in Run 9 to determine the minimum amount of adsorber at the higher flow of gas.

The type of charcoal used in all of this work was Columbia activated carbon, Grade 6G, 8 to 14 mesh.

CONCLUSIONS

The data obtained so far are preliminary and serve mainly to establish the conditions that will be used in subsequent work. The conditions employed in Run 9 should enable us to vary these conditions separately in order to study their effect on the adsorption efficiency of the charcoal trap under test.

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TABLE I

ADSORPTION OF RADON ON CHARCOAL

RUN NO.	RATE FLOW (CC./MIN.)	RADON (MC.)	TYPE	RADON		TYPE	RADON		TYPE	RADON		TYPE	RADON	
				TEMP. (°C.)	REMOVED (%)		TEMP. (°C.)	REMOVED (%)		TEMP. (°C.)	REMOVED (%)		TEMP. (°C.)	REMOVED (%)
1	20	1.0	330 G. SILICA GEL	20	95.6	1 LITER GLASS BEADS	20	3.1	1 G. ACT. CHARCOAL	20	0.9	150 G. ACT. CHARCOAL	20	0.4
2	20	0.17	2H ₂ O TRAPS	-20	NEG.	2 G. SiO ₂	-20	0.5	150 G. ACT. CHARCOAL	20	99.5			
3	20	0.30	2H ₂ O TRAPS	-75	NEG.	1 G. ACT. CHARCOAL	-75	100	150 G. ACT. CHARCOAL	-75	0			
4	20	1.03	2H ₂ O TRAPS	-75	NEG.	1 G. RE-ACT. CHARCOAL	-75	100	150 G. ACT. CHARCOAL	-75	0			
5	20	0.30	2H ₂ O TRAPS	-75	NEG.	1 G. ACT. CHARCOAL	-75	100	1 G. RE-ACT. CHARCOAL	-75	0	150 G. ACT. CHARCOAL	-75	0
6	20	0.60	2H ₂ O TRAPS	-75	NEG.	0.5 ACT. CHARCOAL	20	100	1 G. RE-ACT. CHARCOAL	-75	0	150 G. ACT. CHARCOAL	-75	0
7	40	0.51	2H ₂ O TRAPS	-75	NEG.	AIR STREAM- WARMED 0.5 G. ACT. CHARCOAL	20	96.2	1 G. RE-ACT. CHARCOAL	-75	3.8	150 G. ACT. CHARCOAL	-75	0
8	40	1.03	2H ₂ O TRAPS	-75	NEG.	AIR STREAM- WARMED 0.5 G. ACT. CHARCOAL	0	100	1 G. RE-ACT. CHARCOAL	-75	0.	150 G. ACT. CHARCOAL	-75	0
9	40	0.42	2H ₂ O TRAPS	-75	NEG.	AIR STREAM- WARMED 0.25 ACT. CHARCOAL	20	54.9	1 G. RE-ACT. CHARCOAL	-75	44.9	150 G. ACT. CHARCOAL	-75	0.2

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GAMMA EQUILIBRIUM DURING THE DECAY OF Rn AND GROWTH OF
RaA, RaB, RaC AND RaC¹

FIGURE 1

Problem Title - Determination of Radium Purity

Report By - H. W. Kirby

Work Done By - H. W. Kirby

INTRODUCTION

The decision to purchase radium instead of recovering it from Mallinckrodt's K-65 residues has magnified the economic importance of developing a reliable method for determining the degree of purity of the purchased material.

Although in the case of polonium, a pure alpha emitter, chief reliance for purity analysis is placed on calorimetric methods, a comparable solution to the radium purity problem would be difficult because of the complexity of its decay chain.

Fractional precipitation and ion exchange offer the two most promising methods for the separation of radium from its major impurity, barium. Of the two methods, ion exchange, with its ready adaptability to automatic and remote control operation, would appear to be most nearly suited to the requirements of an analytical scheme.

Accordingly, it is proposed to develop a procedure based on the following successive steps:

1. Separation of barium from radium on an ion-exchange column of appropriate specifications.
2. Concentration of the barium fraction.
3. Determination of the amount of barium present by spectrographic analysis.

Determination of Radium Purity

From a spectrographic standpoint, barium analysis is difficult, for, like all the alkaline earth metals, its spectral lines are few and diffuse. The lower limit of detection for barium is 0.05 microgram, and the precision of measurement about 10 per cent.¹

On the assumption that the purity of radium received will be of the order of 90 to 95 per cent, the total amount of barium in a one-milligram sample will not exceed 100 micrograms. Of this amount, only that fraction which is eluted entirely free of radium may be used; since it is essential to preclude any possibility of contamination in the spectrographic equipment.

For the second step in the proposed scheme (the concentration of barium to a level suitable for spectrographic measurement), it is desirable to have an elutriant which can either be destroyed or be readily volatilized in the process. Although ammonium citrate has been used successfully as an elutriant in the separation of radium from barium,² it is neither volatile nor easily destroyed. Consequently the possibility of using a mineral elutriant, such as hydrochloric acid or ammonium chloride, was considered.

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DETAILED REPORT

Choice of Elutriant

Ammonium chloride (3.5 molar) and hydrochloric acid (from 1.0 to 8.0 normal in 1.0 normal steps) were tested for use as elutriants. In each experiment, 158 milligrams of barium as the citrate was fed onto a short column of Dowex-50 resin and eluted at a rate of one milliliter per minute per square centimeter. The effluent fractions were analyzed for barium by a standard turbidimetric technique, which is discussed subsequently.

Of all the elutriants tested, only the ammonium chloride was satisfactory from the standpoints of distribution of barium and the position of the peak. The best hydrochloric acid concentration was found to be 5.0 normal. When the results of these two elutions are compared (Figure 1) the superiority of ammonium chloride is quite evident.

Separation of Radium from Barium by Ammonium Chloride

A preliminary separation of radium from barium was carried out in order to establish the relative positions of the peaks and the degree of overlapping. A solution containing 140 milligrams of barium and 25 micrograms of radium as the chlorides was fed onto a column and the cations eluted with 3.5 molar ammonium chloride. The effluent fractions were analyzed for barium by the turbidimetric method and for radium by gamma count after 2 weeks (Figure 2).

A clean separation was not obtained, but the distribution indicated that a considerable degree of concentration of barium might be obtained by adjustment of the elution rate and column dimensions.

Use of Barium-140 as a Tracer

The turbidimetric method of analysis for barium consists of adding sulfuric acid or a sulfate solution to a barium solution and examining the resulting turbidity. If the barium concentration is within the proper range (from 40 to 200 parts per million, approximately) the turbidity may be compared with known standards, either in a colorimeter or in matched Nessler tubes, and the amount of barium estimated.

However, the tendency of barium sulfate to form slowly in dilute solution, to be occluded on the glass walls of the comparison cells, and to agglomerate to an unpredictable degree, all combine to make this method of analysis tedious and uncertain at best.

In addition, because of the lower limit of approximately 10 micrograms per 25 milliliter sample, the method is not suitable for use in the present investigation, where the total amount of barium to be determined (less than 100 micrograms) will be divided among a large number of samples.

Consequently, approximately 10 millicuries of barium-140 was obtained from Oak Ridge National Laboratory for use as a tracer.

Barium-140 is a strong beta emitter, decaying with a half life of 308 hours to lanthanum-140, which, in turn, decays by beta emission (40.4 hours half life) to stable cerium-140.

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Slides of barium-140 prepared by the hydrochloric acid-ether precipitation method^s were used to check the calculated decay and growth curve. Good corroboration was obtained (Figure 3).

It was hoped that analysis for radium and barium-140 could be carried out on a single slide by counting alphas emitted from radium and betas from barium. However, slides of pure radium prepared by the hydrochloric acid-ether precipitation methods, were found to have an apparent beta activity about 50 per cent as great as the alpha activity. No satisfactory explanation of this phenomenon has been found, and attempts to absorb this beta activity with thin aluminum absorbers have been unsuccessful. It was, therefore, necessary to carry out separate elutions of radium and barium-140 to establish the conditions for separation.

Simulated Radium-Barium Separation

An elution of 17.85 microcuries (3.86×10^{-4} micrograms) of barium-140 was performed with 3.5 molar ammonium chloride elutriant at an elution rate of 0.5 milliliter per minute per square centimeter. The effluent was collected, allowed to decay for 270 hours, and then gamma-counted. The peak occurred at the 22nd column volume.

A comparison of this elution with the elution of 140 milligrams of inert barium is shown by Figure 4. Because of the decrease in ion concentrations, the peak has shifted from the 13th column volume in the case of the large amount of barium to the 22nd column volume for the smaller amount.

In a separate run on the same column, 45.9 micrograms of radium was eluted with 3.5 molar ammonium chloride at a rate of 0.42 milliliter per minute per square centimeter. The effluent fractions were analyzed by alpha count, the peak occurring at the 32nd column volume.

The combined elution data for the two runs were regarded as simulating an actual separation. They were recalculated for comparison purposes on the basis of column volume (Figure 5). The same data are shown in part as cumulative percentages of the total barium and radium in each run in Table I.

CONCLUSIONS

The preliminary work on this phase of the problem has been completed. Although neither hydrochloric acid nor ammonium chloride is as effective an elutriant as ammonium citrate, ammonium chloride most nearly fulfills the requirements of the proposed analytical procedure.

Only 26 per cent of the barium would be eluted free of radium under the conditions mentioned in Table I; but if this elution procedure is reproducible it will serve to provide a known fraction of the barium, free from radium, for spectrographic analysis.

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TABLE I

SIMULATED SEPARATION OF RADIUM AND BARIUM BY ION EXCHANGE
WITH 3.5 MOLAR NH_4Cl ELUTRIANT; DOWEX-50 RESIN

COLUMN VOLUMES (16.6 ML.)	CUMULATIVE PER CENT OF BARIUM	CUMULATIVE PER CENT OF RADIUM
11	0.24	
12	0.46	
13	1.01	
14	1.52	
15	2.90	
16	6.18	
17	10.49	
18	17.57	
19	26.76	0.00
20	38.16	0.15
21	50.49	0.35
22	64.33	0.53
23	76.46	1.40
24	85.52	2.27
25	91.68	3.43
26	95.15	5.68
27	97.43	8.57
28	98.62	13.41
29	98.76	20.38
30	99.00	29.85
31	99.16	40.04
32	99.42	51.74

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ELUTION OF BARIUM WITH TWO MINERAL ELUTRIANTS

FIGURE 1

RESIN: DOWEX 50, NH₄R
70-100 MESH

FEED: 140 MG. BARIUM + 25 μ C
RADIUM AS CHLORIDES

ELUTRIANT: 3.5M NH₄Cl

DROP RATE: 1 ML./MIN./CM.²

COLUMN VOLUME: 16.6 ML.

SEPARATION OF BARIUM FROM RADIUM BY ELUTION WITH NH₄Cl

FIGURE 2

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NOTE: EACH PLOTTED POINT
IS AN AVERAGE OF COUNTS
FROM FOUR SLIDES.

"A" THEORETICAL DECAY OF BARIUM 140
"B" THEORETICAL GROWTH AND DECAY OF BETA ACTIVITY
FROM INITIALLY PURE BARIUM 140

FIGURE 3

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TWO ELUTIONS OF BARIUM WITH 3.5 M. NH_4Cl

FIGURE 4

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FIGURE 5

Problem Title - Actinium Counting

Report By - E. W. Moshier

Work Done By - N. E. Rogers

INTRODUCTION

In order to assay actinium-227 and to follow the progress of an actinium purification process, a rapid method is needed for determining the amount of actinium present. During this quarter our efforts have been concentrated on the chemical separation of francium-223, thorium-227, and actinium-227 free from all other radioactive elements.

Since the age and purity of an actinium sample will always be uncertain, the first step in an assay method must be the purification of the actinium to a known degree. The second step is the selection of the radioactive element, actinium itself or one of its daughters which lends itself to accurate counting. The third step involves the separation of the selected element from all other radioactive elements. The farther down the chain of daughters an element is, the longer one would need to age the purified actinium from the sample in order to have a sufficient quantity of the element for counting. As a corollary, the nearer the head of the decay chain an element is, the earlier it will grow to an activity sufficiently high for counting. Also the more daughters it produces in its decay chain, the higher the count produced in a given period of time.

From these considerations the purified actinium-227 itself is the logical selection for a rapid assay method. As a second choice, either francium-223, the first daughter from the 1.25-per-cent-alpha decay chain or thorium-227, the first daughter from the 98.75-per-cent-beta decay chain appear most suitable.

DETAILED REPORT

The actinium stock solution is a portion of the actinium-227 prepared at the Argonne National Laboratory. Its age is sufficient to be in equilibrium with its daughters. One milliliter of this solution, purportedly containing 0.01 microcuries, mounted on a 2-inch disk, gave 47,600 alpha and 55,300 beta counts per minute per milliliter. Theoretically this 0.01 microcurie should have given 55,500 alpha and 33,300 beta counts per minute per milliliter at 50 per cent geometry. One milliliter then tentatively contains 0.0086 microcuries based on this alpha count.

In the work described below, for the extractions with TTA, the pipette of West and Carlton¹, as illustrated in Figure 1, was used. Centrifugation was used to separate extraction layers and precipitates. The term filtrate will refer to the supernatant liquor above the precipitate.

Thorium Chemistry and Thorium Counting

The growth and decay of several chemically-isolated thorium samples were followed.

1. Three 0.0086-microcurie samples of actinium stock solution were extracted with thenoyltrifluoroacetone (TTA) in benzene to remove the thorium from an aqueous solution of actinium 0.1 normal in hydrochloric acid, as described by Hagemann.²

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The plot of the growth-decay curves of these samples are very similar in shape. These curves are slightly flatter than the theoretical curve with a half life of 25 days in one case and 34 days in another. The discrepancy is attributed to the presence of an impurity, probably actinium-227. From other considerations it is possible that 1.9 year thorium-228 is present. A study is in progress for determining the presence of the thorium-228 from the decay characteristics of the radium isolated from the aged thorium. The growth-decay curve for the 25-day-half-life sample is shown in Figure 2.

2. One 0.0086-microcurie sample was extracted with TTA at a pH of 3. At this pH, according to Hagemann, the thorium is completely extracted; lead, polonium, and bismuth are less completely extracted; but actinium is not extracted. Although the extracted thorium gave a higher initial count than those extracted at pH of 1, the growth-decay curve was similarly flatter than the theoretical curve.

Extraction of thorium with TTA from a solution one normal in hydrochloric acid is far from complete. The above samples of thorium represent about 50 per cent extraction efficiency.

3. After the experience gained in the TTA extraction, the work was switched to the purification of actinium. Samples of thorium isolated during the purification of actinium were also counted. One such sample obtained from 0.086 microcurie by the original TTA procedure appears to be much purer than the others. Over a 35-day counting study it has followed the theoretical curve very closely as illustrated in Figure 3. It is believed that with the use of a sample 10 times larger the contamination by the impurity, as encountered in earlier work, was no greater than with the smaller samples, and that this impurity was less effective in distorting the growth-decay curve of the larger quantity of thorium. The initial count was 78 per cent of theoretical.
4. The McLane and Peterson³ method of obtaining pure actinium-228 from natural thorium utilizes a pyridine precipitation of thorium as a cleanup step. In following this procedure, slightly modified to suit the actinium-227, it has been found that the precipitated thorium was badly contaminated with actinium. The precipitate when dissolved and reprecipitated was found to be much purer.

One sample repurified in this manner is following the theoretical growth-decay curve very closely, and is comparable to the TTA-extracted sample discussed in the preceding paragraph (3).

Actinium Chemistry and Actinium Counting

1. By the Hagemann procedure attempts were made to obtain radioactively pure actinium from our stock solution.

The procedure consists of the extraction of each radioactive element in the actinium series from aqueous hydrochloric acid solution with TTA solution in benzene at predetermined pH values. Three extractions of

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thorium were made at pH 1; actinium was extracted at pH 6. The actinium was then removed from the benzene with 6 normal hydrochloric acid after each extraction, neutralized to pH 6, and re-extracted with TTA. This procedure was repeated once again. The radium was left unextracted. Lead and bismuth carriers were added, the acidity adjusted to 0.2 normal in acid, and the lead, bismuth, and polonium precipitated with hydrogen sulfide.

The fractions obtained from a 0.0086-microcurie sample were not true to prediction. The thorium extract was somewhat low. Practically no activity was found in the actinium fraction. The radium fraction contained nearly all of the activity. It is possible that conditions were not governed closely enough.

2. By a modified McLane and Peterson procedure attempts were made to obtain pure actinium.

The procedure consisted of adding thorium, lanthanum, and barium carriers to the sample, evaporating to dryness with added nitric acid, and then extracting the actinium from the dry residue three times with isopropyl alcohol, leaving the barium and radium behind. The extract containing the actinium was treated with pyridine to precipitate the thorium. Lead and bismuth were added to the alcohol filtrate and were precipitated along with the polonium by the addition of hydrogen sulfide. The activity in the sulfide precipitate should decay rapidly since no long-lived activity should be present. Actually the activity grew rapidly indicating considerable contamination, probably with actinium. The purified actinium in the supernatant had a very low count, and its behavior was not characteristic of actinium.

- 3 It was decided to combine the better features of both the Hagemann and the McLane and Peterson procedures as follows. The thorium was extracted with TTA at pH 1. To the aqueous layer were added 1 milligram of lanthanum and 4 milligrams of barium carriers, and the solution was evaporated to dryness with added nitric acid. This dry residue was extracted three times with isopropyl alcohol to obtain the actinium. To this alcohol extract were added 1 milligram each of lead and bismuth carriers and the solution was evaporated to dryness with hydrochloric acid to remove the alcohol. The residue, dissolved and adjusted to 0.2 normal with hydrochloric acid, was treated with hydrogen sulfide to precipitate the lead, bismuth, and polonium. The precipitate was dissolved and reprecipitated. The two filtrates were combined and mounted with sulfuric acid for counting. The sulfate is preferable for counting as it is nonhygroscopic.

The actinium fraction obtained by this procedure on a 0.086-microcurie sample has been counted over a 35-day period and follows the theoretical curve after 9 days, as illustrated in Figure 4. The count at zero time was approximately twice what it should have been when calculated

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from the counts obtained subsequently. The nature of this impurity has not been determined. The sulfide precipitate had a low initial count and decayed normally, indicating no loss of actinium in this step.

4. On the basis of the experience gained with the McLane and Peterson method, the method was retested with a larger sample of actinium stock solution. The procedure used was the same as that described under the preceding paragraph (2) except that the sulfide group was precipitated from aqueous solution as described in paragraph (3) rather than from isopropyl alcohol. The actinium fraction obtained from a 0.086-microcurie sample has been counted for 26 days and has followed the theoretical curve very closely from the initial count (Figure 5)

Francium Chemistry and Francium Counting

The procedure of Perey⁴ was used in an attempt to isolate the pure francium daughter from a 0.5-microcurie sample of actinium stock solution.

In this procedure one milligram of barium carrier was added to the sample and precipitated with excess ammonium carbonate to remove the radium. The filtrate was acidified with hydrochloric acid and the precipitate washed, the washings being combined with the original filtrate. This procedure was repeated three times. After the final acidification, the solution was boiled to remove the carbonic acid, a slight excess of ammonium chromate solution was added, and one milligram each of barium and cerium carriers added. The solution was made alkaline with ammonium hydroxide, thus precipitating all but the francium and other alkali metals. This scavenging was repeated once and the final filtrate thus obtained evaporated to a small volume on an oil bath with the aid of a stream of air. The concentrate was mounted, dried, and the ammonium salts volatilized. The sample was counted every 10 minutes for a period of 80 minutes. No changes in either the alpha or beta counts were observed. Since 3 hours were required from the time of the first carbonation to the time of the first count and since 2 of the 3 hours were required for the mounting process, 21-minute francium had pretty well decayed by the time the first count was made. The theoretical francium beta count at the time of the separation from the actinium of this sample was 6,660 beta counts per minute. The actual beta counts remained constant at about 200.

CONCLUSIONS

Our experience has given us a much better and useful knowledge of the chemical behavior of actinium and its daughters. Nearly pure actinium-227 and thorium-227 have been separated from actinium-227 stock solution. Further improvement in the purifications are necessary, and emphasis will be placed on these improvements. Isolation of francium for counting assay was not successful. A much more rapid separation method for francium will need to be worked out before the feasibility of francium counting for assay is considered again. It appears now that the assay of actinium samples will best be done from either pure actinium or pure thorium. Actinium is preferred from the standpoint of quicker assay and fewer operations.

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T. T. A. EXTRACTION PIPETTE.

FIGURE 2

THORIUM—227 FROM ACTINIUM—227

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THORIUM-227 FROM 0.086 MICROCURIES ACTINIUM-227

FIGURE 3

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GROWTH OF PURIFIED ACTINIUM.

FIGURE 4

FIGURE 5

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Problem Title - Extraction of Actinium from Barium Sulfate

Report By - J. B. Otto

Work Done By - J. B. Otto

INTRODUCTION

The extraction of actinium-227 with dilute acid from slow-neutron-irradiated radium-226 sulfate has been discussed¹ as a possible method for separating from radium the actinium produced. The feasibility of such a separation has been studied.

Barium nitrate samples containing about 10 milligrams of inactive barium and tracer quantities of radium-228 have been prepared in this laboratory.^{2,3} Radium-228 (half life, 6.7 years) decays by beta emission to actinium-228 (half life, 6.13 hours); these two isotopes reach radiochemical equilibrium in a little more than one day. The quantity of actinium-228 in equilibrium with the radium-228 in these samples has been determined radiochemically by the Haissinsky, McLane, and Peterson method.⁴ When these barium-radium-228 samples have been converted to the sulfate, they are analogous to neutron-irradiated radium-226 sulfate; i.e., inactive barium simulates the gross excess of radium; and the growth of actinium-228 into equilibrium with radium-228 simulates neutron capture by radium-226 to form radium-227, which subsequently decays by beta emission to actinium-227. These barium-radium-228 samples, when converted to the sulfate, are therefore suitable for the study of the possible separation of actinium-227 from neutron-irradiated radium-226 by the extraction of the actinium in dilute acid.

DETAILED REPORT

An extraction experiment was carried out on a sample of barium-radium-228-actinium-228 nitrate known to contain (at equilibrium) a quantity of actinium-228 equivalent to 22,800 beta counts per minute at 50 per cent geometry. This sample was converted to the sulfate by the following procedure.

1. The sample (in a 15-milliliter centrifuge tube) was dissolved in 10 milliliters of 0.01 normal nitric acid and heated to 90° C.
2. Barium-radium-228 sulfate was precipitated by dropwise addition of enough one normal sulfuric acid (0.4 milliliters or about eight drops) to make the solution about 0.04 normal in sulfuric acid.
3. The resulting suspension was digested at 90° C. with occasional stirring for 2.5 hours. This treatment produced a crystalline precipitate which was easily separable from the solution by centrifugation. The supernatant liquid was discarded.
4. The precipitate was washed with 10 milliliters of 0.05 normal nitric acid at 90° C. The sample was then centrifuged, and the supernatant liquid (wash solution) was discarded.
5. Step 4 was repeated once.

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6. The barium-radium-228 sulfate was finally washed with 5 milliliters of 0.05 normal nitric acid at 90°C. After centrifugation, the wash solution was transferred portionwise to a 2-inch, stainless-steel, Bradley counting slide and evaporated to dryness.
7. The washed barium-radium-228 sulfate precipitate was dried in the centrifuge tube at 110°C.

The residue on the slide prepared as described in Step 6 was counted about 1 hour after preparation on a Nuclear Measurements PC-2 (Bradley) counter at 50 per cent geometry with the following results expressed as counts per minute: alpha - 187, beta - 997. When this slide was counted 24 hours later the following results were obtained: alpha - 192, beta - 730. These results show that a small percent of the total radioactive isotopes known to be present in the sample were still being washed from the precipitate after two previous washings. The relatively small decrease (after 24 hours) in beta activity indicates that only a small fraction of this material was actinium-228. The barium-radium-228-sulfate precipitate was allowed to stand until actinium-228 had grown into equilibrium with the radium-228 (2 days is sufficient). Then an attempt was made to extract the actinium from the sample by the following procedure:

1. The barium-radium-228-actinium-228 precipitate was washed with 5 milliliters of 0.05 normal nitric acid for 2 hours at 90°C. The sample was then cooled and centrifuged (Time - 2:00 P.M., 3/9/51).
2. The supernatant liquid was transferred portionwise to a 2-inch, stainless-steel, Bradley counter slide and evaporated to dryness.

The residue on the slide was counted in a Bradley counter at 50 per cent geometry (Time - 3:30 P.M., 3/9/51) with the following results expressed as counts per minute: alpha - 646, beta - 1,889. When this slide was counted 24 hours later (Time - 3:30 P.M., 3/10/51), the following results were obtained: alpha - 706, beta - 1,205. It may be assumed that the 684 count per minute decay in beta activity is a measure of the quantity of actinium-228 extracted. (6.13-hour actinium-228 decays to about eight per cent of its original activity in 24 hours). By comparison of this result with the quantity of actinium-228 known to be present in the sample, i.e., equivalent to 22,800 beta counts per minute at 50 per cent geometry (corrected for 1.5 hours decay - 19,200), it can be seen that no more than about four per cent of the actinium was extracted. The presence of alpha activity and nondecaying beta activity in the extract sample indicates a high degree of contamination associated with the small fraction of actinium extracted.

Another sample of barium-radium-228 nitrate was converted to the sulfate and extracted by essentially the same procedure as outlined above. In this experiment, however, the barium sulfate digestion step (Step 3, above) was carried out only 10 minutes instead of 2.5 hours. The resulting barium sulfate was partly colloidal, and therefore was not easily separated from solution by centrifugation. The result of this experiment was, however, almost the same as that obtained in the preceding experiment.

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DISCUSSION

The results obtained in these experiments were not unexpected. It has been shown previously in this laboratory² that actinium-228 could not be extracted with absolute ethanol from solid barium nitrate in which it had grown as a result of the decay of radium-228 atoms present in the crystal lattice of the barium nitrate. In this case, the solubility of the daughter compound (actinium nitrate) was governed by that of the parent compound (barium-radium nitrate) which was present in gross excess. By analogy of this with the present situation, it would be surprising if actinium-228 sulfate were not prevented from dissolving by its being dispersed in insoluble barium-radium-228 sulfate. Another reason to believe that the extraction of actinium from barium sulfate should not be possible is the fact that McLane and Peterson⁴ have shown that nearly 100 per cent of the actinium in a solution was carried when barium sulfate was precipitated. These workers have also found that small amounts of lanthanum in solution tend to displace part of the actinium from the barium sulfate.

CONCLUSIONS

Only about four per cent of the actinium in a barium-radium-228-actinium-228 sulfate sample was found to be extractable in dilute acid under the conditions used in this study. For this reason, it is not considered feasible to extract actinium-227 from neutron-irradiated radium-226 sulfate with dilute acid.

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Problem Title Reduction of Lanthanum from Liquid Ammonia

Report By - J. B. Otto

Work Done By - J. B. Otto

INTRODUCTION

Attempts to reduce the lanthanum ion in liquid ammonia, either with sodium metal or polarographically, have been reported previously from this laboratory.¹ A solution of sodium metal did not reduce the lanthanum ion at either the boiling point of liquid ammonia (-33°C.) or room temperature. Polarographic studies at negative potentials from zero to -1.6 volts with reference to the mercury-pool anode gave no indication of a reduction wave for the lanthanum ion.

The present report deals with exploratory studies of the polarographic reduction of the lanthanum ion at potentials more negative than -1.6 volts.

DETAILED REPORT

Previous studies have shown that lanthanum iodide ammonolyzes to form an insoluble ammonolysis product in neutral, liquid ammonia.¹ Ammonium iodide (an acid in the liquid ammonia system) reverses this ammonolytic reaction and makes lanthanum iodide soluble in liquid ammonia to a limited extent.

A lanthanum iodide solution made by dissolving lanthanum metal in an ammonium iodide solution in liquid ammonia at -33°C was found to be roughly 0.14 normal in ammonium iodide and 0.015 normal in lanthanum. The degree of saturation of this solution was not known. These solubility relationships require the presence of ammonium iodide in lanthanum iodide solutions in which the lanthanum ion must have an appreciable concentration, as in the case of polarographic studies.

In the previously reported polarographic studies,¹ 0.1 normal ammonium iodide served both as a supporting electrolyte and as a solubilizing agent for lanthanum iodide. When a solution 0.1 normal in ammonium iodide and 0.007 normal in lanthanum as lanthanum iodide was subjected to polarographic examination, no reduction wave for lanthanum was noted between zero and -1.6 volts with reference to the mercury-pool anode. More negative potentials than -1.6 volts cannot be obtained under these conditions because this is the potential at which the reduction wave of the ammonium ion itself begins. Laitinen and Shoemaker² have shown that a limiting current can be obtained for the ammonium ion and that its half-wave potential is about -1.7 volts with respect to the mercury-pool anode. These workers used tetra-n-butylammonium iodide as a supporting electrolyte. Laitinen and Nyman³ have demonstrated that tetraethyl-, tetrapropyl-, or tetrabutylammonium iodides are nonreducible in liquid ammonia and are suitable for use as supporting electrolytes at potentials up to 2.3 volts with respect to the mercury-pool anode, the potential at which the action of the "electron electrode" begins. By using a quaternary salt as a supporting electrolyte and a minimum amount of ammonium ion to provide for lanthanum solubility, one may explore the region between -1.6 and -2.3 volts to the mercury-pool anode for lanthanum reduction. The lanthanum reduction wave, if present between these potentials, would be superimposed on top of the plateau caused by ammonium ion reduction.

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Tetraethylammonium bromide was used as the supporting electrolyte in the present exploratory polarographic studies. The simple apparatus used in this work has been described previously.¹ All polarographic electrolyses were carried out with about 100 milliliters of solution. Potentials were all measured with respect to the mercury-pool anode. The polarograms shown in Figures 1 and 3 represent the outer envelope (maximum drop size) of the mechanically recorded current-voltage tracings.

In the first series of experiments, the 100 milliliters of liquid ammonia was initially made about 0.005 normal in tetraethylammonium bromide (supporting electrolyte) by addition of 0.100 gram of the solid. A background polarogram was run on this solution (Figure 1-A). The same solution was then made about 0.001 normal in ammonium iodide by addition of 0.020 gram of this material. The presence of the ammonium reduction wave with a half-wave potential of about -1.7 volts can be seen in the polarogram run on this solution (Figure 1-B). Finally, the solution was made about 0.003 normal in lanthanum by addition of 0.050 gram of anhydrous lanthanum iodide, which had been prepared as has been previously described.¹ The insolubility of at least part of this material left doubt as to the concentration of lanthanum ion actually present in solution. The result of a polarographic run on this solution and suspension is shown in Figure 1-C. It can be seen that no lanthanum reduction wave occurred. The erratic nature of the curve may be ascribed to the presence of a precipitate, which increased the boiling of the liquid ammonia solution and may have affected the function of the electrodes. The apparent shifting of the solution-decomposition potential must be caused by changes in the potential of the mercury-pool anode with the composition of the different solutions.

Since the lanthanum iodide used in the previous experiment may not have been completely anhydrous because of storage and handling difficulties, a second experiment was devised in which the lanthanum iodide was prepared directly in liquid ammonia solution. A ten-fold increase also was made in the ammonium ion concentration in an attempt to keep more lanthanum ion in solution. The lanthanum iodide used in this experiment was prepared by the reaction of elemental lanthanum with ammonium iodide in liquid ammonia. This reaction has been found to proceed at a very slow rate at the boiling point of liquid ammonia (-33°C.).¹ To increase the rate of reaction between lanthanum and ammonium iodide in liquid ammonia so that it would go to completion in a reasonable length of time, the reaction was carried out in a sealed tube at 0°C. The apparatus shown in Figure 2 was used. End A of the reaction tube was initially open (dotted lines) and placed up. Into this open end were introduced 0.055 gram of lanthanum chips (enough to make the final 100 milliliters of liquid ammonia solution about 0.01 normal) and 0.306 gram of ammonium iodide (enough to react with the lanthanum and to make the resulting solution about 0.01 normal in ammonium ion). The materials collected on the sintered-glass filter disk. The lanthanum chips had been protected from air by cutting and weighing them under mineral oil which was removed from the chips by washing them in dry xylene immediately before the transfer described above was made. Ammonia gas was then passed through T and out the open end of the reaction tube until all the protective xylene, which had adhered to the lanthanum chips, had volatilized. The stopcock was turned off, and ammonia gas was passed into the open end of the reaction tube through a glass, ammonia-inlet tube, which reached almost to the sintered glass disk. The lower half of the reaction tube (and attached to stopcock) was then immersed in a dry-ice-acetone bath. The gaseous ammonia being passed into the reaction tube via the inlet tube condensed rapidly at the temperature of the dry-ice-acetone bath (-75°C.), but the flow rate of the gaseous ammonia was maintained rapid enough so that there was always an excess of ammonia gas flowing from the open end of the reaction tube to prevent air contamination. After about 10 milliliters of ammonia had been condensed, the ammonia inlet tube

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was removed, and the upper end of the reaction tube was quickly sealed off at point A, Figure 2. The reaction tube was then inverted and the lower half of the tube (end A) immersed in an ice-water mixture (0°C.). The reaction between lanthanum and ammonium iodide was fairly rapid at this temperature as evidenced by the evolution of hydrogen. The quantity of hydrogen gas produced by the reaction was not enough to increase the pressure much above the vapor pressure of the ammonia. The reaction was completed after standing over night (hydrogen evolution had ceased). The solution was clear and colorless, but a small amount of black powder was observed in the bottom of the tube. This powder was some of the black, tightly-adherent coating which covered the piece from which the lanthanum chips were cut. The 10 milliliters of clear solution, about 0.1 normal both in lanthanum iodide and in ammonium iodide produced an appreciable amount of white crystals on cooling to -75°C. which redissolved when the solution was allowed to warm up to 0°C. The white crystals were apparently a lanthanum iodide ammonate. This lanthanum iodide-ammonium iodide solution was now ready for use as described later.

Approximately 0.1 normal tetraethylammonium bromide (supporting electrolyte) was prepared by dissolving 2.1 grams of the salt in about 100 milliliters of anhydrous liquid ammonia contained in the polarographic cell, and a background polarogram was run on this solution (Figure 3-A).

The lanthanum iodide-ammonium iodide solution was transferred to the polarographic cell. The solution in the apparatus (Figure 2) was first cooled to somewhat below -33°C. The apparatus was again inverted (stopcock now at bottom), and tip T connected to the polarographic cell with Tygon tubing. The stopcock was opened, and the solution was pushed by its own vapor pressure through the sintered-glass disk and stopcock into the cell via the Tygon tubing. The medium-porosity filter disk, which served to filter the solution as it passed through, was not fine enough to remove all the black powder previously mentioned. When the lanthanum iodide-ammonium iodide solution mixed with the 100 milliliters of 0.1 normal tetraethylammonium bromide in the cell, a white amorphous precipitate formed. The precipitate, apparently an ammonolysis product of lanthanum, formed when the ammonium ion concentration was decreased by dilution. The resulting 110 milliliters of solution and suspension was then allowed to evaporate to about 100 milliliters. This solution was approximately 0.1 normal in tetraethylammonium bromide, 0.01 normal in ammonium iodide, and 0.01 normal in lanthanum iodide (if completely in solution).

A polarogram was run on the preceding solution and suspension (Figure 3-B). The reduction wave seen between -1.6 and -1.8 volts (Figure 3-B) is due to the ammonium ion, but no reduction wave due to lanthanum is present. The hump with a maximum at about -2.2 volts was found to be reproducible. However, the drop rate becomes extremely rapid and erratic just before reaching this potential range (more negative than -2.1 volts). It is interesting to note in this connection that the action of the "electron electrode"⁹ became visually evident at these higher potentials. At potentials between -2.3 and -3.0 volts, the formation of a dark coating was observed on the surface of the mercury-drop cathode in tetraethylammonium bromide solution (supporting electrolyte). When a drop falls, streaks of the typically blue color due to a solution of electrons in liquid ammonia can be easily seen. The same phenomena is evidenced by the rapid discharge of the blue color and formation of hydrogen bubbles when both tetraethylammonium bromide and ammonium iodide are present in solution. The electrons in the blue solution rapidly reduced the hydrogen ion (from ammonium ion) with the formation of elemental hydrogen. It is quite possible that the erratic, extremely rapid, but uncontrollable drop rate at potentials more negative than -2.1 volts caused the formation of the reproducible hump

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in the polarogram at -2.2 volts (Figure 3-B). The erratic drop rate may have been caused by the "electron electrode" action described above and/or the presence of a precipitate in solution.

DISCUSSION

Solubility studies have shown that it is not feasible to increase the concentration of the components of the solution much above that concentration used in the polarographic study described above, i.e., 0.1 normal in tetraethylammonium bromide, 0.01 normal in ammonium iodide, and less than 0.01 normal in ammonium lanthanum iodide. Tetraethylammonium bromide was found to be soluble in liquid ammonia to the extent of about 5 grams per 100 milliliters (about 0.24 normal) at -33°C. When, however, 100 milliliters of a liquid ammonia solution containing 5 grams of tetraethylammonium bromide was made 0.1 normal in ammonium iodide by addition of 1.4 grams of this substance, a heavy, white, crystalline precipitate formed immediately. Ammonium bromide, under identical conditions of concentration and temperature (-33°C.), produced a similar precipitate to that produced by ammonium iodide. These results indicate that the ammonium ion must exert a "salting out" effect on the tetraethylammonium ion. Since, in polarographic work, the concentration of the supporting electrolyte should be roughly ten times that of the ions for which reduction waves are desired, the above solubility limitations restrict the concentration of the ammonium ion to not much greater than 0.01 normal and that of the tetraethylammonium bromide (supporting electrolyte) to not much greater than 0.1 normal. In connection with the polarographic study described in the previous paragraphs, the solubility of lanthanum as lanthanum iodide was found to be less than 0.055 gram per 100 milliliters (0.01 normal) of a liquid ammonia solution 0.1 normal in tetraethylammonium bromide and 0.01 normal in ammonium iodide. It would be of interest to know the solubility of lanthanum iodide in this solution. If the concentration of lanthanum iodide in a saturated solution was found to be 0.001 normal or greater, it would be possible to prove the existence or nonexistence of a polarographic reduction wave for the lanthanum ion in liquid ammonia with more certainty since the presence of a precipitate in the solution may have adversely affected the function of the electrodes. Such a study would only be of theoretical interest, however, since the electrolysis of lanthanum from liquid ammonia solution has been demonstrated to be impractical from solubility considerations alone. If conditions for such an electrolysis were found, the cathode would have to be mercury because any elemental lanthanum deposited on an inert electrode would immediately react with the relatively concentrated ammonium ion required to prevent the ammonolysis of the lanthanum ion. The presence of the ammonium ion also would probably limit the equilibrium concentration of lanthanum in the amalgam to a very low value. The fact that the ammonium ion because of its higher concentration would be electrolyzed and form an amalgam at a faster rate than the lanthanum ion would further complicate the situation. Consideration of the above facts, together with the existence of a satisfactory method for the electrolysis of lanthanum chloride from ethanol solution into a mercury cathode,⁴ lead one to conclude that a similar electrolytic method in liquid ammonia (if possible) would be only of theoretical interest.

CONCLUSIONS

1. A polarographic reduction wave for the lanthanum ion in liquid ammonia solution could not be obtained under the conditions used in this study.

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2. There is some slight evidence that a polarographic reduction wave might be able to be obtained under different conditions, i.e., absence of a precipitate from solution. This would be of theoretical interest, but electrolysis of lanthanum into a mercury cathode from liquid ammonia solution, even if possible, would be impractical because of solubility limitations and interference from the necessary ammonium ion (solubilizing agent).

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POLAROGRAMS OF LIQUID AMMONIA SOLUTION

FIGURE 1

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POLAROGRAMS OF LIQUID AMMONIA SOLUTION

FIGURE 3

Problem Title - Preparation of Lanthanum Metal by the DeBoer Process

Report By - G. Pish

Work Done By - G. Pish and J. H. Goode

INTRODUCTION

The preparation of lanthanum from the iodide by thermal decomposition was studied to determine suitable conditions for a successful process which could be extended to include actinium. The method necessitated the preparation of anhydrous lanthanum iodide in an inert atmosphere or vacuo. The iodide was then vaporized at low pressure and an attempt made to reduce it thermally on a heated filament, depositing the lanthanum on the filament while the free iodine vapors evolved were removed.

SUMMARY

The experiments conducted were an extension of those reported earlier¹ with a modified DeBoer apparatus (Figure 1). The metal-quartz electrode seals made by the glass shop were not vacuum tight and caused experimental difficulties. A new reaction for the preparation of lanthanum iodide^{2,3} from lanthanum oxide, aluminum, and iodine was investigated and showed considerable promise. This reaction permitted the preparation of lanthanum iodide and its purification within a single, quartz apparatus.

Since vacuum-tight, metal-quartz seals were very difficult to make in the glass shop, atmospheric gases and water vapor present during the reduction process in the DeBoer method have prevented the reduction of lanthanum iodide to metallic lanthanum on the heated filament. To eliminate this source of trouble, the filaments in future DeBoer equipment will be heated indirectly by induction methods.

DETAILED REPORT

Preparation of vacuum-tight, metal-quartz seals was continued with 0.002-inch molybdenum foils, 1/32 to 1/16 inch wide, and 3 inches long. The edges were feathered to a knife-edge with No. 400 emery cloth. These electrodes were sealed into 4-millimeter outside-diameter and 2-millimeter inside-diameter quartz tubes by the vacuum technique.¹ The results of the tests are tabulated in Table 8. Even though vacuum-tight seals could not be relied upon, molybdenum-quartz seals of Series 1 type were used in making DeBoer reaction tubes.

In order to have a supply of anhydrous lanthanum iodide, a method similar to Young and Hastings⁴ was first tried. The procedure differed only in the substitution of a helium atmosphere for the nitrogen atmosphere. The reaction was as follows:

The apparatus used is shown in Figure 2. A mixture of 1 gram of lanthanum oxide and 8 grams of ammonium iodide (dried) was placed in the bottom of a quartz boat containing 1 gram of ammonium iodide. The tube containing the copper turnings was heated to 420°C., and pure helium was passed slowly through the combustion train (atmospheric pressure) as the temperature of the reaction chamber was raised to 350°C. At this temperature the reaction was permitted to proceed for 4 hours. The excess ammonium iodide and reaction products were then removed by maintaining the temperature at 325°C. for 4 hours with the pressure reduced to 0.5

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millimeter of mercury or less. At the same reduced pressure, the temperature was raised to 450°C and the process continued until no vapors of ammonium iodide could be detected. The apparatus was cooled. The reaction product was transferred in a helium atmosphere into sample bulbs, and the bulbs were sealed.

The product was probably not lanthanum iodide, since it could not be volatilized from a quartz tube heated to nearly its softening point at a pressure of 5×10^{-6} millimeter of mercury. Also it did not react with water. After three trials, the lanthanum iodide produced was still of dubious composition so the procedure was discontinued. Problems arising in the transfer of highly reactive lanthanum iodide were unmanageable.

S. Fried's research with actinium and americium compounds^{2,3} looked promising as a method for the preparation of lanthanum iodide, particularly since no transfer problems were involved. The reactions involved were:

The proposed method was to place a mixture of aluminum metal, iodine, and lanthanum oxide into a quartz tube, seal the tube, and heat for several hours at 700°C. After the tube was cooled and the tip broken open in a vacuum, the excess aluminum iodide and iodine could be distilled off below 400°C. Finally lanthanum iodide would be sublimed onto the cooler portions of the tube after the temperature was raised to 800°C. leaving aluminum, aluminum oxide, and lanthanum oxide in the bottom of the tube.

To carry out the entire process of preparing, purifying, and thermally reducing lanthanum iodide to the metal by the DeBoer method, the apparatus shown in Figure 1 was used. Because of this particular design the lanthanum iodide vapors were forced to come into contact with the heated filament during the reduction process

Experiment 1

The DeBoer apparatus was mounted horizontally (from A, Figure 1) to the vacuum line, and a wire-wound resistance furnace was slid over the apparatus to a position that left the electrode terminals exposed. The apparatus was degassed at 800°C., the tungsten filament was flashed several times to white heat, the apparatus was cooled, and the system was filled with dry helium. Then the system was disconnected at the taper joint under helium. The apparatus was charged through end A with 10 milligrams of lanthanum oxide, 50 milligrams of aluminum, and 50 milligrams of iodine (resublimed); replaced into the vacuum line; partly evacuated; and sealed off at the constriction. The apparatus was placed in a resistance furnace and heated to 400°C. for 2 hours, after which it was raised to 800°C. and held for another 3 hours. During the process the taper at B (Figure 1) broke just above the thin quartz bulb. Therefore the experiment was continued at whatever pressure developed in the reaction tube and without an attempt to purify the reaction products. The furnace temperature was set at 800°C. and the filament at 1,000 to 1,100°C. (optical pyrometer). After 3 hours the DeBoer apparatus was cooled and opened under pump oil. The coating from the tungsten filament was examined spectrographically, and the major constituent was found to be tungsten with a moderate amount of aluminum, a weak amount of molybdenum, and traces of titanium, silicon, manganese, magnesium, and lanthanum present.

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X-ray diffraction analysis showed the presence of tungsten, tungsten carbide, and a number of faint lines. No definite lanthanum pattern could be detected.

When some of the coating material was dropped into 5 cubic centimeters of water, a violent reaction developed which produced a white gelatinous precipitate.

Experiment 2

The above experiment was repeated with 10 milligrams of lanthanum oxide, 50 milligrams of aluminum, and 150 milligrams of iodine. All conditions were the same for the reaction in the DeBoer apparatus. After the reaction the DeBoer apparatus was cooled, mounted horizontally from B (Figure 1), and evacuated; and the thin quartz bulb was broken with the magnetic iron plunger. The apparatus was evacuated continuously for 3 hours and at the same time heated with a furnace set at 350 to 400°C. to distill off the excess aluminum iodide and any free iodine. The furnace temperature was then raised to 800°C., the filament raised to 1,000 to 1,100°C. (optical pyrometer), and system pumped continuously at 10^{-4} to 10^{-5} millimeter of mercury. After 1.5 hours of operation the tungsten filament burned out. Therefore the apparatus was cooled, sealed off, and opened under benzene. X-ray diffraction analysis of the coating on the filament showed considerable tungsten and tungsten carbide plus a number of very faint unknown lines. No pattern for lanthanum could be established definitely. Again the coating reacted violently with water and formed a white gelatinous precipitate.

Experiment 3

In this experiment a spiral tantalum filament welded to a molybdenum electrode was incorporated in the DeBoer apparatus. No other changes were made. The experiment was conducted in a manner identical to Experiment 2. During the run the apparatus developed a bad leak, but under continuous pumping the pressure was maintained between 10^{-4} to 10^{-5} millimeter of mercury. However, when the vacuum was momentarily closed, the pressure rose rapidly to 10^{-3} to 10^{-4} millimeter of mercury. In spite of this (leak could not be repaired) the experiment was completed.

X-ray diffraction analysis of the tantalum filament showed over 30 faint lines of unknown origin, but lanthanum could not be detected with any degree of certainty among them.

Since it is impossible consistently to prevent vacuum leaks around the electrodes, a series of experiments is in progress to devise a method in which the trouble will be eliminated. The use of induction heating of a ring within the DeBoer apparatus will allow the reduction to proceed without atmospheric-leakage contamination and will permit one to obtain the 10^{-6} millimeter of mercury pressure necessary for the volatilization of lanthanum iodide at 800°C.

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TABLE I
TESTS ON METAL-QUARTZ SEALS

SAMPLE SERIES	PRESSURE (MM. Hg) DYNAMIC	REMARKS
1	0.5×10^{-5}	ELECTRODE FLAT. SEAL CLEAN, FREE OF BUBBLES, AND CRACKS. ELECTRODE NOT BRITTLE. VERY SLOW LEAK (STAT.C).
2	0.6×10^{-5}	ELECTRODE CORRUGATED. RESULTS SAME AS FOR SERIES 1.
3	0.8×10^{-5}	ELECTRODE WITH SPIRAL TWIST. RESULTS SAME AS FOR SERIES 1.
4	.	ELECTRODE FLAT (NOT FEATHERED). BUBBLES PRESENT, POOR BOND, AND ELECTRODE DISCOLORED.
5		ELECTRODE FLAT (NOT FEATHERED, BUT POLISHED). GOOD APPEARANCE. NOT TESTED.

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FIGURE 1

SPECIFICATIONS OF ALL QUARTZWARE

- ① $4\frac{1}{2}$ " BY $\frac{1}{4}$ " I.D. TAPER JOINTS
- ② $\frac{1}{4}$ " O.D. X 0.006" SPIRAL FILAMENT WELDED TO $\frac{3}{32}$ " BY 0.006" MOLYBDENUM LEADINS
- ③ THIN QUARTZ BULB
- ④ IRON PLUNGER
- ⑤ $1'' - 1\frac{1}{16}''$ O.D. QUARTZ BULB $1'' - 1\frac{1}{2}''$ LONG
- ⑥ CONSTRICTION

MODIFIED DE BOER REACTION TUBE

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FIGURE 2

COMBUSTION TRAIN FOR PREPARATION LaI_3

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Problem Title - The Preparation of Lanthanum with a Modified Calutron

Report By - D. B. Wehmeyer

Work Done By - D. B. Wehmeyer

INTRODUCTION

A small, calutron-type mass spectrometer is being used in an attempt to obtain a sample of pure lanthanum metal. If large enough ion currents are obtainable, this method may be used to deposit lanthanum metal directly from lanthanum chloride in a one-step process. This lanthanum deposition will provide a preliminary test of the practicality of using this method for preparing actinium. Four different experimental models of spectrometers have been run with inconclusive results. Mechanical failures have prevented the formation of an ion beam except for a few seconds in one case. A fifth design is in the process of construction, and it is believed that mechanical difficulties can be eliminated in this model.

DETAILED REPORT

The design of the small (6 inches long), calutron-type mass spectrometer has been described previously.¹ The ion source consists of a stream of electrons oscillating in a magnetic field inside a hole in a carbon block. A sample of lanthanum chloride is vaporized and passes through the electron stream in which lanthanum and chloride ions are formed by electron bombardment. The ions are accelerated by a high voltage to remove them from the block and are separated into lanthanum and chlorine beams as they travel in the magnetic field. A collector plate is placed in the path of the lanthanum ions so that they are deposited on it. It is believed that pure lanthanum metal can be deposited in quantity on a metal target in this manner and that the efficiency of the process will be great enough to be practical for use in preparing actinium.

The first model was built according to the design mentioned above. The Hall-effect magnet² was used for the magnetic field (4-inch diameter gap). A 250-milliamperere, 2,500-volt power supply was available, and it was used for the high-voltage supply for ion acceleration. A small, 200-volt, 1 ampere supply was not available, so that power was run in from a motor-generator set for electron acceleration from the filament into the carbon block. Small filament transformers with Variac control were used for filament and heater power. Since anhydrous lanthanum chloride is very hygroscopic, a new sample must be used for every run. Sample loading must be done quickly, and a long outgassing period is necessary.

A run was started; but after several days of outgassing, one of the filaments shorted to the carbon block; and the run was stopped.

A second run was started with a new charge and new filaments. After outgassing it was found that the filaments were not hot enough. Larger filament and heater power supplies were built. It was found that 50 per cent to 100 per cent overloading of filament transformers did not burn them out. With more power the lanthanum chloride was vaporized, and the electrons now emitted by the filaments permitted the striking of an ionizing arc of more than 150 milliamperes. Within less than 5 seconds the filaments and heater burned out, and since there was not time to turn on the high voltage, it was not possible to observe the ion current. However, the ionizing arc appeared very dense, so large ion currents should be obtainable.

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A new model was constructed with heavier filaments and other electrical connections. The new filaments were 0.015-inch diameter tungsten wire, cylindrically wound on a 6-32 screw. The filaments previously used were 0.008-inch diameter tungsten wire wound spirally in a cone. Heavier (3/16-inch diameter) tungsten leads were used in the metal-glass seal. Two runs were made with this design, but both were terminated because of loose electrical connections between the filaments and filament supports. These mechanical difficulties have led to a more rugged design for the filament and heater supports and electrical connections. Construction is now in progress.

Since a heavy ionizing arc was obtained with the small filaments for a short time, it should be possible to obtain a similar arc for a longer time with the larger filaments. In this case it will be possible to make measurements of the ion current and to calculate the plating efficiency of the lanthanum metal. Still larger filaments may be needed, but a run will first be made with the 0.015-inch diameter tungsten.

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Problem Title - Lanthanum Electroplating From Fused Salts

Report By - B. Blanke

Work Done By - B. Blanke, R. Cote, T. Aponyi, and R. Phillips

INTRODUCTION

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This report concerns electroplating methods of depositing metallic lanthanum from fused-salt mixtures.

DETAILED REPORT

The first method considered was the plating of lanthanum from fused salts. The first type of plating cell (Figure 1) consisted of a quartz crucible of 8-milliliter capacity which contained a closed thermocouple well and a barrier that divided the cell into two sections connected by an opening at the base. The crucible was heated by a resistance coil wound about it and was thermally insulated with alundum cement in a porcelain shell.

Anhydrous lanthanum chloride was prepared from the commercial salt by heating the salt to 70°C. in a vacuum furnace until the pressure of the system dropped to 25 microns. An atmosphere of dry hydrogen chloride was introduced, and the temperature was raised to 250°C. and held there for 8 hours or overnight. The salt was allowed to cool, and the cell was evacuated to remove any trace of the hydrogen chloride. The salt was stored over potassium hydroxide.

Anhydrous potassium chloride, lithium chloride, and cesium chloride were prepared by fusing the salt, allowing it to cool, and grinding. These, too, were stored over potassium hydroxide.

These salts, including the lanthanum chloride, were titrated for their chloride content as an indication of their purity. Results for all salts showed that they were within 1.5 per cent of the theoretical formula value.

A mixture of the anhydrous salts was used to lower the melting point of lanthanum chloride which is reported as being 906°C. For example, 8 milliliters of a mixture of 40.5 per cent lithium chloride and 59.5 per cent potassium chloride, which melts to a slush at 350°C. and is a watery liquid at 450°C., would dissolve more than a 0.5 gram of lanthanum chloride.

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A series of platings were made with an applied voltage of 1.4 to 6.3 volts. Deposits of violet-colored, metallic-like substance formed on the cathode, and these deposits were covered by an adherent film of salt upon removal from the plating bath. Attempts to remove this salt by washing with water and alcohol failed as the plated metal reacted with the solvents. Heating the plated foil in a vacuum at 350°C. caused a metal which, proved to be lithium, to distill. X-ray diffraction studies of foils did not show the presence of lanthanum metal.

At this point the method seemed practical enough to construct a plating apparatus that would permit the deposition of a thin film of lanthanum under conditions somewhat similar to the preparation of polonium films. A smooth surface was plated satisfactorily in this equipment. However, the identity of the material which was plated from the fused salts, and methods of removal of the excess salt solution from the plate were not successfully established.

It became apparent that inconsistent amounts of lanthanum chloride were dissolving in the fused-salt mixtures. A series of solubility measurements were started to determine the condition and amounts of solution.

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not consistent for separate runs although they agree well within each run (Table I). Different batches of anhydrous lanthanum chloride were used in different runs which may account for the erratic results. The temperature setting differed for some runs, but a check at the same temperature gave different values.

To determine the characteristics of the lanthanum prepared by plating, an attempt was made to plate from the pure fused salt. The hydrated lanthanum chloride did not melt at 906°C , (the accepted melting point) or even at 1100°C . It was assumed that it had formed the oxychloride. The anhydrous salt prepared in this laboratory melted at 835°C , well below the accepted value, which indicated the presence of some impurities. With this salt, and nickel wire or tantalum foil as cathodes, plating was attempted at 2.4 volts and 0.25 ampere at 900°C . The plate, on examination, consisted mainly of a mixture of the metal and the lanthanum chloride. X-ray diffraction did not detect the lanthanum metal. Plating could not be continued for any length of time because of the formation of a white sublimate which was not lanthanum chloride. It was thought that this sublimate was formed from contact with moist air and was the oxychloride. To eliminate formation of the oxychloride, the system was enclosed and evacuated (Figure 3). Sublimation of the lanthanum chloride began at three microns pressure at 800°C , so 0.75-millimeter pressure of dry nitrogen was admitted and the temperature raised to 935°C . A liquid nitrogen trap was used to remove the chlorine formed. Plating was accomplished at 2.6 volts with a current of 50 milliamperes for 60 minutes. The plate was nonadherent and formed a dark area about the cathode. On examination, the plate seemed to be a grayish-black metallic substance which under X-ray diffraction examination proved to be mainly lanthanum chloride plus an unidentified substance.

At this point, the fused-salt plating investigations were discontinued, as they were not very promising, as difficulty was experienced in removing the salts adhering to the plate, and as other methods appeared to offer an easier approach.

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TABLE I

SOLUBILITY OF LiAlCl_4 IN FUSED SALT MIXTURES

RUN No	SALT	PER CENT	SALT	PER CENT	SALT	PER CENT	BEGAN MELTING (°C.)	CLEAR SOL ⁿ . (°C.)	FILTERED (°C.)	MG. LA/G. SALT MIXTURE
1	LiCl	25	KCl	75			340	NEVER	550	22
2	LiCl	33	KCl	67			350	NEVER	525	20.4
3	LiCl	40 5	KCl	59 5			330-40	470	480	18.9
4A	LiCl	67	KCl	33			350	410	410	13.0
4B	LiCl	67	KCl	33			300	375	510	40.2
4C	LiCl	67	KCl	33				380	510	31.0
5	LiCl	75	KCl	25			365	450	450	3.71
6A	LiCl	45	CsCl	55			320-330		380	1.75
6B	LiCl	45	CsCl	55			330		350	4.1
7	LiCl	50	CsCl	50						19.97
8A	LiCl	59 3	CsCl	40 7			320	380	425	13.8
8B	LiCl	59 3	CsCl	40 7			340	360	440	25.8
9	LiCl	57	CsCl	25.2	KCl	17.8				3.21
10	LiCl	15	CsCl	25	KCl	60	535			VERY HIGH
11	LiCl	41 7	RbCl	58 3			320		350	4.40
12	LiCl	57	RbCl	25 2	KCl	17 8	330-340		370	4.82

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PLATING CRUCIBLE

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SCALE: FULL

SALTS HANDLING APPARATUS.

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FIGURE 3

VACUUM PLATING APPARATUS.

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Problem Title - Reduction of Lanthanum Chloride with Sodium

Report By - B. Blanke

Work Done By - B. Blanke

INTRODUCTION

Argonne Laboratory reported a method of preparing several of the transuranium elements in metallic-like form by reduction of the halide with calcium vapor in a small vacuum furnace at 1,250°C. in a beryllia crucible. Our purposes would not permit a temperature exceeding 1,000°C. Calcium has too low a vapor pressure at this temperature to be removed by volatilization. It was thought that sodium might be used as it has a fairly high vapor pressure and its additional activity might compensate for the lower reduction temperature.

DETAILED REPORT

The first reduction attempt was made in a small, sealed quartz capsule. Lanthanum chloride in a nickel boat was in the tube and metallic sodium added. The tube was evacuated to 2×10^{-5} millimeter pressure and sealed. The sealed tube was then placed in a small resistance furnace, and the temperature was raised slowly. At 200°C. the sodium covered the quartz surface uniformly, and further internal observation was impossible. The temperature was held at 945°C. for 30 minutes. Sodium vapor pressure at this temperature is 1.8 atmospheres. On cooling, the quartz was cracked and broken because of the formation of silicon or reduced silicon oxides from the quartz. A small button of metallic substance and a large amount of brownish fused salt remained in the boat. X-ray diffraction analysis failed to identify this material.

It was thought that a lower temperature might decrease the count of silica reduced. Lanthanum chloride was placed in an alundum crucible, and the crucible was suspended in a tantalum heating coil (Figure 1). Metallic sodium was introduced, and the equipment evacuated and sealed. The sealed vessel was brought to 400°C. in a resistance furnace to vaporize the sodium, and current was passed through the tantalum heating coil to raise the temperature of the crucible to reaction temperature (950°C.). No reaction was apparent on several runs.

It was thought that a reaction could be obtained if molten sodium was mixed with anhydrous lanthanum chloride. A gram of sodium was placed in a 20-milliliter Erlenmeyer flask with 10 milliliters of xylene (b.p. 137°C.), 0.2 gram of lanthanum chloride was added, and the xylene was refluxed for 20 hours. Then, the sodium pellets were picked manually from the slurry and dissolved in alcohol. Tests were made on the alcohol for lanthanum ion. These tests were all negative. Since the xylene may have wet the lanthanum chloride and prevented sodium contact, the experiment was repeated dry in a helium atmosphere. The reaction vessel was heated in a resistance furnace at 225°C. for 20 hours. Results were inconclusive and the experiments may be repeated.

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FIGURE 1

SODIUM REDUCTION BOMB

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Problem Title - Lanthanum Preparation by Electrolytic Amalgamation

Report By - J. F. Haskins

Work Done By - J. F. Haskins

INTRODUCTION

This discussion covers the preparation of metallic lanthanum by electrolytic mercury amalgamation and subsequent separation by distillation of the mercury. Attempts were made to prepare and handle the metallic lanthanum in the hope that such procedure might be applied to actinium.

It is possible to prepare rare-earth amalgams from aqueous solutions¹ with a mercury cathode; but this procedure is not recommended as the highly reactive amalgams are rapidly decomposed by water, forming hydroxides, and thus the yields are small. Amalgams can, however, be prepared readily by electrolyzing saturated alcoholic solutions of the anhydrous chlorides with a mercury cathode.^{2,3} The latter method is the one which was employed in obtaining the lanthanum amalgams.

Rare-earth metal amalgams may be concentrated with respect to their rare-earth metal content by removal of mercury through distillation under reduced pressure. As mercury distills (235°C.), the liquid or pasty amalgam changes gradually to a greyish-black, powdery mass containing about 15 per cent rare-earth metal by weight. The concentrated amalgam is very pyrophoric, i.e. on contact with air or moisture it takes fire or glows. By further heating to temperatures about 1,000°C in a vacuum furnace, most of the remainder of the mercury may be removed, yielding the rare-earth metal.

DETAILED REPORT

The procedure followed is given in Booth's Inorganic Synthesis, Vol. 1, p. 15. In all cells, a stirrer was used to agitate the surface of the mercury to prevent formation of a solid amalgam and depletion of ions at the cathode.

The first cell employed was an H type (Figure 1) with a platinum anode and mercury cathode in separate chambers but interconnected with a smaller diameter tube. This cell was unsuccessful because of the high internal resistance which caused a very low current density (less than one milliamperere per square centimeter).

A second cell was constructed from a 250-milliliter Erlenmeyer flask with a tungsten lead sealed in to make contact with the mercury (Figure 1). This larger flask was used to increase the surface area of the mercury, which allowed higher current densities to be used. A pure carbon rod served as an anode since the platinum used previously corroded badly and was also a contaminant in the lanthanum amalgam.

The first electrolysis was unsuccessful. The current density was low, about 2 milliamperes per square centimeter, and basic salts were precipitated. The power supply was approximately 80 volts direct current at 200 milliamperes.

A second run was made with a 125-volt direct-current source. This supplied a current of 1.5 to 1.75 amperes. It was necessary to cool the exterior of the cell with a large beaker of ice as the heat evolved was sufficient to boil the alcohol. Electrolysis was continued for 15 hours at a current density of 40 milliamperes per square centimeter.

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Then the amalgam was placed in a quartz boat in a vacuum apparatus. At a pressure of about 10 microns of mercury, the boat was heated at 235°C. in a muffle-type furnace until the mercury had been distilled. The temperature was slowly raised to 850°C. and held for one-half hour, then cooled. A yield of 1.5 grams contained several per cent of mercury. Therefore, about one per cent amalgam by weight was produced by electrolysis.

A third cell was constructed with a water jacket for cooling purposes. Electrolysis, with 82 grams of mercury and a carbon anode, was carried out for 30 hours at a current density of 30 to 50 milliamperes per square centimeter (Figure 2). The mercury was distilled as before. However, the temperature was raised to only 750°C. as the residue solidified. Upon removal the quartz container was found to have been attacked. The yield of lanthanum was about 0.5 gram, again representing a one per cent amalgam.

For further experimentation, a fourth cell was constructed from a 125-milliliter Erlenmeyer flask with a beaker sealed to it for a cooling jacket (Figure 2). This cell and the previous one did not cool the plating solution sufficiently. In this plating run, 122 grams of mercury were used at a current density of 70 to 80 milliamperes per square centimeter at 125 volts direct current. After the electrolysis had proceeded for 6 hours, the current density was increased to 100 milliamperes per square centimeter by decreasing the anode-cathode distance. At the end of 24 hours a very milky electrolyte was observed, and it was presumed that basic salts had begun to form. The solution was withdrawn and fresh electrolyte added. The same milky appearance was observed after an additional 6 hours. Since a new cell with increased cooling facilities (Figure 2) had been constructed, the amalgam was transferred for continued electrolysis.

The cell was operated continuously for a period of 65 hours. Enough electrolyte was evaporated to break the circuit. A very heavy, basic-salt precipitate was observed. The solution was withdrawn and fresh electrolyte added. The electrolysis was carried on for an additional 5 hours. Since, in the previous experiment, the lanthanum had attacked the quartz, an alundum boat coated on the inside with zirconium oxide was used for concentration. However, only a finely dispersed powder was observed after distillation at about 900°C.

The formation of basic salts during electrolysis may cause depletion of the amalgam previously formed.⁴ This phenomenon may have accounted for the very small yield observed in the above mentioned run.

A very successful amalgamation of lanthanum and mercury was made. For this particular run, the cell opening was enclosed with a vented stopper, and the stirrer altered to cause more effective movement of the mercury surface. Within a very short interval of time after the electrolysis was started, the electrolyte turned a very dark yellowish-brown. When this phenomenon occurred the solution was changed. Fresh lanthanum chloride was added periodically. Electrolysis was continued for 48 hours with a resultant viscous liquid amalgam.

The amalgam was heated in an alundum boat coated with zirconium oxide. The mass was successfully heated in the vacuum furnace to 1,000°C. with no deleterious effect on the zirconium oxide, and on the cooling of the mass, the lanthanum metal was left in a cohesive slug. X-ray analysis of the lanthanum showed beta-lanthanum was present with no appreciable impurities such as oxide, residual mercury, or lanthanum-mercury alloy. Considerable surface slag, however, was present. Chemical analysis of the slug showed the presence of mercury. The yield of lanthanum was approximately 6 grams which represented about a four per cent amalgam.

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There are very few materials that will withstand the action of hot or molten lanthanum without reacting or alloying. Most of the pure metals produced in the original works^{1, 2, 3} were handled in crucibles made of the rare-earth oxides with alundum as a binder. Lanthanum either alloys with metals or it wets their surface so thoroughly that it is extremely difficult to remove. The latter is especially true with tantalum and molybdenum. At its melting point, lanthanum reacts with alundum, with calcium oxide, and to a lesser degree with magnesium oxide.

Various refractory materials were received and tested to study their ability to withstand the action of molten lanthanum. The refractories were magnesium oxide, calcium oxide, titanium dioxide, beryllium oxide, zirconium oxide, thorium oxide, and cerium sulfide. All of these materials were fabricated in the form of crucibles except the cerium sulfide, which consisted of portions of a broken cerium sulfide crucible. The refractories were tested with portions of a lanthanum amalgam. The metallic lanthanum adhered to all the ceramic materials except the zirconium oxide and beryllium oxide crucibles. However, the beryllium-oxide crucible appeared to have undergone a change in crystal structure. The various slugs of metal which were obtained had different appearances. The most metallic samples came from the titanium dioxide and zirconium oxide crucibles.

Results obtained by using the zirconium oxide crucible were consistent with those observed previously when an alundum boat was coated with zirconium oxide. A very shiny button of lanthanum was produced.

The beryllium oxide crucible bottom appeared to have undergone a change in crystal structure. The metal obtained was very spongy in nature with considerable slag. A solid button of metal was not produced.

The titanium dioxide crucible was etched, and the color changed from white to dark grey. A solid, cohesive button of metal was produced with very little surface slag.

Magnesium oxide did not show any conclusive results. Two separate runs were made; and, in each case, the sample was expelled from the crucible. This phenomenon occurred below 600°C. and some time after the amalgam became solid. Final stages of reduction to a solid mass of metal took place on a quartz-tube wall.

The hot metallic lanthanum wet the surface and soaked the walls of the calcium oxide and thorium oxide crucibles. It appeared as though a reaction had taken place. In the calcium oxide run, bluish-gold-colored rings appeared on the walls of the quartz tube in the region where the crucible rested. The lanthanum so thoroughly wet the surface of the calcium oxide that it could not be removed. The metal obtained from the thorium oxide was not solid, but rather a spongy mass with considerable slag. The metal was adsorbed by the thorium oxide, and after a period of time in air the crucible shattered.

For further experimentation, a new cell was constructed so that the amalgam could be transferred directly to the reduction tube in the furnace without direct contact with the air (Figure 3). The top of the cell was constructed from a 50/50 standard taper joint and contained four outlets: one for the stirrer, one for the anode, one for a vent, and one for the inlet tube with its stopcock. The inlet tube extended into the cell and could also be used for removal of the electrolyte by aspiration. The main body of the cell contained a water jacket which completely surrounded the chamber holding the electrolyte and

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the mercury cathode. A short length of glass tubing extended from the bottom of the cell and was connected to a three-way stopcock (4-millimeter bore). A tungsten wire was sealed in this glass tubing for contact with the mercury. One outlet of the three-way stopcock was interconnected to a second stopcock (4-millimeter bore) which led into a quartz delivery tube. The quartz delivery tube was an integral part of the quartz reduction tube, and the lanthanum amalgam flowed into a zirconium-oxide crucible located under the outlet of the delivery tube. The three-way stopcock mentioned previously served two purposes, either for delivery of the amalgam to the reduction tube or for complete removal of the contents of the cell. The section of tubing between the three-way stopcock and the stopcock located below served to apportion the amount of amalgam going into the reduction tube. With the three-way stopcock closed and the stopcock below opened, the section of tubing between them was evacuated since it constitutes a portion of the vacuum system. After the evacuation took place, the lower stopcock was closed, and the appropriate outlet of the three-way stopcock was opened to the evacuated section. Mercury was drawn into and completely filled this section. The three-way stopcock was then closed, and the stopcock below opened. The amalgam then flowed through the delivery tube into the zirconium oxide crucible. Once the system was in operation and mercury was being distilled, the amalgam could be continuously added until depleted. After the mercury had been distilled, the crucible was heated to 1,000°C. to complete the distillation. The lanthanum produced by this system was very shiny and free from the surface slag encountered previously.

An investigation of carrier materials to be used in conjunction with the amalgamation of small quantities of lanthanum was undertaken. The quantities of lanthanum used, expressed in terms of the anhydrous chloride, were in the order of 1/4 gram per 100 milliliters of ethyl alcohol.

A suitable carrier material must be soluble in ethyl alcohol, and the metal must boil lower than lanthanum. The alkali metals and cadmium meet the temperature restriction, but the chloride of sodium and potassium are insoluble in ethyl alcohol. The chlorides of the remaining elements, lithium, cesium, and cadmium are soluble in ethyl alcohol to about the same degree as lanthanum chloride.

Carrier experiments with lithium chloride have been unsuccessful. A heterogeneous phase occurred when lithium and lanthanum chlorides were electrolyzed together. The heterogeneous phase appears to be an intermetallic compound of lanthanum, lithium, and mercury with enough surface tension to prevent formation of a uniform liquid mass.

An attempt was made to reduce lanthanum chloride by a displacement reaction between a lithium amalgam and an alcoholic lanthanum-chloride solution. The same heterogeneous phase occurred as noted previously.

Amalgamation of a small quantity of lanthanum without the introduction of another metallic ion was tried. An acidified alcohol solution of lanthanum chloride was used as an electrolyte. The alcohol was acidified by the introduction of dry hydrochloric acid from a Kipp generator. The cell was operated until the current dropped to almost zero (approximately 48 hours). A negligible amount of lanthanum was obtained on reduction.

A series of experiments were made with higher alcohols and a polysaccharol glycerine, as solvents for the lithium chloride and lanthanum chloride mixture. Sodium chloride, which is somewhat soluble in glycerine, was also tried; but, as before, the heterogeneous phase appeared. Results in general were unsuccessful.

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A new experiment was made with lithium chloride again as the carrier, but with the addition of methylamine hydrochloride as a surface-active agent. It was hoped that the addition of this surface-active agent would reduce the surface tension of the heterogeneous phase and allow a homogeneous phase to form. Results at first were promising, but upon distillation of the amalgam, no residue was present. The experiment was repeated only to have the heterogeneous phase recur.

In an effort to determine conclusively if the amalgamation process would work on a microscale, another run was made. The primary object was to determine whether lanthanum plated out. There are three possibilities for the location in which the lanthanum may exist: in the mercury phase, in the heterogeneous phase, or still as the primary constituent in the electrolyte. The mercury phase was treated in two portions. One portion was heated to 1,000°C to determine whether any metallic lanthanum was produced; none was present. The second portion was heated to 250°C. to determine whether any pyrophoric alloy was present; and once again, nothing was obtained. It was noted here, as in previous distillations of the mercury amalgams, that the distilled mercury was never clean, but always had a superficial scum on the surface. It is possible that this scum may be a volatile compound of lanthanum and mercury, which partially accounts for the nonappearance of any lanthanum metal. It was not possible to obtain representative samples of the scum for analysis. The heterogeneous phase was heated to 1,000°C. with no metallic residue present in the crucible. The material which distilled over from the crucible was analyzed by X-ray diffraction techniques and showed primarily mercurous chloride. If any lanthanum was present, it was in quantities of two per cent or less; and the mercurous chloride lines completely blocked out any lanthanum or lanthanum oxide lines that may have been present.

The final results definitely point out that it is impossible to produce lanthanum by amalgamation on the microscale. This process could, apparently, be adapted to large-scale production of lanthanum on a reasonably economic basis.

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FIGURE 1

LANTHANUM PREPARATION BY ELECTROLYTIC AMALGAMATION.

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MERCURY CATHODE ELECTROPLATING EQUIPMENT.

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MERCURY CATHODE ELECTROPLATING EQUIPMENT.

Problem Title - Lanthanum Distillation

Report By - B. Blanke

Work Done By - B. Blanke, R. Cote

INTRODUCTION

A method was desired for depositing small quantities of lanthanum in the form of smooth-surface films. Distillation was investigated although the boiling point of the metal is rather high (1800°C.). The construction of a suitable apparatus which uses electron bombardment for heating made it advisable to investigate the volatilization of several metals with higher boiling points.

DETAILED REPORT

Several samples of lanthanum were heated to temperatures of 1,050°C. to 1,200°C. at pressures of 0.4 to 2.5 microns of mercury for periods of from 30 seconds to 30 minutes. After heating commercial lanthanum for several minutes at 30-second intervals, a dark, gold-colored film was deposited; most of the lanthanum was not moved.

In an effort to distill macroscale amounts of lanthanum, a sample was placed in a tantalum microgun in a quartz holder and subjected to prolonged heating. Only a faint deposit was obtained, although the sample had fused. An apparatus for distillation with induction heating was constructed, but the receiver was over heated through conduction and radiation during the long heating of the microgun.

The next distillation attempt was made with resistance heating. A microfurnace was constructed (Figure 1) by winding a 25-millimeter tantalum heating coil about Lavite $[Al_2(SiO_2)_3]$ core 1/4 inch in diameter. This core was hollowed out to hold a tantalum microgun. The furnace was suspended from a 60-millimeter tungsten support rod in a Pyrex system. The target consisted of a nickel disk held by a brass collar which screwed to a brass fitting soldered to a Housekeeper seal. The seal was used as the bottom of a liquid-nitrogen cold finger and cooled the target by conduction.

At a pressure of 10 microns, the Lavite holder was heated to a temperature of 1,600°C. with a current of 22 amperes at 10 volts. After one minute, the Lavite fused and shorted out the heating coil against the tantalum gun. However, a thin film of lanthanum had been distilled onto the nickel disk.

A physics seminar on ion sources gave the idea of adapting a Shaw-type gun with electron-beam heating for lanthanum distillation. Since fairly high wattage could be applied to a small target, extremely high temperatures could be obtained. An apparatus was constructed (Figure 2) which consisted of a large glass envelope containing a cooled (liquid nitrogen or water) "cold finger" used to hold a collector (disk or foil) and the electron beam elements. These elements consisted of essentially a diode-type tube containing a filament and a plate. These were mounted on three tungsten support rods which were sealed to the base of the tube. The filament was an omega-shaped, 10-mil tantalum wire which was slip-fitted to the support rods. The plate consisted of a 3/16-inch tungsten rod, one centimeter long, which was drilled for 8 millimeters lengthwise to form a microgun. The base was drilled for a short distance and fitted over a tapered, tungsten support rod which was in

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turn supported by a copper set block. The pieces were mounted on a standard-taper ground-glass joint and so constructed that the gun opening faced, and was less than one centimeter from, the face of the collecting apparatus.

The mass-spectrograph power supply was originally used as a power source. However, a specially designed power supply was built which would supply up to 350 milliamperes at 700 volts (Figure 3).

In operation, the tungsten gun was loaded with the metal to be distilled. The apparatus was evacuated to less than a micron pressure, and the filament heated to about 1600°C. After the apparatus was outgassed, the high voltage was applied (500 to 700 volts). Heating of the gun was controlled by varying the temperature of the filament which controlled the electron emission.

Distillations have been made with iron, aluminum, copper, lanthanum, and molybdenum. The gun temperature was greater than 3,300°C, as indicated by the fusion of the tungsten rod.

One major problem with temperatures of this range is material failure. Pyrex "cold fingers," even when water cooled, failed on a few minutes heating. This was corrected by the use of metallic ends attached to the system by means of Housekeeper seals. Later a water-cooled, stainless-steel "cold finger" was constructed. The glass envelope of the system was heated to temperatures over 150°C in less than one minute. This was corrected by water jacketing the envelope.

Another problem was the internal arcing between filament lead wires and the plate lead wire. This was corrected by enclosing the filament leads in glass tubes and by introducing the filament through a different point in the system.

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VACUUM DISTILLATION EQUIPMENT
(ELECTRON BEAM HEATING)

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FIGURE 3

HIGH VOLTAGE POWER SUPPLY.

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