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OF AIRCRAFT REACTORS

UNITED STATES ATOMIC ENERGY COMMISSION

BOILING RUBIDIUM AS A REACTOR
COOLANT. PREPARATION OF RUBIDIUM
METAL, PHYSICAL AND THERMODYNAMIC
PROPERTIES, AND COMPATIBILITY
WITH INCONEL

71013

By
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For The Atomic Energy Commission
H. R. Canale
Chief, Declassification Branch

August 1954

Oak Ridge School of Reactor Technology
Oak Ridge, Tennessee

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CF-55-6-49(Pt. I)

OAK RIDGE SCHOOL OF REACTOR TECHNOLOGY

F. C. VonderLage, Director

"BOILING RUBIDIUM AS A REACTOR COOLANT: PREPARATION OF
RUBIDIUM METAL, PHYSICAL AND THERMODYNAMIC PROPERTIES,
AND COMPATIBILITY WITH INCONEL"

This report contains information generated by a group of ORSORT
students under the leadership of S. Reed Nixon as part of an
assigned summer project. Although other members of the group
contributed in varying degrees to the effort described herein,
the phases reported on were the responsibility of:

Merrill J. Whitman
Don L. Stockton

August 1954

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PREFACE

In September, 1953, a group of men representing various scientific and engineering fields embarked on the twelve months of study which culminated in this report. For nine of these months, formal classroom and student laboratory work occupied their time. At the end of that period, this student group was presented with a problem in reactor design.

This is a summary report of the study, the research, the problems and the solutions which developed during the final ten weeks period of the school term. It must be realized that, in so short a time, a study of this scope can not be guaranteed complete or free of error. This "thesis" is not offered as a polished engineering report but rather as a record of the work done by the group under the leadership of the group leader. It is reproduced for use by those persons competent to assess the uncertainties inherent in the results obtained in terms of the preciseness of the technical data and analytical methods employed in the study. In the opinion of the students and faculty of ORSORT, the problem has served the pedagogical purpose for which it was intended.

As a matter of historical fact and pride we point out that similar investigations by student groups of previous ORSORT classes have led to sufficiently encouraging results to warrant more exhaustive studies; in at least one instance, a reactor first investigated by a student group is soon to become a physical reality. There is also recorded an instance in which calculations contained in a similar report were uncritically abstracted and applied to a study for which they were never intended. It is to avoid the recurrence of the latter experience that we have taken some pains to acquaint the reader with the character of this report.

The faculty wishes to join the authors in an expression of appreciation for the assistance which various members of the Oak Ridge National Laboratory have so generously contributed. In particular, the guidance of the group consultant, E. R. Mann, is gratefully acknowledged.

F. C. VonderLage
for
The Faculty of ORSORT

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INTRODUCTION

0.1.1 Iniation of the Project

This report contains a portion of the information obtained during the course of an investigation to determine the merits of a vapor cycle for aircraft propulsion by use of a nuclear reactor employing a boiling liquid metal as a coolant.

There are certain advantages inherent in a power system utilizing a coolant which undergoes a change of state to transfer the heat energy:

1. Low mass flow of vapor coolant
2. An isothermal system can be approached.

If the change of state is a vaporization or boiling process, there are accompanying disadvantages:

1. The coolant must experience a considerable change in specific volume and the sizes of both equipment and piping become large.
2. Dangers of flow instability and "burnout" of reactor components are present.

Dr. A. P. Fraas, ANP General Design Group, suggested the possibility of using a liquid-vapor cycle with rubidium as the coolant for an aircraft power plant and recommended its study as an ORSORT project.

Rubidium was selected because it is a coolant with a high latent heat of vaporization having an atmospheric boiling point in the temperature range of the current reactor designs for aircraft application. It also has a low melting point which obviates the problem of maintaining a molten coolant. Other physical properties are as might be expected for an alkali metal.

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On June 14, 1954 eight students of the 1953-54 session of ORSORT were assigned this project as a 10-week summer assignment. D. L. Stockton and M. J. Whitman were assigned the portions of the investigation described in this report. Dr. E. R. Mann, ORNL Instrumentation and Control Division, was designated as the advisor.

0.1.2 Scope of the Report

The overall investigation as described in a preliminary report, "Rubidium Vapor Aircraft Reactor" ORNL CF-55-6-49 was devoted primarily to determining the feasibility of using rubidium metal as a heat transfer medium in an aircraft reactor.

The lack of reliable data concerning corrosion, heat transfer, and nuclear properties of rubidium necessitated the expenditure of most of the effort on these subjects. In addition, the unavailability of reasonably pure rubidium metal presented a serious problem.

To overcome these difficulties in order to meet the project objectives, the following programs were initiated:

1. The preparation of rubidium metal.
2. Determination of the physical properties of rubidium.
3. Preparation of thermodynamic diagrams for rubidium.
4. Determination of the compatibility of Inconel and Rubidium at elevated temperatures.
5. A pebble bed boiling experiment.
6. A comparison of sodium and rubidium activation.
7. A power cycle study
8. A reactor study

This report contains the information obtained as the result of efforts to complete the first four programs listed.

It is hoped that the remaining four phases of the investigation will be published in final form in the near future.

0.1.3 Organization of the Report

Since the areas covered in this project are diversified, it is necessary to report the results of each separate section. It is believed that this will result in a suitable presentation of the material. This report therefore is a compilation of several reports. The order in which the subjects are presented does not represent their relative importance, but was selected to give a logical arrangement of the results.

0.1.4 Acknowledgement

Sincere appreciation is extended to the many persons who assisted us in this project. Everyone contacted for assistance was cordial and cooperative. Without the cooperation of these ORNL personnel the investigation and experiments could not have been accomplished. Our thanks are extended to the following:

<u>Division</u>	<u>Personnel</u>	<u>Remarks:</u>
Instrumentation X-10	E. R. Mann	Advisor
ANP Y-12	A. P. Fraas M. Laverne	Chief Consultant Physics
Chem. Tech. X-10	I. R. Higgins J. T. Roberts	Ion Exchange Process
Materials Chem. Y-12	W. R. Grimes C. J. Barton, Sr. R. E. Moore and associates	Supply of Rubidium halides, fusion of RbF dry-box facilities
Stable Isotopes, Y-12	P. S. Baker H. B. Greene Boyd Weaver	Reduction to metal by a special technique
Analytical Chem. Y-12	J. G. White H. P. House Miss Jeanne Rogers	Assays of column eluates, fused salt and metal samples

<u>Division</u>	<u>Personnel</u>	<u>Remarks</u>
Glass Blower Y-12	E. J. Greeley	Fabrication of quartz and pyrex apparatus
Metallurgy X-10	W. D. Manly E. E. Hoffman J. Cathcart R. J. Grey R. M. Steele and associates	Fabrication of loops, purification of rubidium, corrosion tests, metallographic examination, and X-ray analysis
Exp. Eng'g Y-12	H. F. Poppendick S. M. Cohen W. D. Powers	Physical Properties Density Determination Specific Heat Determination

SUMMARY

0.2.1 Conclusions

1. The separation of rubidium from the other alkali metals by ion exchange has been demonstrated. On the basis of experience gained while extracting rubidium metal of high purity from commercial rubidium fluoride, it is concluded that rubidium metal can be produced in quantity at a cost of \$50 per pound as compared to the current price of \$500 per pound.

2. It is concluded on the basis of empirical formulae that more heat can be transferred in a boiling rubidium system than in a comparable boiling water system.

3. It is tentatively concluded that the corrosion of Inconel by circulating, and static, boiling rubidium can be dismissed as insignificant for operating lifetimes of the order likely to be encountered in aircraft nuclear reactors. This conclusion applies through the temperature range in which Inconel warrants consideration as a structural material.

0.2.2 Recommendations

1. It is recommended that research be initiated to determine the nature of the binary and ternary phase diagrams of rubidium and the other alkali metals. This information would prove useful in selecting a reactor coolant composition molten at room temperature in which the desirable physical and nuclear properties would be optimized.

2. A boiling heat transfer system can be operated to transfer heat under essentially isothermal conditions. The constant temperature and liquid-to-vapor transformation should prevent the transport of dissolved container metal from the region of heat input to regions where heat is extracted. It is recommended that many more boiling loops filled with rubidium and with other alkali metals be operated to determine whether boiling systems are inherently less subject to corrosion than circulating liquid heat transfer systems.

1.0 PREPARATION OF RUBIDIUM METAL

1.1 Introduction

It was decided to prepare about 100 grams of high purity rubidium metal for physical property measurements by Dr. H. F. Poppendick's group. In addition, it was desired to have a small amount of metal available for preliminary corrosion tests.

Essentially, the process consisted of removing the major cation contaminants, other alkali metals, from a crude rubidium halide by an ion-exchange process. The cut or fraction of the resin column eluate containing rubidium carbonate was converted to the fluoride by neutralization with aqueous hydrogen fluoride. After concentration and fusion, the anhydrous fluoride was reacted with calcium metal under high vacuum at a temperature of 600° - 800°C. to produce rubidium vapor which was collected in a Pyrex receiver. The rubidium metal was purified by a vacuum distillation (10^{-5} mm Hg) in a Pyrex glass system and the product sealed-off under vacuum.

After completing the preparation of about 100 grams of metal, it was necessary to continue this program for two reasons:

1. The vendor under contract to supply rubidium metal for corrosion tests was unable to meet his schedule so that emphasis was placed on obtaining at least 200 grams of metal at ORNL.
2. A shipment of rubidium fluoride for the ANP fuels program did not meet specifications making it necessary to purify two kilos of crude salt for continuation of current ANP laboratory projects.

We wish to acknowledge the fine spirit of cooperation which was displayed by all the ORNL personnel who contributed to the development of this process. Their valuable assistance, guidance and knowledge were required

to make this process successful.

1.2 Chromatography of Alkali Metals

It was suggested by Dr. E. H. Taylor, as an alternate to the older methods of fractional crystallization of chloroplatinates, oxalates, and tartrates, that chromatography processes be discussed with Dr. Kurt A. Kraus for the separation of rubidium from other alkali metals. Dr. Kraus pointed out that the geometrical similarity of the rubidium ion to the potassium ion would make their separation a difficult one by a cation exchanger. The use of anion exchanger was dismissed because the alkali metals do not have a strong tendency to form complex ions. The extraction of potassium from sea water by a dipicrylamine salt (1) was mentioned as an example of selective removal of alkali metals from a solution.

During a discussion with W. R. Grimes, it was suggested that Boyd Weaver of the Staple Isotopes Division be contacted because Dowex-50 resin (2) had been used to isolate pure fractions of alkali metal compounds suitable for Calutron targets. With the help of Dr. I. R. Higgins a 1-1/2 inch diameter column was set up in Building 4500 for a trial run with a 2.0 liter bed of Dowex-50. When this resin was found to give insufficient separation of rubidium, Dr. Higgins recommended Amberlite IR-105 resin which had been reported by the ORNL Analytical Chemistry Division (3) as giving an excellent separation of alkali metal radioisotopes in tracer amounts.

A "pure" rubidium salt usually contains potassium as the major contaminant. It was found, however, that cesium, at times, also is present in significant amounts. Thus, the original assumption that a process was needed for separating one part of potassium from 100 parts of rubidium

had to be changed to include 10-30 parts of cesium. The first run with Amberlite IR-105 showed that cesium was easily separated for both rubidium and potassium by a fixed-bed ion exchange column. It was then decided to remove the cesium and take the entire cut of rubidium, with the associated potassium, as the product. This was considered satisfactory for both the initial physical measurements and the preliminary corrosion tests.

Subsequent experimental work was performed to prepare analytical standards of rubidium and cesium. High purity salts, containing less than 10-100 p.p.m. of contaminants, were not available from industry either as a stock item or on special order. During the early phase of the rubidium purification work it was necessary to take two cuts near the end of the rubidium elution, containing about 100 p.p.m. of potassium, for the Analytical Division at Y-12 to use as a standard. All of the cesium eluates, called "tail cuts" from Amberlite IR-105 elutions, were held and reworked to prepare about 50 grams of cesium standard. A similar rubidium standard was prepared by reworking the intermediate IR-105 cuts, which contained rubidium with appreciable cesium, and the rework batches of various residues containing rubidium.

It was hoped that time might allow use of a "jerked-bed"(4) continuous ion exchange column in order to obtain a rubidium stream as a product, free of both potassium and cesium. An alternate fixed-bed exchanger of a synthetic zeolite was tried, however, and found to give excellent separation of potassium from rubidium. Thus, a process has been demonstrated by which pure rubidium can be produced for experimental purposes. This was the primary objective of the group in attacking this problem. Future groups should be able to prepare adequate rubidium metal for more physical property measurements, for heat transfer experiments, and for corrosion

loops so that reliable estimate of the power plant system using the rubidium vapor cycle can be made.

1.2.1 Inorganic Exchanger

A fixed-bed column was set up to experiment with the rubidium product containing about one per cent potassium from the Amberlite IR-105 runs. Preliminary experiments with a feed containing equal parts of rubidium and potassium had indicated that a zeolite-type exchanger might have application. The extruded cylindrical pellets of Molecular Sieve 4A from Linde Air Products have a 1/16 inch diameter, a 1/4 inch height and a bulk density of 0.6 gm/cc. These pellets were crushed and screened to obtain a particle size less than 30-mesh. The fines were removed by washing with distilled water and decanting the supernatant liquid after allowing one minute for sedimentation. This cycle of operations was repeated six times before the particles were suitable for charging to the column.

The column consisted of a piece of heavy wall Pyrex tubing four feet high (15/16 inch O.D. with a 1/8 inch wall). A stopcock was attached to the bottom for control of the effluent flow rate. A layer of glass wool served as a support for a one-inch layer of 1/8 inch diameter Pyrex beads. These were covered with two inches of 10-20 mesh Ottawa sand. The 25 inch high bed, about 200-cc nominal bed volume, of the Molecular Sieve 4A exchanger was covered by about nine inches of liquor which overflowed continuously through an 8 mm side arm located six inches down from the top of the column.

The feed pump was connected so that it could be used to backwash the exchanger bed when necessary. This permitted fluidization of the bed so that the colloidal fines could be removed while converting the sodium form of the exchanger to the ammonium form. The elutriant, 0.5 molar (M)

ammonium carbonate, was fed upflow at a rate of 25 cc/min for 12-24 hours until the sodium in the effluent was reduced to 3 ppm.

The conditioned or generated particles were then allowed to settle to form a bed free of channels. The elutriant was fed downflow at 50 cc/min for 2-6 hours to check the flow rate and the removal of sodium. The bed was then washed, downflow, with five bed volumes of distilled water. The water was drained until only 1/4 inch covered the bed and then the alkaline feed solution of rubidium carbonate (about 0.5 M Rb +) was added. The feed liquor was allowed to percolate slowly, about one cc/min. through the exchanger until only 1/4 inch remained above the bed. The column was then washed at a rate of 25 cc/min with two bed volumes of distilled water before the elution was started.

The 0.5 M ammonium carbonate solution is prepared by mixing 15 pounds of reagent $(\text{NH}_4)_2\text{CO}_3$ with 135 liters of distilled water and agitating until all of the salt is dissolved. It was pumped by a "finger" Sigma Motor pump using heavy wall plastic tubing. The elutriant entered the top of the column and overflowed to the make-up storage tank. The discharge rate of the eluate was measured by collection in a graduated cylinder for a period of one minute.

The elution was carried out at 25 cc/min. which is a nominal contact time of eight minutes for a 200 cc bed. The forerun was collected in a 500 cc bottle until a positive test for solids was found by evaporation of a 0.2 cc sample of the eluate on an evaporating dish under a 300 watt lamp. At this point, the eluate was collected for 10 x 100 cc rich cuts and then 2 x 500 cc tail cuts before 2 x 4000 cc of regeneration liquor was collected. The column is now ready for a water wash and another batch of feed. The various cuts were sampled for analysis of the alkali metals (Rb, K, Cs, and Na)

before they were selected for concentration to total solids. A summary of the data for Run 4-A-3 is given in Table 1.1.

The mechanism of the separation by the synthetic zeolite appears to be exclusion of the cesium and rubidium ions from the pores of the exchanger while the potassium ions pass through the interstices because of their smaller diameter. The ammonium ions displace the adsorbed alkali metal ions by the mass action effect during the elution as in the case of an organic resin exchanger.

The MOLECULAR SIEVE allowed the purity of rubidium with respects to potassium to be increased from a ratio of 100/1 to 3500/1 as shown by the results:

<u>RUN</u>	<u>FEED Vol. cc</u>	<u>FEED gm. Rb</u>	<u>FEED Rb/K ratio</u>	<u>PRODUCT Rb/K ratio</u>
4A-1	25	4	100/1	4000/1
4A-2	75	12	100/1	5000/1
4A-3	100	20	100/1	3500/1
4A-4	50	9	1000/1	3500/1
4A-5	50	9	2000/1	3500/1

With an Amberlite IR-105 resin the purity of rubidium with respect to cesium can be made 3000/1 from results in the preparation of a rubidium standard. These results indicate the purity that can be expected of a commercial process using the method covered in this report: first, remove cesium by the Amberlite IR-105 resin column; second, remove potassium by the MOLECULAR SIEVE 4A exchange column.

TABLE 1.1

MOLECULAR SIEVE DATA

SUMMARY OF RUN 4-A-3

<u>Sample</u>		<u>Vol. cc</u>	<u>Rb</u>	<u>Analysis</u> <u>K</u>	<u>mg/ml</u> <u>Cs</u> <u>Na</u>	
Wash Forerun		500	26	5.6	3.0	7.1
		500	7.8	1.1	1.2	7.0
Rich cut	1	100	8,100	4.0	9.4	7.0
	2	100	19,660	3.1	4.0	3.8
	3	100	21,000	7.0	21	4.7
	4	100	23,000	6.4	20	3.0
	5	100	22,000	6.6	16	2.8
	6	100	18,000	5.0	14	2.8
	7	100	14,000	4.5	13	3.6
	8	100	10,000	3.6	8.2	3.8
	9	100	6,800	3.6	6.8	3.2
	10	100	5,100	3.6	4.4	3.2
Tail Cut	1	500	1,780	5.0	2.6	3.2
	2	500	510	7.3	1.4	3.2
Regeneration 1		2000	- Not Sampled -			
2		4000	4.8	13.8	1	3.4

Feeds: Cut 21-F containing 20 gm Rb in 75 cc solution

Elutriant: 0.5 Molar $(\text{NH}_4)_2\text{CO}_3$

Elution: 25 cc/min for a nominal contact time of 8 minutes in the 200 cc bed (25" height).

1.2.2. Synthetic Resin Cation Exchanger

The equation which represents the reversible equilibrium between the rubidium and ammonium ions in aqueous solution with the cation exchanger form of a synthetic resin is:

The equilibrium is shifted in either direction by adjusting the concentration of the respective ion species. Thus, the water-washed ammonium form of the resin is contacted with 0.5M rubidium halide and Rb^+ displaces NH_4^+ from the resin interstices. This process is reversed when the rubidium ion is stripped off the resin by feeding 0.5 M ammonium carbonate solution.

There are similar equilibrium reactions which can be written for the other alkali metal ions present. The equilibrium constants can be evaluated in each case. The differences in the equilibrium constants account for the ability of the resin to separate the various species of the alkali metal cations. The development of the individual bands on the resin shows sodium to be eluted first, then potassium and rubidium which almost overlap each other, followed by cesium which is the most strongly adsorbed member of this family.

The selection of a suitable resin for a given separation is based upon a characteristic called the Separation Factor. This is usually determined experimentally by the use of radioactive tracers. The assay for each component is plotted against the volume of eluate to obtain a probability like curve for each ion species. The Separation Factor is defined as the ratio of the eluate volume corresponding to the maximum concentration for one component to that for a second component. A Separation Factor of 1.00

indicates no separation. It was estimated that the separation factor for the rubidium/potassium system would be in the range 1.0-1.1, which represents a difficult separation. An experiment with Dowex-50 resin using suitable tracers indicated that the separation factors were about 1.1 for rubidium/potassium and 2.0 for cesium/rubidium. When macro amounts were used, however, the Dowex-50 resin was found to be unsuitable with actual values of 1.1 for rubidium/potassium and 1.1 for cesium/rubidium. These data are plotted in Figure 1.1 (Y-12 Photo 22423).

Amberlite IR-105, which has been successfully used for separation of alkali metal tracers (3) was then substituted for the Dowex-50 resin. The results of a typical run are given in Table 1.2 with a plot of the data in Figure 1.2 (22424). The difficulty of separating potassium is shown by the low ratio of $Rb/K = 1.1$. The ease of removing cesium is shown by the separation factor of 2.9 for Cs/Rb . Thus, a convenient method for removing cesium can be seen in Figure 1.2 that there is only a few ppm of potassium near the end of the rubidium curve. The area under the far side of the curve for this fraction represents the small amount of pure rubidium which might be recovered. A cut was taken in this region to serve as a standard for the analytical laboratory.

The irony of the satisfactory performance of the Amberlite IR-105 resin is that it has been discontinued from the line by Rohm and Haas. Verbal discussion with R. Kunin of Rohm and Haas disclosed that IR-105 is quite sensitive to attack by strong alkali. It was noticed during the resin column work that a yellow color was always present in the eluates. The organic material darkens upon charring and it is difficult to remove by carbon treatment. Thus, IR-105 resin would not be suitable over a prolonged period of time for a commercial process because of attack by the hydroxyl ion.

resulting from hydrolysis of the alkali metal carbonate:

More evidence of attack is that there is a small amount of rubidium and cesium irreversibly adsorbed by the resin because material balances are about 90-95 per cent.

As a result, Dr. I. R. Higgins has conducted a few experiments in an effort to find a satisfactory substitute for Amberlite IR-105. Recent experiments have shown Duolite C-3 to have application but with a poor H.T.U. Duolite C-10 is better than C-3 but inferior to Amberlite IR-105. Thus, considerable screening and development work must be done before a commercial process can be established for the manufacture of rubidium using this technique. Emphasis will be placed upon the continuous ion exchange column as other resins are tried out in the laboratory. Eventually, the process might be used to prepare each of the alkali metals as a pure product stream containing less than 5-10 ppm of adjacent family members.

It is felt that the ammonium carbonate elutriant has several advantages over other ammonium salts of weak acids:

1. It is easily decomposed by boiling in the laboratory so that a water solution results. For example, concentrated acetic acid results when ammonium acetate is used.
 2. It can be recovered by the use of carbon steel equipment, since it is non-corrosive, so that it is economical.
 3. It produces a rubidium salt which can be converted easily to the desired halide by neutralization with the respective hydrogen halide.
- The evolution of carbon dioxide serves as a good indicator for the end point of this neutralization.

RESIN :

12 % CROSS LINKAGE ; STRIP : 1.0M $(\text{NH}_4)_2\text{CO}_3$; FEED = 120gm RbCl

Fig. 1.1

TABLE 1.2

ION EXCHANGE SEPARATION - Run 4

2.0 liter resin bed of Amberlite IR-105 (50-100 mesh)

Elution at 20 cc/min with 0.5 M $(\text{NH}_4)_2\text{CO}_3$ Analysis, micrograms per ml

SAMPLE	ELUATE VOLUME, cc	Rb	K	CS	NA
J-23-Feed	600	116,000	830	19000	-
J-23-1	0	<1	<1	4	-
-2	300	<1	<1	2	-
-3	1150	<1	<1	1	-
-4	2025	<1	<1	1	-
-5	2900	120	12	<1	-
-6	3420	1220	57	1	-
-10	4020	4400	110	4	6
-15	4620	10600	154	7	-
-20	5240	16000	162	9	-
-25	5840	17200	150	10	-
-30	6480	20000	84	12	-
-35	7010	16600	29	10	5
-40	7575	11600	8	8	-
-45	8145	7300	3	9	-
-50	8625	4100	2	8	-
-55	9210	2100	1	11	-
-60	9785	980	<1	21	-
-65	10375	370	<1	31	3
-70	10965	112	<1	52	-
-75	11540	13	<1	165	-
-76	11690	5	<1	200	-
-77	12590	<1	<1	300	-
-78	13440	<1	<1	450	-
-79	14290	<1	<1	560	-
-80	15200	<1	<1	560	4
-81	17000	<1	<1	1490	-
-82	17900	<1	<1	2300	-
-83	18800	<1	<1	1450	-
-84	19700	<1	<1	720	-
-85	20600	<1	<1	560	-
-86	21500	<1	<1	240	-
-87	22400	<1	<1	140	-
-88	23300	<1	<1	33	-
-89	24200	2	<1	14	-
-90	25100	<1	<1	9	-
-91	26000	<1	<1	2	-
-92	27000	<1	<1	1	5
-93	27800	<1	<1	3	-

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RESIN :

STRIP: 0.5M $(\text{NH}_4)_2 \text{CO}_3$
 ASSAY, %

	RbX	KX	csX
FEED	86.5	0.8	12.7
PRODUCT	99.0	0.91	0.09

SEPARATION FACTORS :

$$\frac{Rb}{K} = 1.2 \quad \frac{Cs}{Rb} = 2.9$$

ELEMENT	CONC. FACTOR
K	50
Rb	1000
Cs	100

Fig. 1.2

It is convenient to inoculate the crude rubidium halide feed solution with about five drops of a stock solution of cesium 137 tracer. The progress of the cesium band down the resin bed can then be followed by means of a standard Health Physics survey meter. By comparing the position of the cesium band on the bed with flame tests of the column effluent, the beginning and end of the cesium tail cut can be spotted. Since 10-12 bed volumes of eluate are required before the cesium is stripped off, the tracer allows operation to proceed without constant attention. A stock solution of cesium 137 tracer is prepared by obtaining 5 millicuries (2.4 units) from the X-10 Radioisotopes Division. This consists of about 2 drops of solution in a 25 cc glass bottle which is then diluted to about 20 cc. The diluted tracer solution must be stored inside an adequate shield of lead bricks. Rubber gloves must be worn while using a rubber bulb to pipette out about 0.5 cc for adding five drops to the feed solution. An assay sample of the rubidium feed solution should be taken before the cesium 137 tracer is added. The usual safety precautions are also observed in handling the effluent and concentrates from the resin column because of the hazard from the cesium-137 tracer.

Complete separation of cesium from both the rubidium and potassium is possible only when the resin column loading of cesium ion is less than that which results in "break-through." From the data it appears that a nominal loading of about 10 gm cesium per liter of resin bed volume is the maximum permissible.

Some valuable theory and methods for analyzing the ion exchange column data are given in a booklet from the Dow Chemical Company titled, "Tables for Predicting the Performance of Fixed Bed Ion Exchange and Similar Mass Transfer Processes." The authors are Ascher Opler of Dow Chemical Company

and Nevin K. Hiester of Stanford Research Institute.

1.2.3. 1-1/2 inch Diameter Resin Column

The first six runs were made in Building 4500 with a glass column of 1-1/2 inch Pyrex pipe, eight feet long. The two liters of resin formed a bed with a height of about six feet. The column was feed by a 0-200 cc/min variable speed Sigma motor "finger" pump driven by a 1/6 HP motor. At the pump the feed line was 1/4 inch Tugon tubing (heavy wall) with 1/4 inch Saran tubing (thin wall) running to the top of the column. The feed line entered the top of the Pyrex pipe through a rubber stopper which was held in position by a triangular Pyrex pipe flange. The resin bed was supported by 1/4 inch cylinders of Polyethylene plastic packed to a height of two inches at the bottom of the column. A 100-mesh Vinyon plastic screen was over the 1/4 inch outlet line underneath the support of the resin to retain any fines. The effluent stream from the column had a 12-inch section of rubber tubing which could be clamped off when not in operation. The resin bed was kept flooded with an aqueous medium at all times. The nominal load was 120 grams of crude rubidium halide containing 10 per cent cesium for a resin bed volume of 2.0 liters.

1.2.4. 3-inch Diameter Resin Column

When the processing of larger amounts of crude rubidium halide became necessary, it was decided to set up a larger column in Building 9733-2 of the Y-12 area. Essentially, there was no basic change in the arrangement of the column. A cork float was installed at the top of the column through which an off-on liquid level controller was operated. This device obviated constant attention to the balancing of the pump feed rate and the withdrawal rate through a partially opened plug-cock valve at the bottom.

The pumping rate could be set at a constant value, but the swelling and contraction of the resin bed within the column changed the flow rate of eluate markedly. The liquid level controller avoided flooding as well as drainage of the liquid inside the column during an absence of a few hours. It allowed the stripping of cesium to be done at night with only an occasional check to change the eluate collection bottle. A 30 second timer was included with the controller which was connected to the feed pump. The timer eliminated a series of starts and stops which overheated the motor during the first week of operation. A 50-gal stainless steel drum with a 0.5 horsepower Lightnin' mixer was used to prepare and to hold about 180 liters of 0.5 M $(\text{NH}_4)_2\text{CO}_3$ as elutriant. A sketch of this apparatus is shown in Figure 1.3. It should be pointed out that adequate head room is needed to insert a 1/4 inch diameter tube the full length of the eight-foot column when it is necessary to degas the resin bed by agitation for resuspension of the resin particles.

1.2.5. Resin Column Operating Procedure

1. The crude rubidium halide is dissolved in water to give a 0.25-0.50 molar solution. It is neutralized to a pH 8.0 ± 0.5 with concentrated ammonia water using alkacid paper as an indicator. The volume is measured in a graduate and then a 5 ml sample is taken for analysis of all alkali metals except lithium.

2. The slightly alkaline feed solution is inoculated with five drops of cesium-137 tracer solution as described previously. The resin should be washed with water to remove the fines before charging to the column and also generated batch-wise on the ammonium cycle by contacting with 3.0 M ammonium carbonate. There is considerable sodium ion present in the resin which should be displaced completely before operation is begun. The resin

Fig. 1.3

3-INCH DIAMETER RESIN COLUMN

swells upon contact with water and shrinks when feed or elutuant is added. The bed becomes packed after about six runs and requires fluidization and resettling to avoid channeling during operation. This is best done by back washing with water.

3. The feed is then pumped to the top of the resin bed which has been water washed after again converting the resin to the ammonium form. A feed rate which allows a nominal retention time in the column of 20-30 minutes is adequate. A small water rinse is given the feed vessel and then a water wash of 50 per cent bed volume is applied. The position of the cesium band down from the top of the bed is then checked by a survey meter.

4. The elutriant of 0.5 M ammonium carbonate, prepared by diluting five pounds of the salt to each 45 liters of solution, is then fed to the column at a rate to give a nominal retention time of 60-120 minutes. Thus, the flow rate for a 2.0 liter resin bed was 15-30 cc/min.

5. An accurate log should be kept with all the pertinent data as shown by Table 1.3. Regular readings of feed volume, eluate volume, flame test, distance of cesium tracer from top of bed, and the samples taken must be tabulated on a batch sheet.

6. Stream samples are taken in 5-10 cc vials at the bottom of the column. These are best taken at regular intervals of about 1/10 bed volume until the rubidium has been stripped off. Then the frequency of stream samples can be every 1/2 bed volume until the cesium is removed. The concentration of each ~~in species~~ in the stream samples is plotted against the volume of eluate to obtain the distribution curves illustrated in Fig. 1.2 (22424).

7. During the elution it is necessary to collect column holdup until a positive trace of rubidium is observed by the flame test. The fore-run cut is then started and continues until the stream sample shows no sign

TABLE 101

ION EXCHANGE - BATCH No. 4

Resin: Amberlite IR-105

Bed Volume: 2.0 liters

Bed Height: 6' 0" x 1 1/2" dia.

Feed: 100 gm Rb Cl

Flow rate: 30 cc/min

Time	Feed Volume	Eluate Volume	Flow Rate	Flame Test	Cs 137 Distance down col	Stream sample	Remarks
6/23/54							
8:20 pm	600 cc	---	60 cc/min	--	--	feed	adsorption
8:30 p	600	---	60	--	4 in.	--	H ₂ O wash
8:50	4000	0	30	negative	6	J-23-1	start elution
9:00	3700	300 cc	"	"	7	-2	
9:30	2850	1150	"	"	8	-3	
10:00	1975	2025	"	"	9	-4	
10:30	1100	2900	"	"	10	-5	
10:34	4000	3000	30	"	11	added	3000 cc CO ₃ =
10:48	---	3420	"	"	12	-6	
10:52	---	3540	"	positive	14	--	forerun =
11:08	---	4020	"	"	16	J-23-10	3.54 lit
11:28	---	4620	"	"	18	-15	
11:48	---	5240	"	++	20	-20	
12:08	1300	5840	"	++	22	-25	
6/24/54							
8:54 am	---	6480	30	++	24	-30	
9:14	3750	7010	28	++	26	-35	
9:34	3165	7575	-	++	28	-40	
9:54	---	8145	-	++	30	-45	
10:06	---	8490	29	++	31	-47	✓ Cut A = 495 Lit
10:14	---	9625	-	++	32	-50	
10:34	1450	9210	-	++	33	-55	
10:54	---	9785	-	+	34	-60	↓ Cut B = 189 Lit
11:14	---	10375	-	trace	35	-65	
11:34	---	10965	-	negative	36	-70	
11:54	2850	11540	29	"	37	-75	
12:00	2700	11690	-	"	38	-76	
12:30 pm	1800	12590	-	"	40	-77	
1:00	950	13440	-	"	42	-78	
1:30	100	14290	-	trace	44	-79	
2:00	7000	15200	-	positive	46	-80	
3:00	5200	17000	-	"	48	-81	
3:30	4300	17900	-	"	50	-82	
4:00	3400	18800	-	"	52	J-23-83	
7:00	3400	18800	-	"	54	--	
7:30	2500	19700	30	"	56	-84	
8:00	1600	20600	-	"	58	-85	
8:30	700	21500	-	"	60	-86	
9:00	3100	22400	-	trace	62	-87	
9:30	2200	23300	-	"	64	-88	
10:00	1100	24200	-	negative	66	-89	
10:30	700	25100	-	"	68	-90	
11:00	---	26000	-	"	70	-91	
11:30	---	27000	-	"	72	-92	
12:00	---	27800	-	"	72	-93	

of sodium and a definite indication of potassium-rubidium. The product cuts are then made until the flame test shows negative, or low concentration of rubidium. The tail cut is then started and continues until the cesium tracer is off the column after having passed through a definite maximum in color. The resin is then washed with water to displace the ammonium carbonate solution and to leave the resin on the ammonium cycle. It should be mentioned that there is no visible difference in the blue-violet color of the potassium, rubidium and cesium flames. A rough guide for the collection of cuts is:

<u>Eluate</u>	<u>Bed-Volumes</u>
Hold-up	0.5 - 1.0
Forerun	0.5 - 1.0
Product	2.0 - 3.0
Tail Cut	6.0 - 8.0
Water Wash	0.5 - 1.0

These cuts are best collected in calibrated Pyrex bottles. The cuts are labeled after the forerun in alphabetical order. The cuts are well mixed and a 25 cc sample of each is taken for assay to determine the composition of all the alkali metals except lithium. A material balance can then be made based on the assays.

8. Each of the cuts is saved for concentration and those cuts not to be taken for product are accumulated for future disposition. The cesium tail cuts were saved in the hope of reprocessing to obtain an analytical standard of cesium. A summary of a typical set of assays is given in Table 1.2 for Run #4.

1.3. Conversion of Rubidium Carbonate to Rubidium Fluoride

1. The column eluate rich cuts, containing the rubidium and potassium, are concentrated to dryness in 4.0 liter stainless steel beakers on a hot plate. It is convenient to tare the beaker so that the weight of

dried carbonate can be determined immediately upon removal from hot plate before moisture has been absorbed from the air.

2. The carbonate is dissolved in 100-200 cc of water, heated to 50° C and decolorized by adding a suitable carbon equal to 25 per cent by weight of the rubidium present. After agitating for one hour, some Super-Cel admix is added to the carbon slurry and the solution filtered by vacuum through a Super-Cel pad on a medium-pore, sintered glass funnel. The filter cake is saved for recovery of the adsorbed rubidium carbonate. Only the analytical grade of Johns-Manville Super-Cel can be used without introducing cation impurities, especially sodium.

3. The clear filtrate is then transferred to a Polyethylene or Fluorothene beaker for neutralization with aqueous hydrogen fluoride. The standard 60 per cent HF reagent is diluted 1:1 with water before it is used. The amount of HF required is calculated from the alkali metal assay and checked by the weight of carbonate isolated in the cut.

4. The dilute HF is added slowly from a polyethylene wash bottle while stirring the carbonate solution with a plastic rod or tube. The pH is checked with alkacid paper as the end point is approached. Care is taken not to add an excess of HF because it forms a complex with RbF . After about 90 per cent of the HF required has been added, the rate of addition is slowed down and time is allowed for evolution of carbon dioxide. A copious liberation of gas is a good sign that the end point is near. The neutral solution is checked with alkacid paper after standing for 30 minutes to make certain that it is slightly acid - pH 6.5 - 7.0.

5. The aqueous solution of RbF is then concentrated down in a Fluorothene beaker under a 350 watt lamp or in 300 cc Nickel crucible on a hot plate. The heavy magma is then transferred to a 50 cc platinum crucible and dried at 180° C in an oven.

6. The anhydrous RbF is then treated in the fused state to remove as much as possible of the excess HF. An all nickel reaction vessel was used in the ANP Fuels Laboratory for the fusion at 800° - 900° C. The melt is treated for one hour by passing helium over the surface to remove the excess HF. This procedure results in about one per cent of the RbF.HF complex being present in the final product according to a petrographic examination by Dr. McVey of the Ceramics Group.

7. The system is allowed to cool to a temperature of about 150° C before it is placed in a dry box using phosphorous pentoxide as a desiccant. The vessel is opened after it has cooled and the fused mass removed by using a small chisel and hammer to fracture the crystals. The crystals are broken up, if necessary, before they are packaged into a bottled sealed against moisture by Scotch masking tape. A 50-100 milligram sample is also packaged into a weighing bottle for assay of the alkali metals.

1.4. Reduction of Rubidium Fluoride by Calcium

1.4.1 Chemical Reaction

Boyd Weaver and Phil Baker checked the heat of reaction for this equation and reported it to be favorable. By taking the heats of formation and balancing the lefthand side against the right hand side, it is found that the heat of reaction is -11.8 Kcal per gram Mol of rubidium in favor of the desired reaction.

The granular calcium metal, which is stable in air, is charged in excess by 25 per cent of theory. The few runs which have been made did not permit a study of this variable for maximum yield.

Equipment

1.4.2. Quartz Reduction Unit

P. S. Baker and H. B. Greene of the Stable Isotopes Division at Y-12 designed an experimental glass system capable of reacting about 90 gm rubidium fluoride. The unit consists essentially of a 45-mm diameter quartz jacket surrounding a four-inch long stainless steel reactor of 1 1/2 inch tubing suspended from a glass hook by a glass tape. The rubidium vapor flows out of the reactor through a 1/4-inch diameter downcomer into the 25-cc Pyrex cold zone collector. This system is evacuated at the top via a 10-mm diameter side arm. The initial design was modified to permit equalization of the reactor and receiver pressure along with allowance to seal off the receiver under vacuum at the end of the run. The modified design is shown in Fig. 1.4. The induction heating coil consisted of a 3-inch diameter helix with nine turns of 3/8 inch copper tubing through which cooling water flows. A 20-kilowatt Megatherm unit was the source of power for induction heating.

The empty system is assembled and tested for leaks under high vacuum, this is equivalent to 10^{-5} mm Hg being maintained on the system by an oil diffusion pump using a Kinney vacuum pump as the roughing stage. The system is degassed by heating the s.s. (stainless steel) pot to drive off all

absorbed gases. A branch is run off the vacuum line to a tank of argon which serves as a supply of inert gas during shutdown and opening to the atmosphere. A view of the entire assembly and its components is shown in Fig. 185.

The actual operations are carried out behind a full-length, clear-plastic shield because of the hazardous nature of rubidium metal.

An outline of the procedure for operation of the quartz unit is:

1. The dry system is tested for leaks after assembly using Silicone grease on Pyrex standard taper joints at room temperature and then at a temperature for which the stainless steel pot is at red heat (600° - 800°C).

2. Argon was used to vent the evacuated system to atmospheric pressure after obtaining 0.01 microns Hg in a leak-test. The cool S.S. pot was then charged in a dry-box containing phosphorous pentoxide to hold the moisture content of the air to a minimum. The respective weighed amounts of rubidium fluoride crystals (less than 1/4-inch in size) and the calcium metal were then charged to the stainless steel pot. A small cork was used to plug the vapor downcomer line and the screwed cap was sealed around the edge with Scotch Drafting Tape.

3. The S.S. pot was then hung inside the quartz jacket after removing the anti-moisture seals. The system was tested again for leaks at room temperature. After reaching a pressure of 0.01 micron Hg, the system was heated slowly to dry and degas thoroughly. This required about one hour before a pressure less than 0.02 micron Hg is obtained.

4. The reaction is then started by heating up the stainless steel pot to 600 - 800°C . This is accomplished in a few minutes by alternately applying the Megatherm unit power for about 5-10 seconds in both the "on" and "off" condition. The Pirani vacuum gage is observed carefully during this period to make certain that a pressure less than 0.04 microns Hg is being maintained.

FIGURE 1.4 QUARTZ REDUCTION UNIT

Fig. 1.5

REDUCTION-DISTILLATION UNIT FOR RUBIDIUM

SECRET
ORNL-LR-Dwg. 9642

ASSEMBLY

COMPONENTS

5. The reaction is quite rapid after reaching 800°C and the liquid rubidium metal flows out of the downcomer into the Pyrex receiver. The accumulation of metal is observed for about 20 minutes at a temperature of $600^{\circ}\text{--}800^{\circ}\text{C}$. It is necessary in some cases to use a gas flame on the outside of the glass to lower the viscosity of the metal in the downcomer tube until it flows freely.

6. The yield of rubidium metal is estimated by the volume occupied in a calibrated Pyrex receiver. It is then sealed-off under vacuum at the neck followed by sealing the side arm capillary. The ampules should be kept on a cool, dry shelf away from all personnel and solvent. It can be transported by surrounding with Super Cel (a filter aid and insulation material) inside a metal can which is soldered around the top edge if a long trip is to be made.

7. The Quartz jacket is then vented to the atmosphere with argon, and the top and bottom joints opened to the atmosphere - use a hood and adequate safety protection at this point. A torch must be used to heat the joints before they can be loosened. It is good practice to maintain the flow of inert gas inside the jacket while alcohol or water is added to react with the rubidium metal. **BE PREPARED FOR A FLASH FIRE AND A POSSIBLE EXPLOSION DURING THIS OPERATION!** A sample of the aqueous liquor is taken for analysis and the volume recorded to calculate the amount of metal not drained into the receiver.

8. The stainless steel reactor pot (see Section 1.4.3 for description) is handled in exactly the same fashion as the quartz jacket. After any rubidium has been reacted it is necessary to loosen the calcium fluoride sludge, containing 35 per cent calcium and 18 per cent rubidium, by the use of concentrated hydrochloric acid for only a few minutes since it

corrosive. The stainless steel pot is rinsed thoroughly with water then dried. The sludge from the stainless steel pot is held for filtration and the filtrate accumulated for reworking of rubidium unchanged by the reaction. A summary of the data for a typical run is given in Table 14.

TABLE 14
Reduction Run 4

Charge:	Rubidium Fluoride	53.4 gm
	Calcium metal	13.0
	Total rubidium charged	44.0
Reactor:	Product metal	30 gm
	Jacket wash(metal equivalent)	4.2
	Pyrex seal tube metal	1.0
	S.S. pot unconverted metal	4.4
	TOTAL rubidium accounted for	39.6 gm
	Loss in process	4.1 gm

Yield of metal = $\frac{30}{44}$ = 68 per cent of theory

14.3. Stainless Steel Reduction Unit

The use of a stainless steel reduction-distillation unit became desirable when the production of 200 grams-batches of metal was undertaken. It would reduce the number of batches to be run and, at the same time, reduce excessive exposure to the glass system from the standpoint of safety. One design considered was a reactor from which the rubidium vapor would be withdrawn at the top and condensed in a separate vessel. This design was discarded, however, in order to retain the same design as the quartz system which uses a vapor downcomer through the melt. A sketch of the all-metal

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No. 413 HOKE DIAPHRAGM
MONEL VALVE

SECTIONED STAINLESS STEEL REDUCTION-DISTILLATION UNIT

system is shown in Fig. 106. It was constructed of all 316 stainless steel and Heliarc welded.

A major change from the design of the quartz system was the use of Monel diaphragm valves and Swage-Lok fittings in the gas and liquid lines throughout the system. The use of Monel was approved, despite its high content of copper, because none of the valves would be exposed to a temperature above 200°C. The 316 stainless steel tubing was welded to the Monel valves by the use of Inconel filler rod at the suggestion of P. Patriarca of the X-10 Metallurgy Division. In general, this design served as a test model for a commercial reduction unit upon which the cost estimate is based in a later section of the report. It was designed with the advantage that a stainless steel receiver holding about 150 grams of rubidium metal could be transported safely from the Y-12 to X-10 area. Either a vacuum or inert gas atmosphere could be maintained over the metal by the arrangement to blank off the lines with plugs. It was planned to use a dry-box for subdivision directly from the S.S. receiver into Pyrex receivers for the vacuum distillation required for purification.

During the actual operation of this unit, however, it was desired to observe the flow of rubidium as it was being produced and a modification became necessary. A 40-cc Pyrex receiver was attached to the bottom outlet of the stainless steel receiver for collection of metal under vacuum. It turned out that this modification allowed cooling of the rubidium in the stainless steel receiver and, as a result, the bottom outlet line was frozen with metal. It was learned later that the vapor downcomer had also become plugged with calcium fluoride which isolated the receiver. About 75 grams of metal was "milked" out into four separate Pyrex, vacuum sealed ampules about 50-60 grams remained in the stainless steel receiver. A Kovar seal

should have been installed on the inlet side of the S.S. receiver as a sight glass. The Kovar seals are available at the glass blowing shops; it is a graded glass-to-metal seal which is quite sensitive, however, to thermal shock.

The all-metal system was tested for leaks under a pressure of 30 psig and then under high vacuum (0.04 microns Hg) at both room temperature and 800°C. A Chromel-Alumel thermocouple was inserted into the thermowell to estimate the temperature when the induction heating field was not applied. In general, the system was superior to expected performance under high vacuum conditions. The reactor section was insulated with asbestos tape to help retain most of the heat at a temperature of 600°-800°C.

The unit was operated in a parallel manner to the procedure described for the quartz system. One change was in the use of a 300 cc-polyethylene bottle as the charging vessel. This allowed the charge to be prepared in a dry-box and the plastic tubing adaptor plugged with a rubber stopper until ready for use. The plastic tubing was slipped over the 1/2-inch S.S. charge tube and the bottle inverted to drop the charge of 200 gm RbF and 48 gm Ca into the reactor.

It should be mentioned that the rubidium metal from this stainless steel system (Reduction-Run 5) was the highest quality product obtained during the project and superior to that delivered by the commercial supplier. When the downcomer line was found to be plugged, however, it was decided to return to the quartz-glass system.

The stainless steel system was then taken to the vacuum dry-box in X-10 and sectioned perpendicular to the axis for observation. The charge tube and the vacuum line at the top of the stainless steel reactor had a crust of CaF_2 over the openings but the sludge was easily removed without any

ignition of rubidium metal. An assay showed that this material contained 38 per cent calcium and 18 per cent rubidium - as the fluorides weighing 100 grams. Upon sectioning the reactor axially, a plug about 3/8 inch long was found inside the downcomer at the base of the reactor (See Fig. 146). It has been impossible to drill through this section which was assayed as pure calcium fluoride. The vacuum line at the top was then cut and some rubidium residue flashed upon exposure to the atmosphere. The monel valve at this point was sectioned and found to be clean.

The apparent low yield for this run was brought up to normal of about 70-75 per cent when the stainless steel receiver was cut perpendicular to the axis and found to contain about 50-60 grams of rubidium. This material was melted and poured into Pyrex containers for vacuum sealing. The residual metal wetting the walls of the receiver was reacted slowly with ethyl alcohol under a helium atmosphere. Upon opening the bottom outlet valve to the atmosphere, an explosion occurred in the form of a flash fire from the holdup estimated at about 0.1 gram. The receiver was then sectioned parallel to the axis for examination. This experiment proved the utility of an all-metal system but pointed out that a more detailed development of the process must be done to avoid the plugging of lines by calcium fluoride.

1.5 Purification of Rubidium Metal by Vacuum Distillation

Before the metal can be used for corrosion tests, it is necessary to purify it by a high-vacuum distillation. This leaves the non-volatiles, especially oxides and fluorides, as a residue. In the analysis of metal samples the crude metal contains about 2-4 per cent oxygen. After vacuum distillation by Dr. J. Cathcart of the X-10 Metallurgy Division, the oxygen content can be reduced to about 0.1 per cent.

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It is convenient to design a 20-40 cc Pyrex receiver with a side arm of 8 mm tubing, 10 cm in length, having a "break-seal" at the center. The "break-seal" should be custom-made because a commercial unit is too small in crosssectional area and is quite difficult to rupture with a short iron rod. The vacuum sealed ampule is connected to a high-vacuum distillation apparatus through the side arm containing the break-seal joint. Provision should be made to distill the rubidium vapor over into a 20-40 cc Pyrex receiver which is cooled by the ambient air. The source of heat can be a small gas flame moved manually to control vaporization at a temperature of about 100°-200°C under a pressure of 10^{-5} mm Hg. Condensation along the vapor riser occurs easily and requires a follow-up with the gas flame to keep the vapor moving over into the air-cooled receiver. In some cases it is desirable to repeat the distillation to increase the purity. The final product is vacuum sealed in the usual fashion. This procedure is not to be attempted by anyone inexperienced in handling alkali metals because it is hazardous. Complete protection of personnel is imperative and more elaborate safety features might be incorporated in the design of the distillation unit.

1.6 Analytical Procedures for Alkali Metals

1.6.1. Oxygen in Alkali Metals

A new procedure has been developed by the Analytical Division of the ANP program. It is essentially a Wurtz reaction of the alkali metal using an excess of organic halide which leaves the oxides unreacted for a later titration after dilution with water. The procedure was developed by Dr. J. C. White, et al, and is described in Analytical Chemistry Vol. 26, pg. 210, 1954. Other procedures are also discussed in comparison to the new method of using a 40-60 per cent solution of n-butyl bromide in hexane as

an inert atmosphere.

1.6.2. Determination of Na, K, Rb, and Cs by Flame Photometer

It was necessary to carry out between 40-80 assays per day of the alkali metals in resin column eluates to analyze the efficiency of separation and to locate the rich cuts containing rubidium. We are most grateful to H. P. House and Miss Jeanne M. Rogers of the Analytical Division for the courteous, reliable and immediate service which was given throughout the experimental phase of this report. We were pleased to be of service in supplying high purity fractions of rubidium and cesium for use as reference standards.

Description of Procedure:

The alkali metals, Na, K, Rb, and Cs were determined for resin column solutions (feed solutions and eluate fractions) and in product materials, by means of the flame photometer (Beckman Model DU Spectrophotometer with Beckman Flame Photometer Attachment No. 9200). The red-sensitive phototube, Beckman No. 156, was used in the determination of K, Rb, and Cs; for Na, the blue sensitive photomultiplier tube, RCA 1228, together with photomultiplier attachment No. 4300 was used.

The samples which consisted for the most part, of carbonate solutions, were reacted with HCl to convert the carbonate salts to chlorides. The resultant solutions were diluted as required to bring the metal within a suitable concentration range for flame photometry. Portions of the prepared solutions were then aspirated into an oxy-hydrogen flame. Light from the flame was caused to pass through a monochromator, and a narrow band of the emission spectrum including a prominent line of spectrum of the metal was brought to bear on a phototube. The photocurrent thus produced, after electronic amplification, was measured potentiometrically, the reading

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being on the per cent transmission (%T) scale of the spectrophotometer. The magnitude of the reading is proportional to the amount of the alkali metal in the solution aspirated into the flame.

The % T (percent transmission) of a series of standards of varying concentrations were measured in the same manner as was the unknown. A calibration curve, % T versus concentration was constructed. The observed % T for an unknown was then referred to this graph, and from it, the concentration of the metal in the test solution was determined. This value, multiplied by the dilution factor gave the concentration, usually in micrograms (mg) per ml, of the metal in the sample.

Solids, if other than chloride or nitrates, were converted to chlorides and a solution of a specific amount of solid was prepared. The concentration of the desired component in this solution was determined in the same manner as that described above for liquid samples. From this test result, the per cent of ppm of the desired component in the solid was calculated.

Readings of % T for the various alkali metals were made at the following wavelengths:

	Wavelength <u>mu</u>
Sodium, Na	589
Potassium, K	767
Rubidium, Rb	795
Cesium, Cs	852

The detailed procedure, including operational instructions for each of the four metals, Na, K, Rb, and Cs, is outlined in J. M. Roger's Progress Report No. 13 (Appendix C).

1.6.3 Iron, Chromium and Nickel Impurities

These were determined by standard quantitative methods of wet chemistry, or if necessary, semi-quantitative determinations were made by X-ray.

1.6.4 Fused Salts

The purity of these materials was checked by Dr. McVey of the Ceramics Division using petrographic techniques. The amount of HF-complex of rubidium fluoride was checked in this manner. Mixtures of alkali metal halides can also be identified accurately.

1.7 Manufacturing Cost Estimate for Rubidium Metal

1.7.1 Introduction

According to J. W. Mellor (6), R. Bunsen and G. Kirchhoff discovered rubidium in 1863 by identification of a dark red spectrum line not associated with the other alkali metals. Preparation of the metal was not accomplished until H. Erdmann, et al (7) used calcium metal for reduction at 400-500°C in an exhausted glass system. The hydroxide or carbonate can be reduced by an excess of magnesium.

A review of the ore deposits inside the continental United States is reported by R. C. Wells (8). Both light (Muscorite) and dark (Liotite) micas contain non-essential oxides as a source of rubidium. From "Rocks and Rock Minerals" by Pirsson-Knopf (John Wiley 1926 2nd. edition) the light mica in which lithium replaces a large fraction of potassium is lepidolite, a basic ore for rubidium.

Other suitable ores are Biotite, which has the formula $(H,K)_2(Mg,Fe)_2(Al,Fe)_2(SiO_4)_3$ and Zinnwaldite which is rich in iron and has lithium substituting for potassium. Wells (8) listed these assays:

<u>Non-Essential Oxide</u>	<u>Biotite (a)</u>	<u>Zinnwaldite (b)</u>
Li ₂ O	0.65	1.92
Na ₂ O	0.45	0.74
K ₂ O	8.50	9.58
Rb ₂ O	1.46	1.04
Cs ₂ O	1.14	0.10

(a) Custer City, C. D.

(b) Amelia City, Va.

It was planned to study some possible methods of isolating rubidium and other alkali metals directly from the ores. Time did not permit a process to be speculated upon in time for this report. This phase of the project should be studied fully, however, to prepare an ultimate manufacturing cost of rubidium metal. Methods other than ion exchange should be investigated for a survey of the economics.

1.7.2 Rough Manufacturing Cost

The fixed-bed ion exchange process and the small scale batch reduction unit are not applicable for large-scale commercial manufacture of low-priced rubidium metal. At the present time the market price of rubidium fluoride is about 50 cents per gram so that a purchase price of \$1.00 per gram, or \$500. per pound, is reasonable for lots less than five kilos of pure metal.

The ultimate cost for the process operated during the course of this project, with the assumptions that a crude rubidium salt could be produced for five cents per gram and with a 95 per cent recovery of ammonium carbonate, is about ten cents per gram of rubidium metal or \$50 per pound. These values are reliable for a production rate of about 40 kilos per day, and above.

Eventually, continuous (4) ion-exchange and a possible continuous reduction could be developed. The demand will have to be at least 100 kilos per day to justify the development work involved and to place rubidium on the market as a suitable heat transfer fluid.

It should be mentioned that, in addition to the Dutch-Norwegian Pilot Plant at Ijmuiden, Holland (1). The Japanese are also engaged in extracting potassium from sea water (9). The invaluable dipicrylamine salts of rubidium and cesium all co-precipitated out of the potassium. The Japanese have separated the three invaluable alkali metals by selective solvent extraction, amyl alcohol and xylene.

It is doubtful if the ocean is a competitor with igneous rocks, however, as a basic raw material for rubidium. New England granites show an average K/Rb ratio of about 90 with the rubidium content ranging from 0.02 - 0.09 per cent.

1.8 REFERENCES

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- (3) Brooksbank and Leddicotte, J. Phys., Chem. pg. 57, 819 (1953)
- (4) Ion-Exchange, Chemical Eng. Progress Symposium Series, Vol. 50., No. 14, pg. 87 (1954) I. R. Higgins and J. T. Roberts
- (5) Perry's Chem. E. Handbook pg. 237, McGraw Hill, 1950. Values are for 25° C in kilocalories per gram mol.
- (6) Vol II, Reference "A Comprehensive Treatise on Inorganic and Theoretical Chemistry". J. W. Mellor
- (7) J. A. C. S. 21, 259 (1899) H. Erdmann
- (8) I. E. C. Anal. Ed. 6, 442, 1934. R. C. Wells.
- (9) Chemical Abstracts Vol 46, 852 i (1953).

2.0 PHYSICAL PROPERTIES OF RUBIDIUM

2.1 Introduction

It was found by a literature search and reference to the handbooks (1), (2), (3), (4), that data are not available for the physical properties of rubidium metal in the vicinity of the boiling point. Dr. H. F. Poppendick furnished the anticipated relation of the basic properties with temperature for the entire family of alkali metals. In addition, he offered to measure density and specific heat over a temperature range of 50° - 500°C.

The most difficult value to locate was a reliable estimate of the critical temperature for rubidium metal. The values in the literature are from 1800° K to 2700° K in comparison to an estimate of 3000°K by Brewer (5).

2.2 Summary of Data

64

Atomic Number	37
Mol. Wt. monomer (Rb)	85.48
Mol. Wt. Dimer (Rb ₂)	170.96
Natural Isotopic Abundance:	Rb ⁸⁵ 72.2
	Rb ⁸⁷ 27.8
Melting Point:	49°C 102°F (b)
Boiling Point:	688°C 1270°F (b)
	679°C 1252°F (c)
Latent Heat of Fusion:	6.1 cal/gm
Latent Heat of Vaporization:	18.5 <u>kg cal</u> or 383 <u>Btu</u> mole lb
Density of Liquid:	1.52 - 0.00054 (T-39°C) gm/cc
Specific Heat of Liquid:	0.086 Btu/(lb)(°F)
Critical Temperature:	about 3000°K
Critical Pressure:	about 250 atm
Sublimation:	occurs from solid state

2.3 Density

It was arranged to have Mr. Stanly Cohen determine the density of liquid rubidium. The method consisted of operating a Westphal Balance inside an atmospheric dry box. Two different plummets were used to improve the accuracy. The liquid metal was held in an electrically heated nickel

cylinder which had a thermowell drilled down into the heavy wall.

It was difficult to obtain an oxygen-free atmosphere inside the dry box although it was purged with helium which had been passed thru a catalytic combiner for oxygen. The rubidium metal discolored immediately upon removal from the standard taper Pyrex containers.

The liquid metal was then purified to remove oxide particulates by filtration through a fluted glass funnel having a one-inch diameter filter disc of medium pore size. A differential helium pressure of about 10 psi was required to force it through the filter. The rubidium was heated to about 75-100°C before it was poured into the preheated glass filtration system. The filtrate was a clean silvery liquid which rapidly discolored from the trace of oxygen in the ambient gas.

The filtered metal was charged to the nickel cylinder by using a rubber bulb at the end of a piece of glass tubing. A layer of oxide was removed from the top of the metal after it has been charged.

Data were obtained over the range of 50°-400°C as shown by Fig. 2. It was necessary to discontinue this experiment because the vapor pressure of rubidium becomes appreciable above 400°C and it was being lost by vaporization and the interior surface of the dry box became "fogged" with rubidium hydroxide. However, a sufficient range was covered to establish the slope of the straight line relation between density and temperature.

Experimental Relation for Density as a Function of Temperature

$$\rho_{Rb} = 1.52 - 0.00054 (T - 39^\circ\text{C})$$

This equation is slightly different from the predicted curve based upon the same volume change during fusion as occurs for sodium, potassium and NaK.

0000000000

Predicted Relation

$$\rho_{Rb} = 1.475 - 0.00025 (T - 39)$$

A graph is shown in Fig. 2.2 for the density of all the alkali metals over a wide range of temperature.

2.4 Specific Heat

Mr. W. D. Powers determined the average specific heat of the liquid between 60° C and 550° C using sealed capsules. The data gave a linear curve which showed $\left(\frac{\partial H}{\partial T}\right)_p = C_p = 0.086 \frac{\text{Btu}}{(\text{lb})(^\circ\text{F})}$. A summary of the published data (2) is:

<u>Metal</u>	<u>Cp</u>	<u>T°C</u>	<u>M.W.</u>	<u>Molar Heat</u>
Li	1.0	200	6.9	6.90
Na	0.3305	100	23.0	7.60
	0.3030	800	23.0	6.90
K	0.1956	75	39.1	7.65
	0.1884	800	39.1	7.15
Rb	0.0913	39-126	85.5	7.8
	0.085	100-800	85.5	7.3
Cs	0.060	28.5	132.9	8.0

2.5 Viscosity

The family of curves for the viscosity of the alkali metals given in Fig. 2.3 is based on data from the Liquid Metals Handbook. It is of interest to note that a recent measurement of the viscosity of rubidium metal (6) was made with metal containing 0.5 per cent sodium and potassium. The difficulty of obtaining pure rubidium was discussed in this paper.

Fig. 2.1

ORNL-IR-DWG-9644
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Fig. 2.2

ORNL-LR-Dwg.-9645
SECRET

DENSITY OF ALKALI METALS

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Extrapolation of data for 300-800°C gives equation: $\mu = 0.0666 e^{-\frac{813}{T}} \text{ cp}$

μ = viscosity centipoise

The constants were determined as follows:

$$T_1 = 573^\circ\text{K} \quad \mu_1 = 0.275 \text{ cp}$$

$$T_2 = 1073^\circ\text{K} \quad \mu_2 = 0.142 \text{ cp}$$

$$B = \frac{T_1 T_2}{T_2 - T_1} \ln \frac{\mu_1}{\mu_2}$$

$$B = \frac{(573)(1073)}{500} \ln \frac{.275}{.142}$$

$$= 1230 (0.66114)$$

$$= 813$$

$$A = \mu_1 e^{-B/T_1} = (0.275) e^{-\frac{813}{573}}$$

$$A = 0.0666$$

2.6 Thermal Conductivity (See Fig. 2.4 for summary of literature data.)

$$K = 0.075 - 0.00038 T (^\circ\text{C})$$

$$K = \frac{\text{cal}}{(\text{sec})(\text{cm})(^\circ\text{C})}$$

	MW	$k_{500^\circ\text{C}}$	MW $k_{500^\circ\text{C}}$	$\frac{K_{1000^\circ\text{C}}}{K_{500^\circ\text{C}}}$	$\frac{k_{500^\circ\text{C}}}{K_{500^\circ\text{C}}}$
Li	6.94	0.090	6.25	-	-
Na	23	0.212	4.9	1.28	1.32
K	39.1	0.115	4.5	1.25	1.27
Rb	85.5	0.0725	6.2	-	-
Cs	133	0.045	6.0	-	-

2.7 Vapor Pressure of Rubidium

A plot of vapor pressure in atmospheres against the reciprocal of the absolute temperature is given in Fig. 2.5 for each member of the

VISCOSITY OF ALKALI METALS

FIG. 2.3

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ORNL-IR-DWG-9616

THERMAL CONDUCTIVITY OF ALKALI METALS

Fig. 2.4

ORNL-IR-DWG.-9647
SECRET

Fig. 2.5

ORNL-LR-Dwg.-9648
SECRET

alkali metals family. These data are taken from page 30 of N.N.E.S.

2.7.1 ORNL DATA

A check on the values for rubidium was made by Dr. R. E. Moore of the Materials Chemistry Division. The procedure followed was designed by Rodebush and Dixon (7). About 8-10 grams of rubidium metal was charged to the quartz vapor pressure apparatus in the X-10 vacuum dry box. The data are given in Table 2.1. The extrapolated boiling point, 683°C, and the heat of vaporation, 18.5 kg. cal/mole agree closely with values found in Kelley's compilation (2), 679°C and 18.8. The analytical expression for the vapor pressure is:

$$\log_{10} P \text{ (mm Hg)} = -\frac{4024}{T(^{\circ}\text{K})} + 7.091$$

TABLE 2.1

<u>Temp.</u> <u>(°C)</u>	<u>Observed Pressure</u> <u>(mm Hg)</u>	<u>Calculated Pressure</u> <u>(mm Hg)</u>
428	23	22
440	31	28
464	41	42
485	60	60
517	97	98
540	143	138

2.7.2 Battelle Data

About 25 grams of rubidium was shipped to Battelle Memorial Institute for vapor pressure measurements. A summary of the data is given (Tab. 2.2) for comparison with the ORNL data and to validate the calculations that the amount of dimer is negligible. The Battelle transpiration method would have indicated a higher molecular weight if the dimer were significant.

TABLE 2.2
BATELLE VAPOR PRESSURE DATA

<u>V.P. mg Hg</u>	<u>Temp ° C</u>
219	573.5
57.3	481.8
25.5	429.3
7.76	371.7

$$\log p \text{ (mm)} = 6.942 - \frac{3900}{T(^{\circ}\text{K})}$$

$$\text{Boiling Point} = 687^{\circ} \text{ C}$$

$$\Delta H_v = 17.85 \quad \frac{\text{K cal}}{\text{gm mole}}$$

2.8 Dimer Content of Vapor

It was planned to conduct some experimental measurements of the vapor density of rubidium vapor in the range of 100° to 800° C to determine the molecular weight of the vapor however, time did not permit the measurements. These data are needed to calculate the amount of rubidium dimer in the vapor. This information is required for accurate calculations of thermodynamic data. It was assumed, however, on the basis of literature search (8) (4) that the amount of rubidium dimer was less than five per cent and could be neglected in the preparation of the T-S and H-S diagrams. This is not the case with sodium which has as much as 20 per cent dimer in the vapor (NAA-SR-62).

In order to validate the assumption that rubidium is, essentially, a monatomic vapor, Dr. Leo F. Brewer of the Department of Chemistry and Chemical Engineering at the University of California, Berkely Campus, was contacted. We wish to thank one of his students, John Engleke, who furnished sample calculations for us to follow in proving that the rubidium dimer is a

a negligible component of the vapor. These calculations included an extrapolated beyond the reported (9) temperature range of 2000°K to the estimated critical temperature of about 3000°K.

The vapor pressure of both the monomer and dimer can be calculated separately from available thermodynamic data. At the low pressures under study for the jet engine cycles, the rubidium vapor can be treated as an ideal gas. It can then be assumed that the equilibrium constant for either vapor species, in equilibrium with rubidium liquid, is equal to the partial pressure of the respective vapor molecule:

$$\text{Equation : } Rb(l) = Rb(g)$$

$$\text{Equilibrium constant: } K = \frac{\text{activity } Rb(g)}{\text{activity } Rb(l)} = \text{Fugacity } Rb(g)$$

$$K \approx \text{partial pressure } Rb(g)$$

Since the standard free energy and equilibrium constant are given by the equation:

$$\Delta F_T = -RT \ln K$$

the partial pressure of $Rb(g)$ may be calculated:

$$\ln pp Rb(g) = -\frac{\Delta F_T}{1.98T}, \text{ where}$$

$$\Delta F_T = \text{standard free energy, Kg cal/}(^{\circ}\text{K})(\text{mole})$$

$$R = \text{gas constant, 1.98}$$

$$T = \text{absolute temperature, } ^{\circ}\text{Kelvin}$$

$$K = \text{equilibrium constant}$$

$$pp = \text{partial pressure, atm.}$$

The free energy function, which must be found at the temperature under consideration for each molecular species, is calculated by the equation:

$$\text{Eq. A} \quad \frac{F_T - H_{298}}{T} = \frac{H_T - H_{298}}{T} - (S_T - S_{298}) - S_{298}, \text{ where}$$

F_T = free energy at temperature T, Kg cal/(°K)(mole)

H_T = heat content at T, Kg cal/(mole)

S_T = entropy at T, kg. cal/(°K)(mole)

T = temperature of system, °K

Subscript 298 is standard state of 25°C

The standard entropies at room temperature for both species are given on pp 78 and 112 of Kelley's Bulletin, No. 477 (10). The heat content and entropy differences are from Kelley's Bulletin No. 476 (9) page 194.

Since the specific heat of a liquid does not change appreciably with temperature, the data for Rb (ℓ) on p. 194 of Bulletin No. 476 can be employed as follows:

$$\begin{aligned} \text{Rb}(\ell) : \quad (H_T - H_{298}) &= 1310 + 7.80 (T - 400) \\ (S_T - S_{298}) &= (S_{400} - S_{298}) + \int_{400}^T \frac{C_p}{T} dT \\ &= 395 + 7.80 \ln \frac{T}{400} \end{aligned}$$

C_p = molar specific heat of liquid, $7.80 \frac{\text{Kg Cal}}{(\text{°K})(\text{mole})}$

For the monomer vapor it is satisfactory to use the data for Argon from page 19 for

$$(H_T - H_{298}) \quad \text{and} \quad (S_T - S_{298})$$

For a temperature of 1000°K the vapor pressure of the monomer is calculated to be 1.62 atmospheres:

$$\begin{aligned} R_b(\ell) &= R_b(g) \\ \text{Liquid} = R_b(\ell) : H_T - H_{298} &= 1310 + 7.80 (1000 - 400) \\ &= 1310 + 7.80 (600) \\ &= 1310 + 4680 \\ &= 5990 \text{ Kg cal/mole} \end{aligned}$$

$$S_T - S_{298} = 3.95 + 7.80 \ln \frac{1000}{400}$$

$$= 3.95 + 7.80 \ln 2.50$$

$$= 3.95 + 7.80 (0.92)$$

$$= 3.95 + 7.15$$

$$= 11.10$$

$$S_{298} (\ell) = 16.6 \pm 1.0$$

Eq. (A)

$$\frac{F_T - H_{298}}{1000} = \frac{5990}{1000} - (11.10) - 16.6$$

$$= 5.99 - 27.70$$

$$= 21.70 \frac{\text{Kcal}}{(\text{mole})(^\circ\text{K})}$$

Vapor Monomer = R_b (g)

$$H_T - H_{298} = 3487 \quad \text{p. 19 Table}$$

$$S_T - S_{298} = 6.01 \quad \text{p. 19 Table}$$

Eq. (A)

$$\frac{F_T - H_{298}}{1000} = \frac{3487}{1000} - 6.01 - 40.64$$

$$= 3.49 - 46.65$$

$$= -43.16 \frac{\text{Kcal}}{(\text{mole})(^\circ\text{K})}$$

Assuming $\Delta H_{298} = 20,505 \frac{\text{cal}}{\text{mole}}$, as the standard latent heat of vaporization, allows the function $\frac{\Delta F_T}{T}$ to be calculated:

$$\text{for } 1000^\circ\text{K} \quad \left[\frac{F_T - H_{298}}{1000} \right]_{R_b (g)} - \left[\frac{F_T - H_{298}}{1000} \right]_{R_b (\ell)} = -43.16 + 21.70$$

$$\frac{\Delta F_T}{1000} - \frac{\Delta H_{298}}{1000} = -21.46$$

$$\frac{\Delta F_T}{1000} = -21.46 + \frac{20,505}{1000}$$

$$= -2.146 + 20.50$$

$$= -0.96 \text{ Kg cal/}(\text{mole})(^\circ\text{K})$$

$$\ln pp \text{ Rb}_b(g) = + \frac{0.96}{1.98} = 0.485$$

$$pp \text{ Rb}_b(g) = 1.62 \text{ atm at } 1000^\circ\text{K}$$

For the dimer partial pressure at 1000°K , the calculation are:

$$2 \text{ Rb}(l) = \text{Rb}_2(g)$$

$$\text{Rb}_2(g) :$$

$$H_T - H_{298} = 6275$$

$$S_T - S_{298} = 10.83$$

$$\frac{F_T - H_{298}}{1000} = \frac{6275}{1000} - 10.83 = -63.1$$

$$\text{with } S_{287} = S_{298} = 63.1 \text{ K cal/}(\text{mole})(^\circ\text{K})$$

$$\text{or } \frac{F_T - H_{298}}{1000} = 6.28 - 73.93 = -67.65$$

Then for the equation representing dimer in equilibrium with the liquid:

$$\frac{\Delta F_T - H_{298}}{T} = -67.65 + 2(21.70)$$

$$\text{Free energy Function} = -24.26$$

$$\Delta H_{298} = 29.1 \pm 1.0 \text{ for Gaydon (4)}$$

so that

$$\frac{\Delta F_T}{1000} = -24.26 + \frac{29.100}{1000} = -4.84$$

$$\ln pp \text{ Rb}_2(g) = - \frac{4.84}{1.98} = -2.45$$

$$pp \text{ Rb}_2(g) = 0.086 \text{ atm}$$

This procedure is repeated at other values of temperature and then

interpolation of the free energy function, $\frac{\Delta F_T - H_{298}}{T}$, can be made

linearly with temperature since it is a slowly varying function.

A somewhat different method must be used to estimate the $\text{Rb}_2(\text{g})$ fugacity, partial pressure in this case, at 3000°K . Since the ~~fully~~ data end at 2000°K , the assumption is made that the difference in heat capacity between the product, $\text{Rb}_2(\text{g})$ and reactant, $2\text{Rb}(\text{l})$, is constant between 2000°K and 3000°K and that it is given from the data on p. 149,

$$\Delta C_p = 8.95 - 2 \times 7.80 = -6.65 \text{ cal/deg/mole}$$

From the free energy function the heat content and entropy change at 2000°K can be obtained.

$$\Delta H_{2000} - \Delta H_{298} = 15.22 - 2 \times 13.87 \\ = -12.52$$

$$\Delta H_{298} = 29.1$$

$$\Delta H_{2000} = 16.58 \text{ K cal/mole}$$

$$\Delta S_{2000} = \frac{\Delta H - \Delta F}{T} = \frac{16,580}{2,000} + 5.63 = 13.92 \text{ e.u.}$$

$$\Delta H_{3000} = \Delta H_{2000} + \int_{2000}^{3000} \Delta C_p dT \\ = 16,580 - 6,650 = 9,930 \text{ cal/mole}$$

$$\Delta S_{3000} = \Delta S_{2000} + \int_{2000}^{3000} \frac{\Delta C_p}{T} dT \\ = \Delta S_{2000} - 6.65 \times 2.303 \log \frac{3000}{2000} \\ = 13.92 - 2.70 = 11.22 \text{ entropy units}$$

$$\Delta F_{3000} = \Delta H_{3000} - T \Delta S_{3000} = 9,930 - 3,000 \times 11.22 = -23,730 \text{ cal/mole}$$

$$\log f = \frac{23730}{4.575 \times 3000} = 1.730$$

$$f_{\text{Rb}_2(\text{g})} = 53.7 \text{ atm}$$

The following is a summary of the calculations made:

Temp ° K	Fugacities (atm)		Total atm	Dimer %
	Rb (g)	Rb ₂ (g)		
1000	1.62	0.087	1.707	5.1
1073	2.996	0.197	3.193	6.19
1200	7.16	0.58	7.74	7.5
2000	115	17	132	12.85
3000	363	53.7	416.7	12.90

These values are for saturated vapor so that the dimer content will decrease from a shift in equilibrium constant as the superheat region is entered at constant pressure. By use of the corrected molecular weight of the rubidium vapor, the change in specific volume can be calculated and found to be negligible for preliminary studies based on all the other assumptions made.

2.9 Surface Tension of Rubidium

The following equation is an approximation which compares the surface tension of "anomalous" liquids. Liquid metal, as well as water is "anomalous".

$$\frac{\sigma_1}{\sigma_2} = \frac{(P_c^{2/3} T_c^{1/3})_1}{(P_c^{2/3} T_c^{1/3})_2} \quad (3.1)$$

where: σ = surface tension (dynes /cm)
 P_c = critical pressure (atmosphere)
 T_c = critical temperature ($^{\circ}\text{C}$)

A specified condition for equation (3.1) above is that:

$$\left[\frac{T}{T_c} \right]_1 = \left[\frac{T}{T_c} \right]_2 \quad (3.2)$$

where: T = temperature at which the surface tension is given:

The surface tension of Rb was calculated by comparing it with Na in equations (3.1) and (3.2) above. The critical temperature (T_c) of Rb was obtained by averaging two values reported in the literature*(4) (i.e., 1886°C and 1650°C , average = 1767°C). The surface tension of Na is 200 dynes/cc at 250°C (11). Using the above values in equation (3.2), the temperature at which the Rb surface tension is given is calculated to be 220°C . Substituting these values in equation (3.1), the Rb surface tension is calculated as 102 dynes/cm.

To calculate the surface tension of Rb at 700°C , a temperature of interest for reactor application, the following equation (12) was used:

$$\sigma = k \left(\frac{\rho}{M} \right)^{2/3} (T_c - T) \quad (3.3)$$

where: σ = surface tension (dynes/cm)

k = constant, usually 2.12

p = density (g/cc) at a corresponding temperature T ($^{\circ}$ C)

M = molecular weight

T_c = critical temperature ($^{\circ}$ C)

From equation (3.3) the following relation is obtained:

$$\frac{\sigma_1}{\sigma_2} = \frac{k \left(\frac{\rho_1}{M_1} \right)^{2/3} (T_c - T_1)}{k \left(\frac{\rho_2}{M_2} \right)^{2/3} (T_c - T_2)} \quad (3.4)$$

From equation (3.5) the surface tension of Rb at 700° C is calculated to be 66 dynes/cc.

The following table lists results obtained above.

	Critical Pressure P_c (atmosphere)	Critical temperature T_c ($^{\circ}$ C)	Surface Tension (dynes/cc)	Temperature for which the surface ten. is ($^{\circ}$ C)
Na	340 (7)	2000 (7)	200 (7)	250
Rb	131.7 (9)	1767 (6)	66 102	700 220

(9) This report see page (see original draft)

(7) see preceeding page (NAA)

(6) reference for values used in averaging

A second method of calculating surface tension was used in order to conform the results obtained by the preceeding equations (3.1) thru (3.5) This method involves the use of a "Parochor" (10) which is defined by the equation:

* This value should be revised to conform with more recent calculation found on page of this report. At the time of this cacl. these were available however, the error in the surface tension would not exceed 10%.

$$[P] = M \sigma^{1/4} (D - d) \quad (3.6)$$

where $[P]$ = "Parochor"

M == molecular weight

σ = surface tension, (dynes/cm)

D = liquid density (g/cc)

d = vapor density (g/cc)

The "Parochor" is given in the reference (13) for several common elements and compounds. A plot of (P) vs atomic weight shows that the P for elements of the same family is a straight line for atomic weights above 35. Also, these straight lines are roughly parallel. These observations were used to obtain a value of (P) for Rb.

The (P) for Na and K was found by evaluating equation (3.6). These values were plotted and a straight line drawn thru them on a linear plot. This line was roughly parallel to those for other families. A value of (P) for Rb was obtained by interpolating according to its atomic weight (85.48) on the line for other members of the family. The value obtained for (P) was 158. Substituting this value for Rb in equations (3.6) the surface tension value was calculated to be 34 dynes/cm. This compares favorably with 66 dynes/cm, the value obtained by using equations (3.1) thru (3.5). For other calculations, the value of 66 dynes/cm is used for Rb surface tension.

2.10 Coefficient of Cubical Expansion for Rubidium

The coefficient of volume expansion is defined by the following equation:

$$\beta = \frac{dV(T)}{V(T) \cdot dT} \quad (4.1)$$

where: β = coefficient of volume expansion

$V(T)$ = volume in cc at a specified temperature

T = temperature, °C

The density of Rb varies linearly with temperature as shown by Fig. 2.2 Rb density vs. temperature. It can be shown that equation (4.1) can be expressed as:

$$\beta(T) = - \frac{\Delta \rho(T)}{\rho(T) \Delta T} \quad (4.6)$$

where: $\frac{\Delta \rho}{\Delta T}$ = slope of the density vs. temperature curve

From Fig. 2.2, the coefficient of volume expansion for Rb is determined to be:

$$\text{Rb } \beta(688^\circ\text{C}) = 4.68 \times 10^{-4}$$

2.11 Heat Transfer Properties

For reference in determining the heat transfer properties of Rb the following table lists some of the physical properties of Rb at its boiling point (688°C) under a pressure of one atmosphere. Water and mercury also listed for comparison and assistance in the following calculation.

	Boiling temp. (°C)	Density (g/cc) B.P.	Viscosity (g/sec - cm)	Heat Cap. Cp (Cal/g cm)	Thermal Cond. k (cal/sec-cm°C)	coeff. of volume expansion (°C ⁻¹)	Latent heat of vaporization (cal/g)	Surface ten. dynes/cm
H ₂ O (14)	100	0.959	2.838 x 10 ⁻³	1.011	1.68	750	540	59
Rb	688(2)	1.1675	1.55 x 10 ⁻³	0.085	0.049	4.68 x 10 ⁻⁶	212	66
Hg	357(2)	12.881 (2)	1.01 Cp	0.0325 (2)	0.0303 (2)		69.7 (2)	394 (2)

Analytical correlation of boiling rubidium to boiling water and boiling mercury is found as follows:

a. Method of Approach

Some data are known for boiling water. Since almost nothing is known about Rubidium, data for this metal were estimated by correlating the water and mercury data to rubidium through dimensionless parameters.

b. Results

The results of a dimensionless parameter correlation between boiling water, mercury and rubidium are listed below and compare the heat flux (Btu/hr. ft^2) and/or the heat transfer coefficient ($\text{Btu/hr.ft}^2\text{-}^\circ\text{F}$) at a pressure of one atmosphere. The terms "mild" and "violent" boiling are defined in the reference (15) and are based, in general, on the magnitude of the temperature differential between the wall and the fluid mean temperature. For formulae and calculations for these results, see Appendix .

TABLE

HEAT FLUX COMPARISONS FOR BOILING RUBIDIUM,
BOILING WATER, AND BOILING Hg AS IT IS RELATED
TO BOILING WATER TAKEN AS 1.0

	<u>Mild boiling (1)</u> <u>(for same ΔT)</u>	<u>Violent boiling (1)</u> <u>(for same ΔT)</u>	<u>Peak Heat flux</u> <u>(without film boiling)</u>
H ₂ O	1.0	1.0	1.0
Rb	6.27	10 ^{8*}	4.12
Hg			

c. Conclusions

The results tabulated above indicate that more heat can be transferred in a boiling Rubidium system than in a comparable boiling water

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system. It should be strongly emphasized, however, that these results were obtained from empirical formulae that have not been experimentally tested for use with liquid metals. Therefore, they should be used qualitatively and with caution to indicate trends only.

The ability to wet a surface is an important factor in film boiling. It was observed that liquid Rb wets a glass surface very well, and much better than water.

2.12 References

- (1) Chemical Rubber Handbook
- (2) Liquid Metals Handbook
- (3) N. N. E. S., L. L. Quill
- (4) Gmelins Handbook
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3.0 THERMODYNAMIC DIAGRAMS FOR RUBIDIUM

3.1 Introduction

The power cycle analysis of the feasibility of using boiling rubidium as a heat transfer medium could not be accomplished without reference to thermodynamic data on rubidium, liquid and vapor. To facilitate the cycle analysis, temperature-entropy (T-S) and enthalpy-temperature (H-S) diagrams were constructed utilizing the data available in the literature.

For a first approximation it was assumed that all of the rubidium liquid dissociated completely into a monatomic vapor. Using this major assumption the idealized temperature-entropy (T-S) (Fig. 3, 4) and enthalpy-entropy (H-S) diagrams (Figure 3.6) were constructed. The following additional assumptions were made in constructing the diagrams:

1. The latent heat of vaporization, L_v , is constant.
2. The superheated rubidium vapor is a perfect monatomic gas and its specific heat is equal to $5/2 R$ (R is the ideal gas constant).
3. In the liquid-vapor region, the specific volume of the liquid is negligible as compared to the specific volume of the vapor.

The following fundamental thermodynamic values for rubidium were used in the preparation of the temperature-entropy and enthalpy-entropy diagrams:

1. Vapor pressure versus reciprocal of absolute temperature data, (Figure 3.1) (Ref.1) (Table 3.1) and the derived vapor versus temperature curve. (Figure 3.2)
2. Specific heat of rubidium liquid, $C_{p1} = 7.80 \text{ cal/gm mol} = 380.56 \text{ BTU /#}$, (Ref. 2).

3. Latent heat of vaporization, $L_v = 18,120 \text{ cal/gm mol} = 380.56 \text{ BTU/\#}$. (Ref.2)
4. Specific heat of rubidium vapor, $C_{pv} = 5/2 R = .0581 \text{ BTU/\#, } ^\circ\text{F}$.
5. Melting point $= 39.0^\circ\text{C} = 312.2^\circ\text{K} = 102^\circ\text{F} = 562^\circ\text{R}$.
6. Molecular weight of rubidium $= 85.48$
7. Estimations of the critical temperature vary from 1800°K (2780°F) when estimated by the method of Watson to over 3000°K (Ref.5). The latter value is considered to be closer to the actual critical temperature.
8. The critical pressure is estimated to be over 250 atmospheres. (Ref. 5)

The reference temperature used in the construction of the temperature entropy and enthalpy-entropy diagrams was the melting point of rubidium, 102°F .

3.2 Temperature - Entropy Diagram

Using the fundamental thermodynamic values given above, the data required to construct the temperature-entropy diagram were calculated and the chart plotted (See Fig. 3.3 and 3.4) (Table 3.2). The equations used and the method of calculating the necessary points to establish the constant-pressure line on the diagram for two atmospheres is as follows:

3.2.1 Entropy of the saturated liquid, S_1

$$S_1 = \int_{T_0}^{T_b} C_{pl} dT/T = C_{pl} \ln T_b / T_0$$

$$C_{pl} = \text{specific heat of the liquid} = 7.80 \text{ cal/gm mol. } ^\circ\text{C} = .0912 \text{ BTU/\#, } ^\circ\text{F}$$

$$T_b = \text{boiling temperature of Rb at 2 atmospheres} = 747^\circ\text{C} = 1020^\circ\text{K} = 1380^\circ\text{F} = 1840^\circ\text{R}$$

$$T_0 = \text{reference temperature} = 39.0^\circ\text{C} = 312.2^\circ\text{K} = 102^\circ\text{F} = 562^\circ\text{R}$$

$$S_1 = 7.80 \ln 1020/312.2 = 9.24 \text{ cal/gm mol, } ^\circ\text{C,} = 0.108 \text{ BTU/\#, } ^\circ\text{F}$$

2. Entropy of vaporization, ΔS_{lv}

$$\Delta S_{lv} = L_v/T_b$$

$$L_v = \text{latent heat of vaporization} = 18,122 \text{ cal/gm mol} = 380.56 \text{ BTU/\#}$$

$$T_b = \text{temperature of vaporization} = 747^\circ\text{C} = 1020^\circ\text{K} = 1380^\circ\text{F} = 1840^\circ\text{R}$$

$$\Delta S_{lv} = 380.56/1840 = 0.207 \text{ BTU/\#, } ^\circ\text{F}$$

3. Entropy of saturated vapor, S_v

$$S_v = S_l + S_{lv}$$

$$S_v = .108 + .207 = .315 \text{ BTU/\# } ^\circ\text{F}$$

4. Entropy of superheated vapor, ΔS_{sv}

$$\Delta S_{sv} = \int_{T_b}^{T_{sv}} C_{pv} \frac{dT}{T} = C_{pv} \ln T_{sv}/T_b$$

$$C_{pv} = \text{specific heat of vapor} = .0581 \text{ BTU/\#, } ^\circ\text{F}$$

$$T_b = \text{temperature of vaporization} = 1840^\circ\text{R}$$

$$T_{sv} = \text{temperature of superheated vapor} = 2100^\circ\text{F} = 2560^\circ\text{R (selected temperature)}$$

$$\Delta S_{sv} = .0581 \ln 2560/1840 = .0191 \text{ BTU/\# } ^\circ\text{F}$$

The variation of temperature with entropy at constant pressure in the superheated vapor region was found to be very nearly linear when plotted on the scale used in Figure 2.21 and all such curves were drawn as straight lines.

The data needed for the construction of lines of constant specific volume in the vapor region were obtained by using the Ideal Gas Equation. The specific volume of the saturated vapor at a selected pressure was calculated and then, maintaining this calculated specific volume as a constant, the pressure corresponding to an arbitrarily selected temperature was calculated. By reference to a crossplot of pressure versus entropy for various constant temperatures (Figure 2.22) the entropy corresponding to the originally calculated specific volume at the selected temperature was

determined. By repeating this procedure for several selected temperatures, with the specific volume constant, data necessary to construct the constant specific volume line in the vapor region were obtained: (Table 3.3)

$$P_t \bar{V} = RT/W$$

$$\bar{V} = \text{specific volume, ft}^3/\#$$

$$R = \text{Ideal Gas Constant} = .729 \text{ atmospheres ft}^3/\# \text{ mol } ^\circ\text{R}$$

$$T = \text{temperature, } ^\circ\text{R}$$

$$W = \# \text{ atomic weight} = 85.48 \#/\text{mol}$$

$$P_t = \text{pressure, atmos.}$$

$$P_t = .729T/85.48 \bar{V} = .008528T/\bar{V}$$

$$\bar{V} = .008528 T/P_t$$

Example

When the pressure equals 0.5 atmospheres the saturated vapor temperature equals $1130^\circ\text{F} = 1590^\circ\text{R}$.

$$\bar{V} = .008528 \times 1590 / .5 = 27.12 \text{ ft}^3/\text{lb}$$

Using $P_t = .008528 T/\bar{V}$ and holding $\bar{V}$ constant at $27.12 \text{ ft}^3/\#$ while selecting temperatures corresponding pressures are found. By referring to Figure 3.2 the values of entropy for these pressures are taken from the constant temperature lines.

Temperature, $^\circ\text{R}$	Pressure, atmos.	Entropy, Btu/ $\#^\circ\text{F}$
1660	.522	.336
1860	.585	.342
2-60	.648	.345
2260	.711	.350
2560	.805	.355

A plot of these temperatures versus corresponding values of entropy determines the location of the line of constant specific volume of $27.12 \text{ ft}^3/\#$

The lines of constant quality in the liquid-vapor region were determined graphically by taking the direct proportion of the length of a given constant

temperature line. Thus all points of 50% vapor fall on the midpoints of the constant temperature lines between S_L and S_V .

Since the region of interest lies in the quality range of from 50 to 100 per cent it may be assumed that the specific volume of the liquid in the liquid-vapor region is very small as compared to the specific volume of the vapor. In this case the specific volume of the liquid-vapor mixture is equal to the specific volume of the vapor and can be represented by the following equation:

$$\bar{V}_V = f\bar{V}$$

$\bar{V}_V$ = specific volume of vapor in the liquid-vapor region

f = fraction of vapor in the liquid-vapor mixture, or quality in percent.

$\bar{V}$ = specific volume of saturated Rb vapor

By dividing a selected value of $\bar{V}_V$ by the value of $\bar{V}$ corresponding to a given T and P_t combination the value of f for the known $\bar{V}_V$ value can be calculated. (Table 3.4 and 3.5). This establishes the point on the temperature-entropy diagram where constant T , f and $\bar{V}_V$ lines intersect.

Example

For a temperature of 1060° F (1520°R) and a corresponding P_t of 0.31 (Fig. 3.2) calculate the value of $\bar{V}$.

$$\bar{V} = .008528 T/P_t = .008528 \times 1520 / .31 = 41.81 \text{ cu ft/lb.}$$

Selecting $\bar{V}_V$ to equal 27.12 fixes the value of the constant $\bar{V}_V$ line to be drawn.

$$f = \bar{V}_V / \bar{V} = 27.12/41.81 = 0.649 = 64.9\%$$

These values of $T = 1520^\circ\text{R}$, $f = .649$ and $\bar{V}_V = 27.12$ fixes a point on the constant $\bar{V}_V$ line.

3.3 Temperature - Enthalpy Diagram

The data required for the construction of the enthalpy-entropy diagram for rubidium (Fig. 3.5 and 3.6) were also calculated using the available thermodynamic

values of C_p , L_v , C_{pv} , and choosing the base temperature for zero enthalpy to be 102°F , the melting point of rubidium (Tabs. 3, 6, 3-7). The equations used and the method of calculating data required for the construction of the enthalpy-entropy diagram using as an example a constant pressure of two atmospheres is as follows:

3.3.1. Enthalpy of saturated liquid, H_l

$$H_l = \int_{T_o}^{T_b} C_{pl} dT = C_{pl} (T_b - T_o)$$

$$C_{pl} = 7.80 \text{ cal/gm mol}, ^\circ\text{C} = .0912 \text{ Btu/}\#, ^\circ\text{F}$$

$$T_b = \text{boiling temperature}, ^\circ\text{F} = 1380^\circ\text{F}$$

$$T_o = \text{reference temperature} = 102^\circ\text{F}$$

$$H_l = .0912 \times (1380 - 102) = 116.55 \text{ Btu/}\#$$

3.3.2. Enthalpy of vaporization

L_v , has been assumed to be constant and is equal to $380.56 \text{ Btu/}\#$.

3.3.3. Enthalpy of vapor due to superheat, H_{sv}

$$\Delta H_{sv} = \int_{T_b}^{T_{sv}} C_{pv} dT = C_{pv} (T_{sv} - T_b)$$

$$T_b = \text{temperature of vaporization} = 1380 ^\circ\text{F}$$

$$T_{sv} = \text{temperature of superheated vapor} = 2100 ^\circ\text{F (selected)}$$

$$C_{pv} = \text{specific heat of vapor} = .0581 \text{ Btu/}\# ^\circ\text{F}$$

$$\Delta H_{sv} = .0581 (2100 - 1380) = 41.83 \text{ Btu/}\#$$

3.3.4. Enthalpy of saturated vapor, H_v

$$H_v = H_l + L_v$$

$$H_v = 116.55 + 380.56 = 497.11 \text{ Btu/}\#$$

3.3.5. Total enthalpy, H

$$H = H_l + L_v + \Delta H_{sv}$$

$$H = 116.55 + 380.56 + 41.83 = 538.94 \text{ Btu/}\#$$

The entropy corresponding to all the above enthalpy values can be obtained from the temperature-entropy diagram since the pressure, two atmospheres, and the temperatures are known.

The lines of constant quality may be transposed directly from the temperature-entropy diagram (Fig. 3a) by reading the intersection of constant quality, pressure, and entropy lines.

The lack of P-V-T data in the literature makes it impossible to plot complete diagrams for T-S and H-S relations from the melting point of the liquid to the critical temperature for the vapor as shown by Fig. 3b and 3c. Fortunately, the region of interest is far removed from the critical region so that enlarged sections were drawn for reference as shown by Fig. 3d and 3e.

TABLE 3.1

VAPOR PRESSURE-TEMPERATURE DATA FOR RUBIDIUM

<u>Vapor, Pressure, atmospheres</u>	<u>T, °K</u>	<u>T, °F</u>	<u>Reference</u>
1×10^{-6}	403	266	Brewer (1)
1×10^{-5}	445	341	"
1×10^{-4}	496	433	"
1×10^{-3}	561	544	"
1×10^{-2}	650	710	"
1	952	1254	"
1.32×10^{-3}	567	561	Liquid Metals Hand-
1.32×10^{-2}	660	729	book (2)
1.32×10^{-1}	792	966	"
2.63×10^{-1}	842	1056	"
5.26×10^{-1}	901	1162	"

TABLE 3.2

ENTROPY OF RUBIDIUM IN THE SATURATED REGION

$T, ^\circ F$	$T, ^\circ R$	$S_1, \text{Btu}/\#^\circ F$	$\Delta S_{1v}, \text{Btu}/\#^\circ F$	$S_v, \text{Btu}/\#^\circ F$
102	562	0	.677	.677
122	582	.003	.654	.657
212	672	.016	.566	.582
392	852	.038	.447	.485
572	1032	.056	.369	.425
752	1212	.073	.314	.387
932	1392	.083	.273	.356
1112	1572	.094	.242	.336
1292	1752	.104	.217	.321
1380	1840	.108	.207	.315
1454	1914	.112	.119	.311
1472	1932	.113	.197	.310
1652	2112	.121	.180	.301
1832	2292	.129	.166	.295
2000	2460	.135	.155	.290
2732	3192	.159	.119	.278

TABLE 3.3

ENTROPY OF SUPERHEATED RUBIDIUM VAPOR

<u>Pressure, P_t, Atmos.</u>	<u>T, °F</u>	<u>T, °R</u>	<u>S_v</u>	<u>ΔS_{sv}</u>	<u>S_{total}</u>
.01	706	1166	.396		.396
	1400	1860		.027	.423
	2000	2460		.043	.439
.02	770	1230	.383		.383
	1400	1860		.024	.407
	2000	2460		.040	.423
.04	832	1292	.372		.372
	1400	1860		.021	.393
	2000	2460		.037	.409
.10	922	1382	.358		.358
	1400	1860		.017	.375
	2000	2460		.034	.392
.20	1000	1460	.348		.348
	1400	1860		.014	.362
	2000	2460		.030	.378
.50	1130	1590	.334		.334
	2000	2460		.025	.359
1.0	1254	1714	.323		.323
	2000	2460		.021	.344
2.0	1380	1840	.315		.315
	2000	2460		.017	.332
3.0	1454	1914	.311		.311
	2000	2460		.015	.326
4.0	1500	1960	.308		.308
	2000	2460		.013	.321
6.0	1609	2069	.303		.303
	2000	2460		.010	.313
8.0	1670	2130	.301		.301
	2000	2460		.006	.307

TABLE 3.4

SPECIFIC VOLUME OF SUPERHEATED RUBIDIUM VAPOR

$\bar{V}$, ft ³ /#	T , °F	T , °R	P , atmos	S_{total} , Btu/#°F
997.8	710	1170	.010	.396
997.8	1000	1460	.0125	.403
997.8	1200	1660	.0142	.405
997.8	1600	2060	.0176	.412
997.8	1800	2260	.0194	.417
997.8	2100	2560	.0219	.424
524.5	770	1230	.020	.383
524.5	1000	1460	.0237	.390
524.5	1400	1860	.0303	.396
524.5	1800	2260	.0366	.405
524.5	2100	2560	.0416	.413
275.7	832	1293	.040	.372
275.7	1000	1460	.0452	.378
275.7	1400	1860	.0576	.385
275.7	1800	2260	.0699	.393
275.7	2100	2560	.0792	.400
117.9	922	1382	.100	.315
117.9	1200	1660	.120	.365
117.9	1600	2060	.149	.372
117.9	2000	2460	.180	.381
62.25	1000	1460	.200	.348
62.25	1400	1860	.255	.356
62.25	1800	2260	.310	.365
62.25	2100	2560	.351	.371
27.12	1130	1590	.500	.334
27.12	1200	1660	.522	.336
27.12	1400	1860	.585	.342
27.12	1800	2260	.711	.350
27.12	2100	2560	.805	.355
14.62	1254	1714	1.00	.323
14.62	1600	2060	1.20	.335
14.62	2000	2460	1.435	.340
7.85	1380	1840	2.00	.315
7.85	1600	2060	2.24	.323
7.85	2000	2460	2.67	.327
5.44	1454	1914	3.00	.311
5.44	1800	2260	3.54	.318
5.44	2000	2460	3.86	.320
4.18	1500	1960	4.00	.308
4.18	1800	2260	4.61	.314
4.18	2000	2460	5.02	.315
2.94	1609	2069	6.00	.303
2.94	2000	2460	7.14	.308
2.27	1670	2130	8.00	.301
2.27	2000	2460	9.24	.302

TABLE 1.5

SPECIFIC VOLUME OF THE LIQUID-VAPOR MIXTURE

<u>$\bar{v}_v$, ft³/#</u>	<u>T, °F</u>	<u>T, °R</u>	<u>P_t, atmos</u>	<u>$\bar{v}$, ft³/#</u>	<u>f, quality</u>
524.5	710	1170	.010	997.8	.526
524.5	740	1200	.015	682.2	.769
275.7	770	1230	.020	524.5	.526
275.7	800	1260	.028	383.8	.718
117.9	850	1310	.048	232.7	.506
117.9	900	1360	.080	145.0	.813
62.25	900	1360	.08	145.0	.429
62.25	930	1390	.10	118.5	.525
62.25	960	1420	.14	86.50	.720
27.12	1000	1460	.20	62.25	.436
27.12	1060	1520	.31	41.81	.649
27.12	1100	1560	.41	32.45	.836
14.62	1100	1560	.41	32.45	.451
14.62	1200	1660	.74	19.13	.764
7.85	1200	1660	.74	19.13	.410
7.85	1300	1760	1.30	11.55	.680
5.44	1350	1810	1.74	8.77	.613
5.44	1400	1860	2.27	6.98	.779
4.18	1400	1860	2.27	6.98	.599
4.18	1450	1910	3.10	5.25	.796
2.94	1400	1860	2.27	6.98	.421
2.94	1450	1910	3.10	5.25	.560
2.94	1500	1960	4.00	4.18	.703
2.27	1550	2010	4.9	3.50	.649
2.27	1600	2060	6.0	2.925	.776
1.88	1600	2060	6.0	2.925	.641
1.88	1700	2160	8.7	2.115	.887

TABLE 3.6

ENTROPY AND ENTHALPY OF RUBIDIUM IN THE SATURATED REGION

<u>T, °F</u>	<u>T, °R</u>	<u>S_l, Btu/#°F</u>	<u>S_v, Btu/#°F</u>	<u>H_l, Btu/#</u>	<u>H_v, Btu/#</u>
102	562	0	.677	0	380.56
122	582	.003	.657	1.825	382.39
212	672	.016	.582	10.04	390.60
392	852	.038	.485	26.46	407.02
572	1032	.056	.425	42.89	423.45
752	1212	.073	.387	59.31	439.87
932	1392	.083	.356	75.74	456.30
1112	1572	.094	.336	92.16	472.72
1292	1752	.104	.321	108.59	489.15
1380	1840	.108	.315	116.62	497.18
1454	1914	.112	.311	123.37	503.93
1472	1932	.113	.310	125.01	505.57
1652	2112	.121	.301	141.44	522.00
1832	2292	.129	.295	157.86	538.42
2000	2460	.135	.290	173.19	553.75
2732	3192	.159	.278	239.99	620.55

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TABLE 3.7

ENTROPY AND ENTHALPY OF RUBIDIUM IN THE SUPERHEAT REGION

<u>P_t, atm</u>	<u>T_b, °F</u>	<u>H_v, Btu/#</u>	<u>T_{sv}-T_b</u>	<u>ΔH_{sv}, Btu/#</u>	<u>H, Btu/#</u>	<u>S, Btu/#°F</u>
.01	706	435.5	1294	75.18	510.7	.439
.02	770	441.5	1230	71.46	513.0	.423
.04	832	447.0	1168	67.86	514.9	.409
.10	922	455.0	1078	62.63	517.6	.392
.20	1000	462.5	1000	58.10	520.6	.378
.50	1130	474.5	870	50.55	525.1	.359
1.0	1254	485.5	746	43.34	528.8	.344
2.0	1380	497.0	620	36.02	533.0	.332
3.0	1454	504.0	546	31.72	536.7	.326
4.0	1500	508.0	500	29.05	537.1	.321
6.0	1609	518.0	391	22.72	540.7	.313
8.0	1670	523.5	330	19.17	542.7	.307
10.0	1740	530.0	260	15.11	545.1	.301

T_b = temperature of vaporization

T_{sv} = temperature of superheated vapor = 2000°F (selected)

H = H_v + ΔH_{sv} = total enthalpy

S = total entropy

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3.4 REFERENCES

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Fig. 3.1

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Fig. 3.2

Fig. 3.4

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4.0 COMPATIBILITY OF INCONEL AND RUBIDIUM AT ELEVATED TEMPERATURES

4.1 Handling of Rubidium Metal

Rubidium metal discolors immediately upon exposure to an inert atmosphere containing trace amounts of oxygen and/or water. There is considerable heat generated by these reactions which can become explosive in nature if not arrested by an exhaustion of the oxygen containing material.

It was found by experience that the solid metal does not always ignite spontaneously upon exposure to the atmosphere. A mixture of yellow and black oxides is produced on the surface as a protective crust for the metal underneath if water vapor is absent. Four of the oxides listed in the literature are:

monoxide	Rb_2O	yellow
dioxide	Rb_2O_2	yellow
trioxide	Rb_2O_3	black
tetroxide	Rb_2O_4	yellow

In all of this work it was considered safe to keep the rubidium metal in a Pyrex glass container which had been sealed under vacuum. Care was taken, however, to maintain the temperature below 25°C to avoid fusion and to store the sample in an isolated space in case of fire or explosion. A face shield must be worn upon exposure to any size sample because of the hazard involved. The glass ampules were not annealed after sealing so that a failure would occur occasionally.

Hydrogen is evolved by rubidium metal upon contact with either water or alcohol. The reactor can be violent with serious consequences if the proper precautions are not taken. Water must be excluded in the liquid state and all necessary treatments made to remove water vapor from the system for handling

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the metal. The mercury-like surface of the rubidium turns a dull gray upon contact with water vapor in a drybox. The Battelle Memorial Institute uses a molten alkali metal trap to remove water and oxygen from the fresh inert gas being supplied to a drybox. Ethyl alcohol is considered a convenient method of reacting the metal prior to disposal. This is best done, however, under a mixture of hexane and alcohol with an inert gas blanket of argon to exclude oxygen. This procedure was employed while recovering small samples of rubidium metal for rework. All the necessary safety precautions are employed because of the fire hazard, with remote operation preferred.

It is recommended that the liquid metal be handled inside a suitable drybox. This includes a vacuum system capable of 10^{-5} mm Hg for "pumping down" and an inert gas purifier of activated charcoal at the temperature of liquid nitrogen. Two or three flushes are required to purge the oxygen and water to a tolerable value for handling the molten metal. A Plexiglas dome is convenient for observing all operations. Shown in Figure 4.1 is the vacuum-dry-box made available at X-10, Bldg. 2000 by the courtesy of the Metallurgy Division. Experience with an atmospheric dry box equipped with an oxygen removal unit (catalytic) for the inert purge gas was not satisfactory.

The Pyrex ampules are opened inside the drybox by scratching the glass tubing and breaking off the end opposite to the charge of metal. The metal is then melted on a small hot plate with the Pyrex container standing inside a metal beaker having the bottom covered with a layer of shot for balancing. It is necessary to preheat the Pyrex funnel with an insulated electrical heating tape to avoid solidification upon pouring from the ampule to the new container. A temperature of about 75-100°C is preferred to permit easy flow of the liquid metal.

No success was experienced in an attempt to cast the rubidium metal into small diameter rods as is done with sodium. The solid was friable and did not retain its cylindrical shape. Amounts are best judged by comparison to a known volume in a similar vessel.

Samples of the liquid metal can be collected in vacuum-sealed tubes which are enlarged at one end to hold about 0.5 cc. Preheating of the capillary suction tube is needed to allow rapid flow of the metal into the evacuated chamber after breaking off the pointed tip under the surface of the metal.

The liquid metal can be filtered through a sintered glass funnel by arranging to apply about 5-10 psig pressure differential across the filter medium while maintaining a temperature of 75-100 °C. This is used to remove dirt and insoluble oxides of the crude metal if a vacuum distillation cannot be performed.

The tubular metal capsules used for corrosion tests were closed inside the dry box by attaching a rubber hose with a clamp. It was then evacuated outside the dry box and crimped in a hydraulic press to close using about 20,000 psig. The excess tubing was removed with a hack saw prior to sealing by Heliarc welding along the cut edge. Rubidium metal must be excluded near the zone of crimping to permit a satisfactory weld.

Residues from capsule corrosion tests and/or ampules were removed from the dry box with the metal in the solid state. The residual metal was reacted with alcohol under an argon blanket as described previously. In some cases it is necessary to dilute the alcohol with water to remove the hydroxide and/or oxide protective layer. Extreme care is required to avoid accumulation of metal and alcohol in a "pocket" which will eventually be exposed to air. Keep other solvents away, especially acetone.

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In general, extreme care must be taken by those handling alkali metals. Hydrocarbons such as mineral oil and kerosene are standard agents used to protect the metal by preventing contact with air, but this practice leaves much to be desired where purity of the metal is important. Shipment over long distances can be made in sealed containers which have an inert packing around the ampule containing the alkali metal.

4.2. The Corrosion of Inconel by Rubidium

4.2.1 Introduction

Before rubidium can be seriously considered as an engineering material, its corrosiveness to possible container materials, at proposed operating temperatures, and under conditions as nearly simulating proposed operating conditions as possible, must be obtained.

The accepted procedure for evaluating an alloy proposed for use as a container material for a liquid metal is to first conduct static capsule tests in which the liquid is sealed within a small container of the alloy and held at the desired temperature for an extended period of time. If the alloy successfully passes this screening test it is next exposed to the liquid metal in a system which incorporates contact with flowing liquid metal at elevated temperature, with a temperature gradient present in the system.

The wholehearted cooperation of the Metallurgy Division, ORNL, made it possible to complete two Inconel-Rubidium static capsule tests and one dynamic-closed-loop test during the time allotted for this project.

The entire fabrication and operation of the capsule and boiling loop tests were conducted by E. E. Hoffman and associates. The rubidium metal was vacuum distilled by John V. Cathcart. Metallographic examinations of the sectioned capsules and loop were conducted by R. J. Grey and associates.

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X-ray analysis of a rubidium-sodium alloy and the precipitate found in the boiling loop was conducted by R. M. Steele.

J. C. White and associates, ANP Analytical Chemistry Division, conducted the chemical analyses of the rubidium.

4.2.2 1540 Degree F. Inconel-Rubidium Capsule Test

The first capsule test consisted of an Inconel tube 10" long, having a 1" inside diameter with heliarc welded end plugs, and a heliarc welded thermocouple well of 1/4" tubing extending upward from the base of the capsule to above the bath level. The capsule was hydrogen annealed at 1950°F for 20 minutes. The volume of rubidium during the test is estimated to be 1.5 cc. The exact volume is unknown because a portion of the rubidium distilled out of the capsule early in the test through a capillary tube attached to a bourdon-tube pressure gage connected to the top of the capsule. The rubidium was placed in the capsule and the capsule sealed by heliarc welding in a drybox which had been purged by alternately evacuating and flushing with purified helium. The assembled capsule was evacuated to approximately 100 microns pressure and sealed by crimping and heliarc welding the evacuated tube.

The capsule was placed in a Globar electric furnace and heated to a temperature of 1560 degrees F. This temperature was maintained for 101 hours. The control temperature of 1540 degrees F. was measured by a thermocouple placed in a thermocouple well in the center of the base of the capsule which extend into the capsule to above the level of the rubidium bath. The capillary tube extending from the top of the capsule outside the furnace to a pressure gage became plugged during the first five hours of heating before equilibrium furnace temperature was attained.

After removing the capsule from the furnace the capillary tube was crimped and cut close to the capsule. The capsule was placed under inert atmosphere in a drybox, and the upper inch removed with a tube cutter. The opened capsule was heated to a temperature of approximately 150°F, which is well above the melting point of rubidium, and inverted. No rubidium liquid could be poured from the capsule, nor could any liquid, or solid, be seen by looking through the plastic drybox cover into the capsule. The capsule was removed from the drybox and after a few seconds exposure to the air it was noticed that a liquid was now present in the capsule. The capsule was immediately returned to the drybox and approximately 1.5 cc of a golden colored metallic liquid, very clean in appearance, was readily poured from the capsule. The approximate freezing point of the liquid was determined to be 14°F and the melting point 23°F. These temperatures were determined by immersing the glass bottle containing the rubidium alloy in an acetone and dry ice bath.

The small amount of golden liquid that clung to the walls of the test capsule was rapidly attacked upon exposure to air and a white hygroscopic film, probably RbOH, formed.

The gold colored liquid was analysed to contain:

<u>%</u>	<u>Relative Error %</u>
91.4% Rb	1
7.8% Na	1
.52 K	10
.25 Ca	10
2.05 O ₂	10

No significant amount of Fe, Cr, or Ni could be detected. Since 7.8% sodium is far in excess of the percentage found in any of the other rubidium samples analyzed it is postulated that the sample became enriched in sodium, as well as potassium and calcium by the distillation of rubidium out of the capsule into the bourdon-tube and capillary while the capsule was being heated to the test temperature.

Although the rubidium had been slightly contaminated by very short exposure to air prior to insertion in the test capsule during handling, after reduction of the RbF, it was silver in color with a melting point of approximately 95 degrees F.

Evidently increasing the concentration of sodium, or oxygen, in rubidium markedly lowers the melting point of the alloy in the composition range considered. The Rb-Na binary diagram (Reference 1) exhibits a low melting eutectic having about the same Rb-Na composition and melting point as the liquid analyzed. However, the fact that the liquid was not molten until it had been exposed to the air indicates that the addition of oxygen to rubidium in concentrations of between 0 to 2% lowers the melting point. This lowering of the point is accompanied by a gradual color change from silver to gold. This lowering of the melting point to below room temperature, accompanied by the color change, has been noted on several occasions when small quantities of Rb metal in the bottom of open flasks were exposed to air.

A metallographic examination of the surface of the Inconel capsule which was exposed to the rubidium alloy reveals that corrosion by the mechanisms of void formation and, or, intergranular penetration is not excessive.

In the vapor zone general void corrosion is evident to the depth of only .0005 inch with no sign of grain boundary corrosion (Figure 4.1).

In the region of the bath-vapor interface subsurface void formation was observed to a depth of .001 inch. (Figure 4.2).

The subsurface corrosion penetration in the zone below the liquid level was less than .0005 inch. (Figure 4.3).

A sample of the Rubidium-Sodium liquid was submitted for X-ray Analysis - The analysis was conducted by R. M. Steele.

The sample was carefully frozen by a jet of He passed through coils of copper tubing immersed in liquid N_2 . A Debye Scherrer pattern was taken and the measured defraction lines are listed in Table 4.1.

TABLE 4.1

Line Intensity	λ	Rb_2O	RbO_2	RbN_3	RbOH
M	8.715				
M	7.761				
S	7.025		001		
W+	6.559				
W	6.006		100		002
M	5.293				
M	4.495		101	100	
S	4.055		110		011,003
S+	3.743			001	
S+	3.504		002		012
S+	3.378	200			
W-	3.145			110	
W+	2.943			101	013
W+	2.826				
S	2.661		201		
W+	2.565				
W	2.472				104,014
S+	2.387	220			113
W	2.341		003		
W	2.241			200	
W-	2.142		212		200,114
W-	2.095		220		105
M	1.953	222		201	202
M-	1.884			002	121,115
W	1.787			211	212
W	1.755		004,213		024
M-	1.704		302	102	007,123
W+	1.593			220	214
W-	1.554				
M	1.512	420	204	300	117
M	1.380	422	402	212	300
W-	1.286				312
W-	1.250			320	313
W-	1.199	440			
W+	1.127	600			
W+	1.071	620			
W	1.054	533			
W-	.9786	444			
W	.9394	640			

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Figure 4.1 Inconel Exposed to Rubidium Vapor for 101 Hours
at 1540°F. Magnification: 1000X

Figure 4.2 Inconel from The Region of The Bath-Vapor Interface
Following an Exposure of 101 hours at 1540°F.
Magnification: 1000X Specimen was Nickel Plotted
Following Test.

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Figure 4.3 Inconel Exposed to Liquid Rubidium for 101 Hours
at 1540°F. Magnification: 1000X Etchant:
Glyceria Regia

Figure 4.4 Intergranular Corrosion of Inconel by Rubidium Vapor.
Section of A Weld Following Exposure for 101 Hours
at 1540°F. Magnification: 1000X

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Wyckoff lists the following values:

Rb	body centered cubic	a = 5.709 Å°		
RbOH	orthorhombic	a = 4.15 Å°	b = 4.30 Å°	c = 12.2 Å°
Rb ₂ O	face centered cubic	a = 6.742		
RbO ₂	Tetragonal	a = 6.00		c = 7.03
RbN ₃	Tetragonal	a = 4.497		c = 3.707

It is believed that this sample contains Rb₂O, RbO₂, and possibly some RbN₃ and RbOH. A number of diffraction lines are unexplained indicating at least one other phase was present.

The attack in the region of the liquid-vapor interface, although deeper, is not as general as the attack in the liquid and vapor region. Subsurface voids were more widely scattered. Evidence of intergranular void penetration was found in the weld sealing the tip of the thermocouple well. This tip was in the vapor zone approximately .25 inch above the bath level. The only visible corrosion in the weld metal was intergranular voids to a depth of .001 inch. (Figure 444).

Although no change in weight measurements were made to determine the amount of general surface corrosion, the absence of appreciable percentages of Be, Cr, and Ni in the residual alloy indicates that little general surface corrosion occurred.

The surface to volume ratio was large enough to allow saturation of the alloy with Fe, Ni and Cr in a short time if solution corrosion was present and the vapor would not transport Fe, Cr, or Ni so that corrosion could continue by mass transfer.

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4.2.30 1650 Degree F Inconel - Rb Capsule Test

The capsule for the second Inconel-Rb capsule test was a .10" long section of .5" outside diameter Inconel tubing, having a .035 inch wall thickness which had been hydrogen annealed at 1950 °F for 20 minutes. One end of this tube was pressed flat and sealed by heliarc welding. A sample of Inconel having dimensions .035" by .25" by .5" cut from tubing and flattened was placed in the tube and 3 cc (4.5 grams) of vacuum distilled Rb was loaded into the capsule under a helium atmosphere in a drybox. A rubber tube was attached to the capsule and sealed with a hose clamp. The loaded tube was removed from the dry box, attached to a vacuum pump and the top pressed flat, crimped, and heliarc welded. The sealed Inconel tube containing Rb under a vacuum was then placed inside a section of heavy wall 304 stainless steel pipe, and closed by heliarc welding in air.

The assembly was placed in a cold furnace, heated in 3 hours to 1650 °F and this temperature was maintained for 100 hours, not including time lost by one shutdown of the furnace due to an electrical malfunction.

When the assembly was removed from the furnace the 304 stainless steel cylinder ends were found to be distorted due to internal pressure during the heating. In a dry-box under a helium atmosphere the outer cylinder was opened with a tube cutter. Upon examining the Inconel tube it was found that the internal pressure due to Rb vapor, of approximately 110 psi at 1650°F, had deformed the upper end of the Inconel tube, which had been pressed flat, to a configuration almost cylindrical. The sharp reversed bending at the edge of the flattened tube parallel to the tube axis had resulted in a failure of the metal and Rb vapor had leaked into the outer cylinder to equalize the pressure. The leak did not occur in the weld.

It is not believed that any of the air within the outer container entered the interior of the Inconel capsule since the break in the wall was very small and at the test temperature the air should react immediately with the escaping Rb.

A partial analysis of the Rb metal removed from the capsule at the conclusion of the test revealed the following composition:

Na	350 parts per million
O	.11 %
Fe	20 parts per million
Ni	less than 10 parts per million
Cr	less than 10 parts per million

No indication of corrosion of the Inconel specimen that was immersed in the Rb bath during the test could be found. The weight of the specimen at the conclusion of the experiment was the same as that recorded before immersion in the Rb. A metallographic examination of the sample did not disclose any sign of corrosion (Figure 4.5).

A metallographic examination of the wall of the Inconel capsule in the region that was exposed to Rb liquid (Figure 4.6) disclosed general surface roughening and intergranular voids to a depth of .0025 inches. A band of the precipitates appears parallel to the surface at a depth of from .015 to .003 inches. A possible explanation of the difference in corrosion of the tube wall and that of the specimen is that the tube wall was stressed during an undetermined portion of the 100 hours by the 110 psi internal pressure. The corrosion of the Inconel by Rb at 1650 °F may be increased if the Inconel is under stress. Further evidence to support this contention may be seen in Figure 4.7 which is a photograph of the fracture that allowed the Rb vapor to escape and equalize

Figure 4.5 Inconel Exposed to Liquid Rubidium at 1650°F for 100 Hours. Specimen was Nickel Plated Following Test. Magnification: 1000X

Figure 4.6 Inconel Capsule Wall Exposed to Liquid Rubidium at 1650°F for 100 Hours. The Capsule was Stressed by an Internal Pressure of 110 psi. Magnification: 1000X

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Figure 4.7 Region of Fracture in Inconel Tube Following Exposure to Rubidium Vapor for 100 Hours at 1650°F. Magnification: 150X Etchant: Glyceria Regia

the pressure on the Inconel tube wall. This area was exposed to Rb vapor. The metal adjacent to the fracture which was subjected to the highest stresses has been generally attacked along the grain boundaries. It may be generally concluded that the static corrosion of Inconel by Rb at 1650°F is not excessive if the Inconel is not simultaneously subjected to high stresses.

4.2.4 Boiling Rubidium - Inconel Loop

The resistance of Inconel to corrosion by flowing liquid, and vapor, rubidium in a closed system incorporating a temperature gradient was determined by means of a dynamic loop apparatus somewhat similar in appearance to the conventional "thermal harp". The loaded loop is shown in Figure 4.8 prior to attaching the thermocouples and resistance furnaces.

The loop was constructed entirely of Inconel. The boiler and vapor separator section and the superheated vapor line were of 0.500 inch outside diameter tubing with 0.049 inch wall thickness. The remainder of the loop was of tubing having a 0.250 inch outside diameter and 0.035 inch wall thickness. The tapered sections at the ends of the .500 inch tubing were formed by swagging. The upper end of the boiler section was left open to provide a means of loading and evacuating the loop.

The loop was placed in a drybox and loaded with 8 to 9 cc of vacuum distilled rubidium in a helium atmosphere. This quantity of rubidium filled the loop to the level indicated in Fig. 4.8. A short section of rubber tubing was attached to the open tube and sealed with a hose clamp. The loop was now removed from the drybox and the short section of rubber tubing was connected to a vacuum system, the hose clamp removed, and the loop evacuated. With the vacuum system still connected the charging tube was pressed flat and crimped. The vacuum line was removed and the end of the tube sealed by heliarc welding. Chromel-alumel thermocouples were next spot welded to the outside of the loop. The

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location of the thermocouples and the overall dimensions of the assembly are shown in the line drawing, Figure 4.8a.

A 12 inch clam shell resistance furnace was installed on the boiler and vapor separator section of the loop in the location indicated on Figure 4.9. This furnace was insulated and the remainder of the loop left bare. When current was applied to the furnace the boiler leg rapidly heated to the desired test temperature but the thermocouple located on the superheated vapor line remained cold. When heat was applied with a torch to the condenser and aftercooler section to insure that the rubidium was molten the temperature of the superheated vapor line suddenly rose to over 930 °F and the temperature in the top of the boiler dropped from 1490 to 1200°F. The rubidium cooled so rapidly in the condenser region that the loop again plugged and circulation ceased. It now appeared that the heat output of the single furnace was not sufficient to supply the heat that would be transferred by the circulating boiling rubidium at the desired test temperature of 1500°F unless the heat loss in the system was reduced by insulating, or adding another furnace. At the end of the working day on which the assembly was brought to temperature the loop was left with the boiling rubidium circulating at a maximum temperature of 1200°F. Within an hour the rubidium in the condenser and aftercooler solidified, the boiler temperature increased and the boiler section operated as a capsule test with a hot zone temperature of 1520°F for 15 hours. The next morning a 8 inch clamshell resistance heater was placed over the center of the superheated vapor line and the loop was insulated by wrapping with asbestos tape from the rubidium exit end of the 8 inch furnace to the center of the condenser and aftercooler section. The base of the loop was now heated to thaw the solidified rubidium. After a very slight amount of heating circulation was initiated and the equilibrium loop surface temperatures indicated on Figure 4.9 were rapidly attained.

Two of the equilibrium temperature values indicated are not strictly accurate since the temperature measurement 4 inches down from the top of the boiler section varied sinusoidally with a cycle time 9 minutes and a total temperature gradient over the cycle at this location of 80°F (from 1470 to 1550°F). The surface temperature at a point 3 inches from the base of the boiler leg varied cyclically from 1030 to 1075°F with the same cycle time. No temperature cycling was detected in the superheated vapor line but the temperature measured 3 inches below the upper end of the condenser leg followed the same cycle with a maximum recorded temperature spread of 18°F. This cycling of temperature was not a result of the cyclic control of electrical power input into the furnace but was probably brought about by the boiling conditions prevailing within the loop.

After 312 hours of circulation under the conditions indicated on Figure 3.9 the loop was cooled, placed in a drybox under a helium atmosphere where it was opened with a tube cutter, drained of rubidium, and sectioned.

A sample of the rubidium removed from the apparatus was submitted to J. C. White of the ANP Analytical Chemistry Division for chemical analysis. The sample was analysed for iron, nickel, and chromium in an attempt to determine whether any of the main constituents of Inconel were being selectively dissolved, and for sodium as a check on the analysis of the vacuum distilled rubidium that was loaded into the loop. The following chemical analysis was reported:

iron	-	100 parts per million
nickel	-	less than 25 parts per million
chromium	-	less than 25 parts per million
sodium	-	300 parts per million

Since the vacuum distilled rubidium should be free of iron it appears that the iron in the Inconel was selectively dissolved by the rubidium. This dissolution attack would be expected to occur either in the boiler by the liquid being heated, or in the condenser by the newly condensed liquid rubidium.

In the former case the iron would not be carried over by the vapor, but would precipitate from the boiling liquid and tend to settle to the base leg of the loop. In the latter case it would be possible for mass transfer to occur by precipitation of the iron in solution in the rubidium as the liquid cooled in moving down the condenser and aftercooler. There is strong evidence that this solution and precipitation of iron at a very slow rate did occur. A very small amount of finely divided black powder was removed from the base leg of the loop when the loop was rinsed with alcohol after the rubidium had been drained. This powder, which was insoluble in both alcohol and water, was submitted to R. M. Steele for X-ray analysis and although the actual diffraction lines could not be identified, excessive scattering of the X-ray beam occurred when a copper target was used. This is a general indication of the presence of iron or chromium in the specimen.

The loop was sectioned and representative specimens of the tubing were mounted, polished, and examined metallographically. The surface of the Inconel loop in the region of the liquid-vapor level in the boiler section is shown in Figure 4.10. The corrosion penetration in this region did not exceed .001 inch and was intergranular. In the area shown a surface grain has been separated from the tube wall apparently as a result of the intergranular corrosion.

No evidence of corrosion penetration, or measureable amount of surface erosion was found in the vertical boiler section. Figure 4.11 depicts a representative section of the loop wall 6 inches above the liquid level. The large

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grain size can be attributed to grain growth during the extended heating at a temperature of approximately 1500°F.

Very little indication of corrosion of the Inconel could be detected along the superheated vapor line of the loop or in the welds at each end of this leg. The maximum surface attack in this leg was .0005 inches and no noticeable erosion had occurred.

In the condenser and after cooler section of the loop slight surface irregularity to a depth of .00025 inches was noted. Figure 4.12 is a photomicrograph of the Inconel-rubidium interface at a point approximately 3 inches below the bend in the loop separating the superheated vapor line and condenser and after cooler section. This region was exposed to condensing rubidium, liquid and vapor, which had been distilled. The slight corrosion may be attributable to erosion of the Inconel by the rubidium, or it may be due to preferential leaching of a constituent of the Inconel followed by recrystallization and grain boundary attack which allowed the small grains to become separated from the surface of the tube.

No corrosion attack could be detected in the loop in any region below the liquid rubidium level. The welds that were exposed to only liquid rubidium were completely free from attack. Figure 4.13 shows a section of the weld at the base of the tapered region in the boiler and vapor separator section.

It may be tentatively concluded that the corrosion of Inconel by circulating, boiling, rubidium can be dismissed as insignificant for operating lifetimes of the order likely to be encountered in aircraft nuclear reactors. It should be possible to successfully circulate boiling rubidium in an Inconel system at temperatures and pressures so high as to be limited by the strength properties of the Inconel.

4.2.5. Quartz-Rubidium Capsule Corrosion Test

Approximately .5 cc of Rb was vacuum distilled into a quartz tube having an outside diameter of 9 mm and an inside diameter of 7 mm. The quartz tube containing the Rb was sealed under vacuum. The loaded capsule was 13 cm long with 1.25 cm of this length filled with Rb. The quartz capsule was then sealed in air in an Inconel tube having an inside diameter of .5 inches and held in a furnace at 1650 °F for one hour.

Upon opening the outer protective Inconel capsule it was discovered that the Rb had reacted completely with the quartz and the quartz had shattered. The quartz capsule had ~~retained~~ its shape but was broken into many fragments.

No reaction was noted when the broken capsule was exposed to air. The Rb had reacted so completely with the quartz that no visible reaction occurred when the inner capsule surface was washed with alcohol or water.

Five distinct color bands were observed in an examination of a cross-section of the quartz capsule. Progressing from the inner wall outward layers of light brown, light grey, dark grey, golden brown glasses, and unattached transparent quartz were present. All of the layers were glassy in appearance and a petrographic examination by T. N. McVay, consultant to Ceramic Laboratory, Metallurgy Division, ORNL, indicated that the material was of isotropic ~~form and similar~~ to the silicate glasses. X-ray analysis divulged that the material was non-crystalline, either amorphous or vitreous.

A plane of weakness existed between the clear quartz and the golden brown layer and separation along this plane was in evidence.

An attempt to polish a specimen for metallographic analysis failed because the Rb-silicate glass apparently reacted chemically with the water used in polishing. When left over night the reaction proceeded and the accompanying

Fig. 4.8. Loaded Rubidium-Inconel Loop Prior to
Attaching the Thermocouples and Resistance Furnaces.

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Fig. 4.8a DIMENSIONS OF RUBIDIUM-INCONEL LOOP AND LOCATIONS
OR THERMOCOUPLES

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BOILING RUBIDIUM - INCONEL LOOP

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NOTE: EQUILIBRIUM LOOP SURFACE TEMPERATURES ARE GIVEN

Fig. 4.9. Sectioned Boiling Rubidium-Inconel Loop Following Completion of 312 Hours of Operation Showing Operating Conditions and Heater Locations.

Figure 4.10 Rubidium-Inconel Interface in the Region of The Liquid-Vapor Level in The Boiler Section of The Boiling Rubidium-Inconel Loop. Magnification: 1000X Etchant: Aqua Regia

Figure 4.11 Rubidium Vapor-Inconel Interface Representative of
the Surface Six Inches Above the Liquid Level in the
Vertical Boiler Section Magnification: 1000X
Etchant: Aqua Regia

Figure 4.12 Rubidium-Inconel Interface in The Region Exposed to
Condensing Rubidium. Magnification: 1000X Etchant:
Aqua Regia

Figure 4.13 Rubidium Liquid-Inconel Interface At A Weld
Located at The Base of The Tapered Region in The
Boiler and Vapor Separator Section. Magnification:
500X Etchant: Aqua Regia

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expansion fractured the plastic mount. When the remainder of the capsule, that had been stored in a jar in air, was observed after a period of 3 weeks it was discovered that the colored glass had expanded and separated from the clear quartz and was now dark brown in color, and no longer glassy but with a dull surface.

REFERENCES

1. Liquid Metals Handbook, NAVEXOS p. 733 (Rev), June 1952
2. Crystal Structures, Wyckoff, Vol I, 1951

APPENDIX A

DETERMINATION OF SODIUM BY THE FLAME SPECTROPHOTOMETER

Stock Solution

1000 ppm of Na. Prepare by dissolving 2.541 g of NaCl in water and diluting to 1000 ml with water.

Standard Solutions

Prepare as follows:

	<u>Na, ppm</u>
100 ml stock solution diluted to 1000 ml	100
2 ml 100 ppm Na solution diluted to 100 ml	2
4 ml 100 ppm Na solution diluted to 100 ml	4
6 ml 100 ppm Na solution diluted to 100 ml	6
8 ml 100 ppm Na solution diluted to 100 ml	8
10 ml 100 ppm Na solution diluted to 100 ml	10

Equipment

Beckman Model DU Spectrophotometer with Beckman No. 9200 flame photometer attachment.

Procedure

I. Preparation of Flame Photometer

(Check for closure of oxygen and fuel gages of flame photometer before and after using photometer).

1. Set oxygen tank gage at 5 pounds pressure.
2. Set hydrogen tank gage so that it is just off the zero mark.
3. Light a match and quickly light the burner. (Keep water in the cup under the burner at all times when the burner is on).
4. Make final adjustment of pressure of oxygen at 20 pounds pressure and hydrogen at 6 pounds pressure. The flame photometer oxygen and hydrogen gages indicate these pressures.

II. Preparation of Standard Curve

1. Set the resistor on No. 2 position.
2. Turn photomultiplier box in "on" position and switch on No. 3 position (350 volts).
3. Pull out phototube lamp knob to set photomultiplier tube in proper position.
4. Turn sensitivity switch to 0.1 sensitivity setting.
5. Set the wavelength scale at 589 $m\mu$.
6. Set the slit width knob at 0.030 mm.
7. Zero null point needle by adjusting the dark current knob.
8. Pour approximately 4 ml of the standard solution containing 10 ppm of Na into a 5 ml cup and place under the burner by means of the elevator lever. Turn phototube switch to "on" position.
9. While the Na is burning, set % T scale at 75 and zero the null point needle by adjusting the sensitivity control knob (upper left hand corner).
10. Turn off the phototube switch.
11. Pour 4 ml of the standard solution containing 2 ppm of Na into a 5 ml cup and place under the burner by means of the elevator lever.
12. Zero the null point needle by adjusting the dark current knob.
13. Turn on the phototube switch and zero the null point needle by adjusting the % T knob.
14. Turn off the phototube switch and record the % T.
15. Repeat steps 11 thru 14 for the standard solutions containing 4, 6, and 8 ppm of Na.
16. Prepare a standard calibration curve by plotting % T as the ordinate versus ppm of Na as the abscissa on linear graph paper.

III. Preparation of the Sample

A. Ammonium Carbonate Solutions

1. Transfer a 5 ml aliquot of the carbonate solution to a 10 ml volumetric flask.
2. Neutralize the solution with concentrated HCl. (Add dropwise with gentle shaking of the flask after each drop of HCl. The sample is neutralized when the addition of HCl produces no gas evolution.
3. Dilute to volume with water.
4. Take an aliquot of this solution and dilute to a volume which will contain 2 to 10 μg of Na per ml.

B. Solid Samples

1. Weigh out a sample which will contain at least 100 μg of Na.
2. Dissolve in H_2O and add HCl until the solution is just acid.
3. Dilute the solution to a suitable volume in a volumetric flask.
4. Take an aliquot of this solution and dilute to a volume which will contain 2 to 10 μg of Na per ml.

IV. Determination of Sodium in the Sample

1. Repeat steps 1 thru 4 under, "Preparation of Flame".
2. Repeat steps 1 thru 10 under, "Preparation of the Standard Curve."
3. Pour approximately 4 ml of the sample solution into a 5 ml cup and place under the burner by means of the elevator lever.
4. Zero the null point needle by adjusting the dark current knob.
5. Turn on the phototube switch and zero the null point needle by adjusting the % T knob.
6. Turn off the phototube switch and record the % T.

7. From the standard calibration curve, determine the μg of Na per ml corresponding to the observed % T. Record this value.

8. Calculation:

Let $R = \mu\text{g Na per ml}$ as determined in step 7

$D = \text{dilution factor}$

$W = \text{weight of the sample, g}$

then $R \times D = \mu\text{g Na per ml in sample (for solutions)}$

also, $\frac{R \times D}{W} \mu\text{g Na per g in sample (for solids)}$

DETERMINATION OF POTASSIUM BY THE FLAME SPECTROPHOTOMETER

Stock Solution

1000 ppm of K. Prepare by dissolving 1.912 g of KCl in water and diluting to 1000 ml with water.

Standard Solutions

Prepare as follows:

	<u>K, ppm</u>
100 ml stock solution diluted to 1000 ml	100
2 ml 100 ppm K solution diluted to 100 ml	2
4 ml 100 ppm K solution diluted to 100 ml	4
6 ml 100 ppm K solution diluted to 100 ml	6
8 ml 100 ppm K solution diluted to 100 ml	8
10 ml 100 ppm K solution diluted to 100 ml	10

Equipment

Beckman Model DU Spectrophotometer with Beckman No. 9200 flame photometer attachment.

Procedure

I. Preparation of Flame Photometer

(Check for closure of oxygen and fuel gages of flame photometer before and after using photometer)

1. Set oxygen tank gage at 5 pounds pressure.

2. Set hydrogen tank gage so that it is just off the zero mark.
3. Light a match and quickly light the burner. (Keep water in the cup under the burner at all times when the burner is on.)
4. Make final adjustment of pressure of oxygen at 20 pounds pressure and hydrogen at 6 pounds pressure. The flame photometer oxygen and hydrogen gages indicate these pressures.

II. Preparation of Standard Curve

1. Set the resistor on No. 3 position.
2. Check to determine that the photomultiplier box is in "off" position.
3. Push in phototube lamp knob to set red-sensitive phototube in proper position.
4. Turn sensitivity switch to 0.1 sensitivity setting.
5. Set the wavelength scale at 767 mμ.
6. Set the slit width knob at 0.070 mm.
7. Zero null point needle by adjusting the dark current knob.
8. Pour approximately 4 ml of the standard solution containing 10 ppm of K into a 5 ml cup and place under the burner by means of the elevator lever. Turn phototube switch to "on" position.
9. While the K standard is burning, set % T scale at 75 and zero the null point needle by adjusting the sensitivity control knob (upper left hand corner).
10. Turn off the phototube switch.
11. Pour 4 ml of the standard solution containing 2 ppm of K into a 5 ml cup and place under the burner by means of the elevator lever.
12. Zero the null point needle by adjusting the dark current knob.

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13. Turn on the phototube switch and zero the null point needle by adjusting the % T knob.
 14. Turn off the phototube switch and record the % T.
 15. Repeat steps 11 thru 14 for the standard solutions containing 4, 6, and 8 ppm of K.
 16. Prepare a standard calibration curve by plotting % T as the ordinate versus ppm of K as the abscissa on linear graph paper.

III. Preparation of the Sample

A. Ammonium Carbonate Solutions

1. Transfer a 5 ml aliquot of the carbonate solution to a 10 ml volumetric flask.
2. Neutralize the solution with concentrated HCl. (Add dropwise with gentle shaking of the flask after each drop of HCl. The sample is neutralized when the addition of HCl produces no gas evolution.
3. Dilute to volume with water.
4. Take an aliquot of this solution and dilute to a volume which will contain 2 to 10 μg of K per ml.

B. Solid Samples

1. Weigh out a sample which will contain at least 100 μg of K.
2. Dissolve in H_2O and add HCl until the solution is just acid.
3. Dilute the solution to a suitable volume in a volumetric flask.
4. Take an aliquot of this solution and dilute to a volume which will contain 2 to 10 μg of K per ml.

IV. Determination of Potassium in the Sample

1. Repeat steps 1 thru 4 under, "Preparation of Flame."

2. Repeat steps 1 thru 10 under, "Preparation of the Standard Curve."
3. Pour approximately 4 ml of the sample solution into a 5 ml cup and place under the burner by means of the elevator lever.
4. Zero the null point needle by adjusting the dark current knob.
5. Turn on the phototube switch and zero the null point needle by adjusting the % T knob.
6. Turn off the phototube switch and record the % T.
7. From the standard calibration curve, determine the μg of K per ml corresponding to the observed % T. Record this value.
8. Calculation:

Let $R = \mu\text{g K per ml}$ as determined in Step 7

$D = \text{dilution factor}$

$W = \text{weight of the sample, g}$

then $R \times D = \mu\text{g per ml in sample (for solutions)}$

also, $\frac{R \times D}{W} = \mu\text{g K per g in sample (for solids)}$

DETERMINATION OF RUBIDIUM BY THE FLAME SPECTROPHOTOMETER

Stock Solution

1000 ppm of Rb. Prepare by dissolving 1.415 g of RbCl in water and diluting to 1000 ml. with water.

Standard Solutions

Prepare as follows:

	<u>Rb, ppm</u>
100 ml stock solution diluted to 1000 ml	100
5 ml 100 ppm Rb solution diluted to 100 ml	5
10 ml 100 ppm Rb solution diluted to 100 ml	10
15 ml 100 ppm Rb solution diluted to 100 ml	15
25 ml 100 ppm Rb solution diluted to 100 ml	25

Equipment

Beckman Model DU Spectrophotometer with Beckman No. 9200 flame photometer attachment.

Procedure

I. Preparation of Flame Photometer

(Check for closure of oxygen and fuel gages of flame photometer before and after using photometer)

1. Set oxygen tank gage at 5 pounds pressure.
2. Set hydrogen tank gage so that it is just off the zero mark.
3. Light a match and quickly light the burner. (Keep water in the cup under the burner at all times when the burner is on.)
4. Make final adjustment of pressure of oxygen at 20 pounds pressure and hydrogen at 6 pounds pressure. The flame photometer oxygen and hydrogen gages indicate these pressures.

II. Preparation of Standard Curve

1. Set the resistor switch on No. 3 position.
2. Check to determine that the photomultiplier box is in "off" position.
3. Push in phototube lamp knob to set red-sensitive phototube in proper position.
4. Turn sensitivity switch to 0.1 sensitivity setting.
5. Set the wavelength scale at 795 mμ.
6. Set the slit width knob at 0.12 mm.
7. Zero null point needle by adjusting the dark current knob.
8. Pour approximately 4 ml of the standard solution containing 25 ppm of Rb into a 5 ml cup and place under the burner by means of the elevator lever. Turn phototube switch to "on" position.
9. While the Rb standard is burning, set % T scale at 75 and zero the null point needle by adjusting the sensitivity control knob (upper left hand corner).

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10. Turn off the phototube switch.
 11. Pour 4 ml of the standard solution containing 5 ppm of Rb into a 5 ml cup and place under the burner by means of the elevator lever.
 12. Zero the null point needle by adjusting the dark current knob.
 13. Turn on the phototube switch and zero the null point needle by adjusting the % T knob.
 14. Turn off the phototube switch and record the % T.
 15. Repeat steps 11 thru 14 for the standard solutions containing 10 and 15 ppm of Rb.
 16. Prepare a standard calibration curve by plotting % T as the ordinate versus ppm of Rb as the abscissa on linear graph paper.

III. Preparation of the Sample

A. Ammonium Carbonate Solutions

1. Transfer a 5 ml aliquot of the carbonate solution to a 10 ml volumetric flask.
2. Neutralize the solution with concentrated HCl. (Add dropwise with gentle shaking of the flask after each drop of HCl. The sample is neutralized when the addition of HCl produces no gas evolution.
3. Dilute to volume with water.
4. Take an aliquot of this solution and dilute to a volume which will contain 5 to 25 μg of Rb per ml.

B. Solid Samples

1. Weigh out a sample which will contain at least 250 μg of Rb.
2. Dissolve in H_2O and add HCl until solution is just acid.

3. Dilute the solution to a suitable volume in a volumetric flask.
4. Take an aliquot of this solution and dilute to a volume which will contain 5 to 25 μg of Rb per ml.

IV. Determination of Rubidium in the Sample

1. Repeat steps 1 thru 4 under, "Preparation of Flame."
2. Repeat steps 1 thru 10 under, "Preparation of the Standard Curve."
3. Pour approximately 4 ml of the sample solution into a 5 ml cup and place under the burner by means of the elevator lever.
4. Zero the null point needle by adjusting the dark current knob.
5. Turn on the phototube switch and zero the null point needle by adjusting the % T knob.
6. Turn off the phototube switch and record the % T.
7. From the standard calibration curve, determine the μg of Rb per ml corresponding to the observed % T. Record this value.
8. Calculation:

Let $R = \mu\text{g Rb per ml as determined in step 7}$

$D = \text{dilution factor}$

$W = \text{weight of the sample, g}$

then $R \times D = \mu\text{g Rb per ml in sample (for solutions)}$

also, $\frac{R \times D}{W} = \mu\text{g Rb per g in sample (for solids)}$

DETERMINATION OF CESIUM BY THE FLAME SPECTROPHOTOMETER

Stock Solution

1000 ppm of Cs. Prepare by dissolving 1.267 g of CsCl in water and diluting to 1000 ml with water.

Standard Solutions

Prepare as follows:

	<u>Cs, ppm</u>
100 ml stock solution diluted to 1000 ml	100
5 ml 100 ppm Cs solution diluted to 100 ml	5
10 ml 100 ppm Cs solution diluted to 100 ml	10
15 ml 100 ppm Cs solution diluted to 100 ml	15
25 ml 100 ppm Cs solution diluted to 100 ml	25

Equipment

Beckman Model DUSpectrophotometer with Beckman No. 9200 flame photometer attachment.

Procedure

I. Preparation of Flame Photometer

(Check for closure of oxygen and fuel gages of flame photometer before and after using photometer)

1. Set oxygen tank gage at 5 pounds pressure.
2. Set hydrogen tank gage so that it is just off the zero mark.
3. Light a match and quickly light the burner. (Keep water in the cup under the burner at all times when the burner is on.)
4. Make final adjustment of pressure of oxygen at 20 pounds pressure and hydrogen at 6 pounds pressure. The flame photometer oxygen and hydrogen gages indicate these pressures.

II. Preparation of Standard Curve

1. Set the resistor switch on No. 3 position.
2. Check to determine that the photomultiplier box is in "off" position.
3. Push in phototube lamp knob to set red-sensitive phototube in proper position.
4. Turn sensitivity switch to 0.1 sensitivity setting.

5. Set the wavelength scale at 852 mμ.
6. Set the slit width knob at 0.13 mm.
7. Zero null point needle by adjusting the dark current knob.
8. Pour approximately 4 ml of the standard solution containing 25 ppm of Cs into a 5 ml cup and place under the burner by means of the elevator lever. Turn phototube switch to "on" position.
9. While the Cs standard is burning, set % T scale at 75 and zero the null point needle by adjusting the sensitivity control knob (upper left hand corner).
10. Turn off the phototube switch.
11. Pour 4 ml of the standard solution containing 5 ppm of Cs into a 5 ml cup and place under the burner by means of the elevator lever.
12. Zero the null point needle by adjusting the dark current knob.
13. Turn on the phototube switch and zero the null point needle by adjusting the % T knob.
14. Turn off the phototube switch and record the % T.
15. Repeat steps 11 thru 14 for the standard solutions containing 10 and 15 ppm of Cs.
16. Prepare a standard calibration curve by plotting % T as the ordinate versus ppm of Cs as the abscissa on linear graph paper.

III. Preparation of the Sample

A. Ammonium Carbonate Solutions

1. Transfer a 5 ml aliquot of the carbonate solution to a 10 ml volumetric flask.
2. Neutralize the solution with concentrated HCl. (Add dropwise with gentle shaking of the flask after each drop of HCl. The sample is neutralized when addition of HCl produces no gas evolution.)

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3. Dilute to volume with water.
4. Take an aliquot of this solution and dilute to a volume which will contain 5 to 25 μg of Cs per ml.

B. Solid Samples

1. Weigh out a sample which will contain at least 250 μg of Cs.
2. Dissolve in H_2O and add HCl until solution is just acid.
3. Dilute the solution to a suitable volume in a volumetric flask.
4. Take an aliquot of this solution and dilute to a volume which will contain 5 to 25 μg of Cs per ml.

V. Determination of Cesium in the Sample

1. Repeat steps 1 thru 4 under, "Preparation of Flame."
2. Repeat steps 1 thru 10 under, "Preparation of the Standard Curve."
3. Pour approximately 4 ml of the sample solution into a 5 ml cup and place under the burner by means of the elevator lever.
4. Zero the null point needle by adjusting the dark current knob.
5. Turn on the phototube switch and zero the null point needle by adjusting the % T knob.
6. Turn off the phototube switch and record the % T.
7. From the standard calibration curve, determine the μg of Cs per ml corresponding to the observed % T. Record this value.
8. Calculation:

Let $R = \mu\text{g}$ Cs per ml as determined in step 7

$D =$ dilution factor

$W =$ weight of the sample

then $R \times D = \mu\text{g}$ Cs per ml in sample (for solutions)

also, $\frac{R \times D}{W} = \mu\text{g}$ Cs per g in sample (for solids)

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