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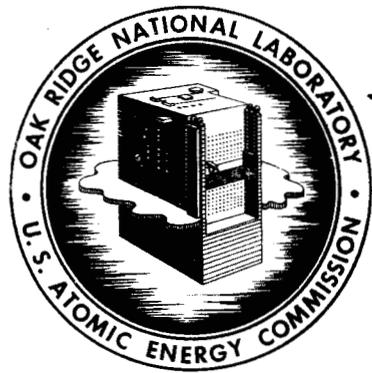
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UC-25 - Metallurgy and Ceramics

THE SOLUBILITY OF NITROGEN AND OXYGEN
IN LITHIUM AND METHODS OF
LITHIUM PURIFICATION

E. E. Hoffman

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THE SOLUBILITY OF NITROGEN AND OXYGEN IN LITHIUM
AND METHODS OF LITHIUM PURIFICATION

ABSTRACT

Nitrogen and oxygen are two of the most common impurities found in commercially available lithium. Experiments were conducted to determine the solubility of these elements in lithium in the temperature range from 250 to 450°C and to determine which of several possible purification methods was most effective in reducing the nitrogen and oxygen content of lithium.

The solubility of nitrogen in lithium increased from 0.04 wt % at 250°C to 1.31 wt % at 450°C. The solubility of oxygen was found to be 0.010 wt % at 250°C and increased to 0.066 wt % at 400°C.

Vacuum distillation, low-temperature filtration, cold-trapping, and gettering with active metals were investigated as possible purification methods to reduce the nitrogen and oxygen content of lithium. Of the techniques studied, gettering with active metals was found to be the most effective method of reducing the nitrogen concentration, while cold-trapping and low-temperature filtration were most effective in reducing the oxygen concentration.

I. INTRODUCTION

There is considerable interest in the application of the low-melting alkali metals as potential coolants for nuclear reactors and other heat-transfer applications. Lithium has many properties which make it most attractive as a high-temperature, high-performance coolant;¹ however, one problem which has discouraged its use has been the severe corrosion encountered in elevated-temperature corrosion tests. The observed corrosion has in some cases been attributed to impurities in the lithium.

The most common impurities found in commercial lithium, either dissolved or mechanically dispersed as lithium compounds, are nitrogen,

¹Hoffman, E. E., and W. D. Manly, "Comparison of Sodium, Lithium, and Lead," Problems in Nuclear Engineering, 1 (Pergamon Press, New York, 1957) p 128.

oxygen, carbon, chlorine, hydrogen, aluminum, calcium, iron, silicon, and sodium.² Very little quantitative information which relates the effect of these impurities to the corrosiveness of lithium exists in the literature.

It has been shown that nitrogen additions to lithium increase its corrosiveness to stainless steel, resulting in grain-boundary attack of the alloy.³ Recent corrosion tests⁴ have been conducted on tensile-test specimens of type 316 stainless steel exposed to pure lithium,⁵ to lithium contaminated with 2 wt % lithium oxide, and to lithium contaminated with 2 wt % lithium nitride.⁶ The addition of lithium nitride to lithium resulted in grain-boundary attack of the stainless steel with corresponding decreases in the room-temperature tensile strength and ductility of the specimens following test. The specimens exposed to pure lithium were essentially unaffected by the test, while the specimens tested in lithium contaminated with lithium oxide were attacked, but to a very slight degree compared to specimens tested in the nitrogen-contaminated lithium.

Since both nitride and oxide additions to lithium were found to affect the corrosiveness of lithium, a program was initiated to determine the solubility of nitrogen and oxygen in lithium, and also to determine which of several possible purification methods was most effective in removing these impurities.

²Lyon, R. N., (ed.) Liquid Metals Handbook (rev. ed.), Office of Naval Research, NAVEXOS P-733, p 158 (June 1952).

³Hoffman, E. E., "Liquid Metal Corrosion," Corrosion Fundamentals (Univ. of Tenn. Press, 1956) pp 79, 80.

⁴Corrosion test conditions: Static tests at 816°C for 100 hr.

⁵Lithium contained 25 ppm N₂ and 135 ppm O₂.

⁶Hoffman, E. E., unpublished work.

II. REVIEW OF PAST WORK

Solubility of Nitrogen and Oxygen in Lithium

No information could be found in the literature relative to the solubility of nitrogen and oxygen in lithium.

Purification of Lithium

Numerous investigators have attempted to purify lithium. Rogers and Viens^{7,8} refined lithium by vaporization at low pressure, but only the lowering of sodium and potassium contents was considered. Epstein and Howland⁹ purified a small quantity of lithium by distillation of the metal onto a "cold finger," but no quantitative determinations of the oxygen and nitrogen contents of the purified metal were given. Baker et al.,¹⁰ also prepared "high-purity" lithium by vacuum distillation, but again no determinations of the oxygen and nitrogen contents were included in the study. Horsley¹¹ made an extensive study of the theoretical factors which should influence the production of high-purity lithium and although both nitrogen and oxygen removal were discussed, no experimental work was done to substantiate the proposed purification procedures.

An attempt was made to reduce the nitrogen and oxygen contents of large quantities of lithium by low-temperature filtration but the results were inconclusive.¹² The potential usefulness of this method of purification was unknown since no solubility data for nitrogen or oxygen in lithium as a function of temperature were available in the literature.

⁷Rogers, R. R., and G. E. Viens, "Refining Lithium by Vaporation at Low Pressure," Can. Mining and Met. Bull., p 15-20 (Jan. 1951).

⁸Rogers, R. R., and G. E. Viens, "Effect of Pressure on the Refining of Lithium by Distillation," J. Electrochem. Soc., 98(12), 483-487 (1951).

⁹Epstein, L. F., and W. H. Howland, "The Distillation of Lithium Metal," Science, 114, 443-444 (1951).

¹⁰Baker, P. S., F. R. Duncan, and H. B. Greene, "Preparation of High-Purity Lithium Metal by Vacuum Distillation," Science, 118, 778-780 (1953).

¹¹Horsley, G., The Purification of Commercial Lithium, Atomic Energy Research Establishment, Harwell, England, Report No. AERE-M/R-1251 (Sept. 26, 1953).

¹²Crocker, A. R., R. L. Potter, R. J. Spera, T. D. McLay, and S. H. Esleeck, Design and Operation of a Sodium-to-Lithium-to-Air Heat Transfer System, Office of Technical Services, U. S. Department of Commerce, Washington 25, D. C., APEX-327 (Dec. 1954) p 117.

III. SAMPLING METHOD; ANALYTICAL PROCEDURES,
AND PURITY OF COMMERCIAL LITHIUM

Inconsistencies in analytical results on duplicate samples of lithium taken from purification systems were observed throughout the early portions of this study. In addition, the concentrations of nitrogen and oxygen in given lithium samples often were found to be inconsistent with the past history of the lithium. Although analytical difficulties were thought to be responsible for some of the inconsistencies observed, it was recognized that inadequate sampling procedures also contributed to the experimental errors.

The sampling procedure developed to overcome these problems is illustrated in Fig. 1. In order to obtain meaningful analytical results, it was necessary to take samples in inert containers at the temperatures of interest, quench them rapidly from the test temperature to avoid segregation of the impurity elements, and protect them from atmospheric contamination at all times. The procedure consisted of the following steps:

1. Pressurization of the container to be sampled with argon, forcing lithium into a heated sampling tube.
2. Removal of the furnace from around the sampling tube and rapid quenching of the sample by means of a chilled-oil bath.
3. Cutting of the sampling tube¹³ and transference to the inert-atmosphere chamber for sectioning and loading of samples into the transfer capsules which were submitted for chemical analysis.

The analytical method used to determine the nitrogen content of lithium samples was that reported by Gilbert and co-workers¹⁴ and was found to be quite satisfactory. Two analytical procedures were used initially to determine the oxygen content of lithium samples. A method described by Sax and Steinmetz¹⁵ utilizing methanol and Karl Fischer reagent was investigated

¹³Air-contaminated ends of the sampling tubes were discarded.

¹⁴Gilbert, T. W., Jr., A. S. Meyer, Jr., and J. C. White, "Spectrophotometric Determination of Lithium Carbide in Metallic Lithium as the Acetylene-Silver Perchlorate Complex," Anal. Chem., 29, 1627-1630 (1957).

¹⁵Sax, N., and H. Steinmetz, Determination of Oxygen in Lithium Metal, ORNL-2570 (Oct. 15, 1958).

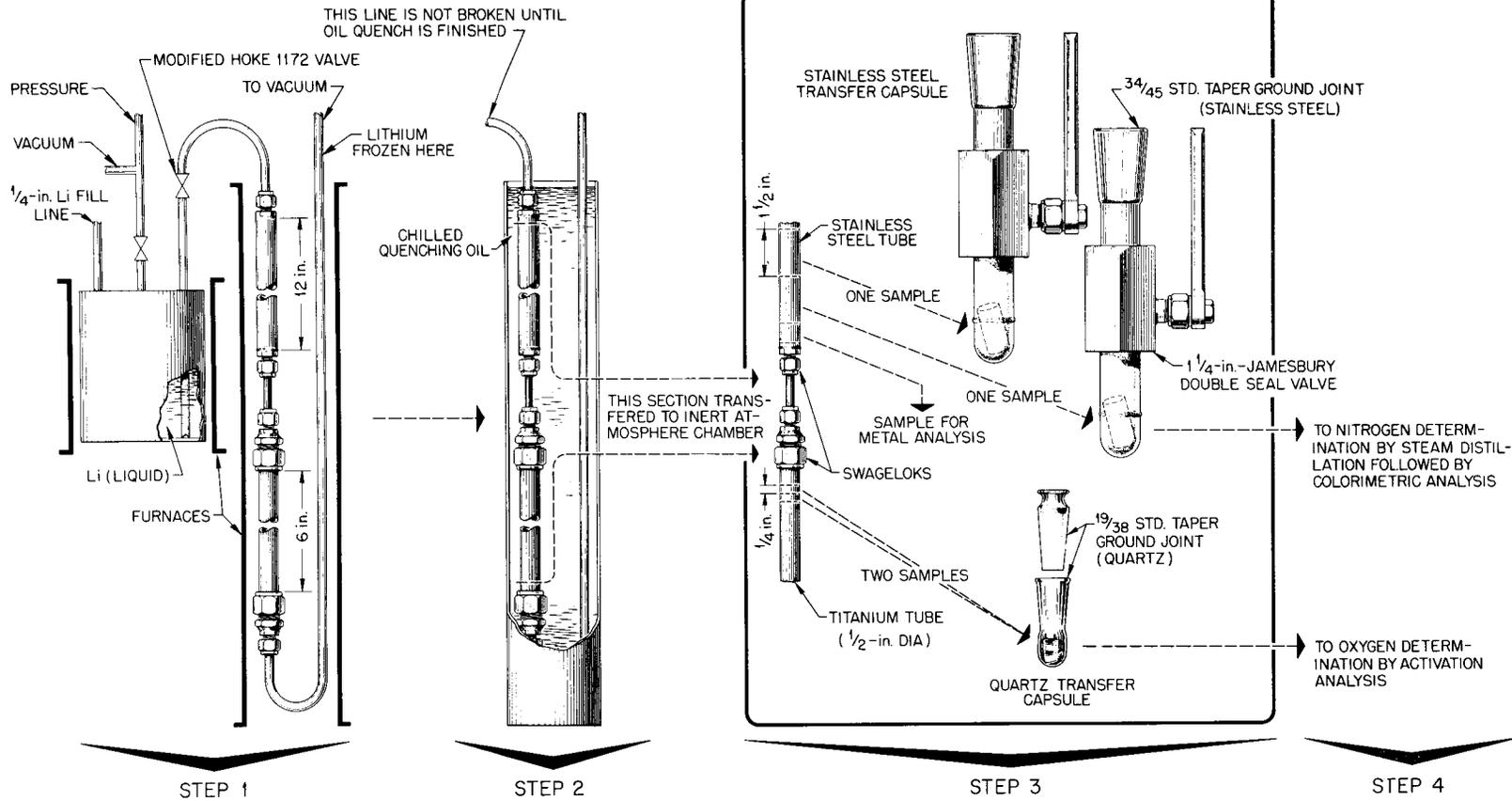


Fig. 1. Lithium Sampling Procedure.

but did not yield oxygen results which were as reproducible as those which were obtained by the activation analysis technique reported by Ieddicotte.¹⁶ The reproducibility and sensitivity particularly at low oxygen concentrations, which were obtained by activation analysis, are illustrated by the results of the analyses of samples taken during the determination of oxygen solubility in lithium.

The lithium used in these studies was obtained from the producer in gas-tight stainless steel containers packed under an argon atmosphere. The as-received purity of several typical shipments of metal is given below:

<u>Shipment</u>	<u>Nitrogen (ppm)</u>	<u>Oxygen (ppm)</u>	<u>Quantity (lb)</u>
A	600	390	20
B	1940	415	46
C	3310	1980	46

IV. SOLUBILITY OF NITROGEN AND OXYGEN IN LITHIUM

No information was found in the literature relative to the equilibrium solubilities of nitrogen or oxygen in molten lithium. Such information was needed in order to determine the potential usefulness of low-temperature filtration or cold-trapping¹⁷ as methods of purifying lithium.

The solubility experiments were conducted in the sampling apparatus illustrated in Fig. 2. For each solubility determination, sufficient lithium oxide or lithium nitride was added to bring the nitrogen or oxygen content of the bath to 5 wt %. Samples of the lithium were taken by forcing the lithium through a 20- μ stainless steel filter after allowing the system to equilibrate at the sampling temperature for 24 hr. The samples were quenched and prepared for analysis by the sampling technique previously described.

¹⁶Ieddicotte, G. W., and L. C. Bate, "Determination of Oxygen by Activation Analysis," Anal. Chem. Prog. Rep., Dec. 31, 1957, ORNL-2453.

¹⁷Cold-trapping is a method of liquid-metal purification which is based upon the temperature dependence of solubility of impurities in the liquid metal.

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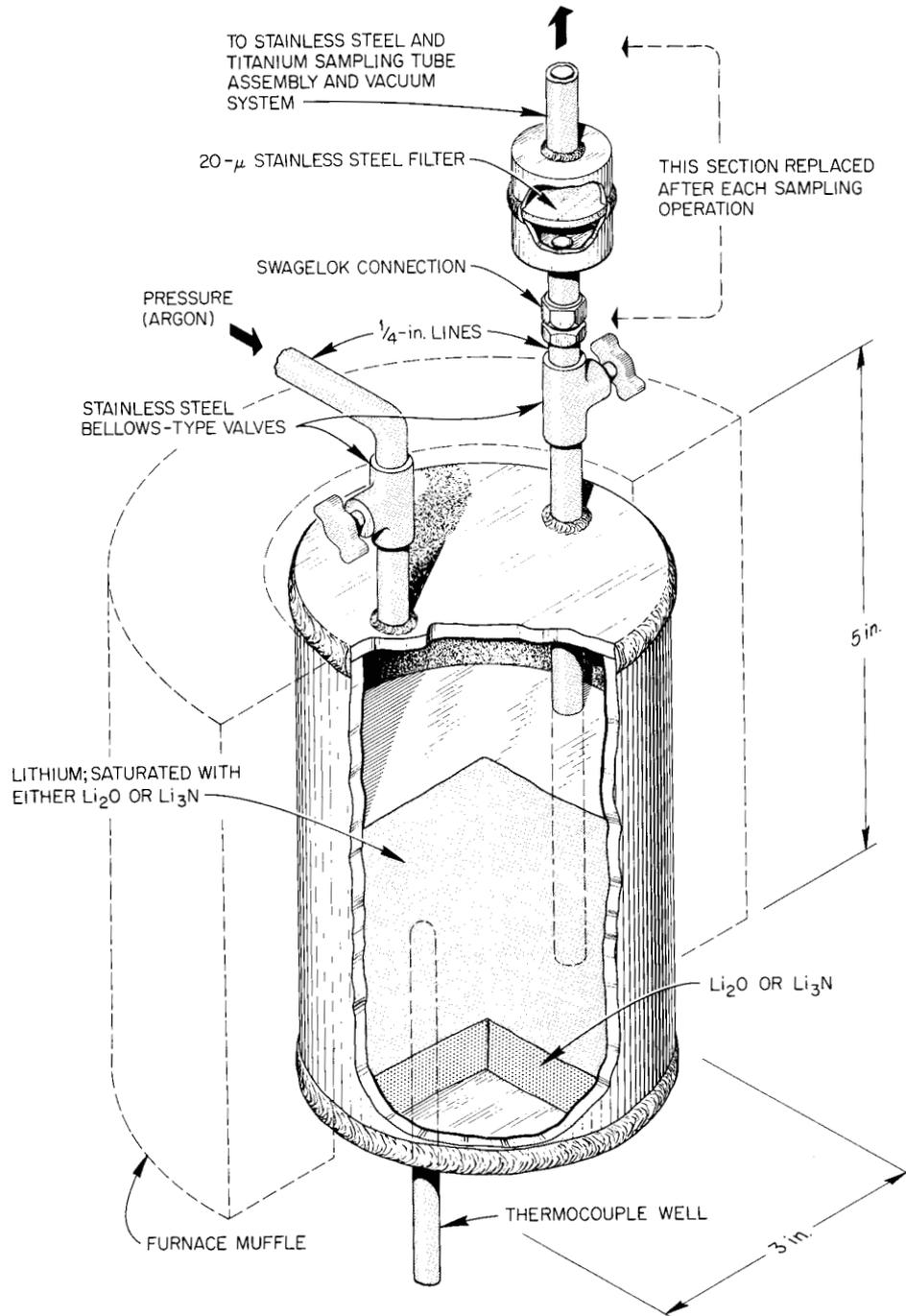


Fig. 2. Solubility Sampling Rig.

The lithium nitride¹⁸ and lithium oxide¹⁹ used in these experiments were quite pure. Lithium nitride was prepared by passing nitrogen gas over lithium which was held in a tantalum boat inside a gas-tight stainless steel container at 800°C. Lithium oxide was prepared by vacuum treatment of a pure grade of lithium hydroxide monohydrate in a nickel container at 600°C.

The results of experiments to determine the solubility of nitrogen in lithium are:

<u>Sampling Temperature (°C)</u>	<u>Nitrogen Content* (wt %)</u>
250	0.04
300	0.16
350	1.19
400	1.21
450	1.31

* Nitrogen content is average of four determinations at each temperature.

It may be noted that the solubility is appreciable (~ 400 ppm) at 250°C (482°F) and increases quite rapidly with increasing temperature.

The solubility of oxygen was determined at four temperatures with a minimum of seven samples taken at each temperature. The results, which are listed and plotted in Fig. 3, show that the solubility of oxygen at temperatures slightly above the melting point of lithium is less than 100 ppm.

V. EXPERIMENTAL METHODS OF PURIFICATION AND RESULTS

Typical batches of high-purity commercial lithium were found to vary in nitrogen and oxygen content from several hundred to several thousand parts per million. The methods investigated to purify lithium of these impurities included vacuum distillation, low-temperature filtration, cold-trapping and

¹⁸Lithium nitride analysis: 99.9 wt % Li₃N

¹⁹Lithium oxide analysis: 99.8 wt % Li₂O

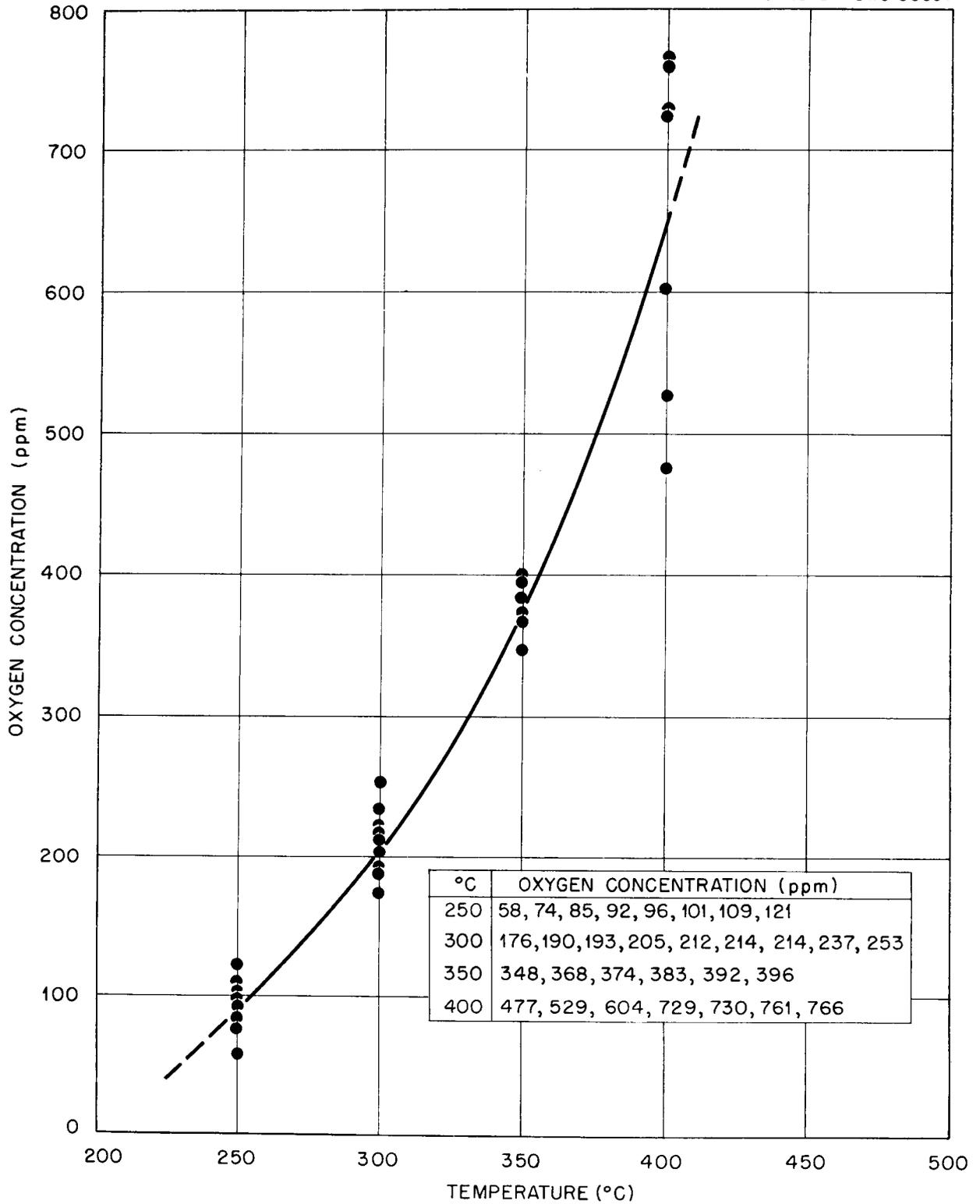


Fig. 3. Solubility of Lithium Oxide in Lithium.

gettering with active metals. Emphasis will be placed on those methods which were found to be most efficient and practical in reducing the nitrogen and oxygen contents of large quantities of lithium to levels of 100 ppm or less.

Vacuum Distillation

Vacuum distillation of lithium at 650°C in the apparatus illustrated in Fig. 4 was found to be ineffective in lowering the nitrogen and oxygen concentrations of the lithium. The results of these experiments are listed in Table I. The failure of this method of purification is not fully understood but may indicate the need for operating such a system at a lower pressure than the 10^{-4} mm Hg that was used in these experiments. Distillation at lower temperatures might have resulted in a purer product; however, the distillation rate was only 30 g/hr or 2.5 g/hr/in.² of liquid-vapor interface area when the distillation temperature was 650°C.

Recent experiments by Berkowitz et al.,²⁰ regarding the sublimation of lithium oxide, indicate that effective separation of lithium oxide from the metal by vacuum distillation should be possible. No definite information could be found regarding the volatility of lithium nitride; however, estimates based on the free-energy relationships suggest that there can be no effective separation of the nitride from lithium at distillation temperatures of 600°C and above.²¹

Low-Temperature Filtration

If it is assumed that the solubilities of nitrogen and oxygen in lithium are quite low at temperatures slightly above the melting point of lithium, it should be possible to purify lithium by forcing the metal through a filter. This method of purification is effective in decreasing the oxygen content of sodium.²²

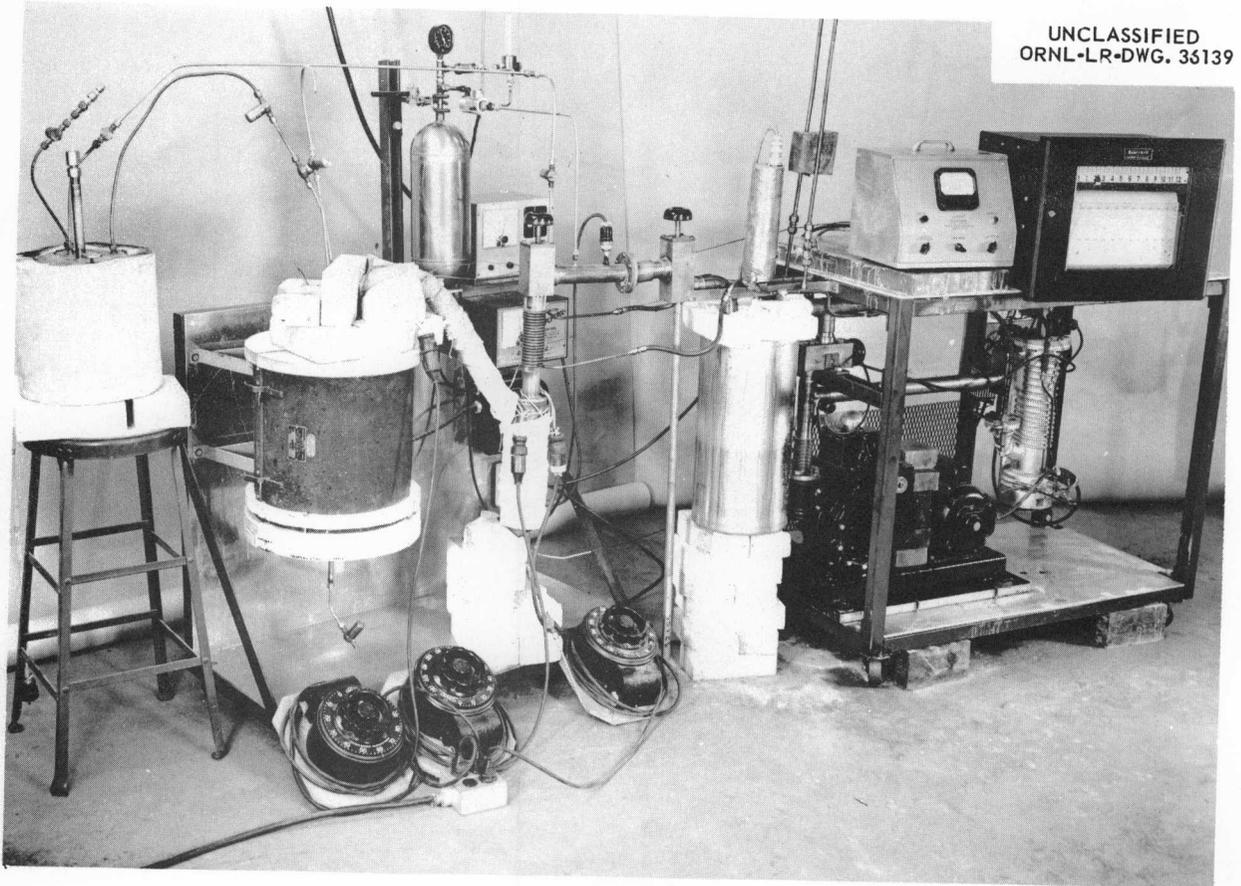
The effectiveness of low-temperature filtration in reducing the oxygen and nitrogen content of lithium is illustrated by the solubility results which have been presented (Section IV). Filtration at 250°C of lithium contaminated with 5 wt % oxygen reduced the oxygen concentration to less than 100 ppm. Since the solubility of nitrogen is quite high (~ 400 ppm)

²⁰Berkowitz, J., W. A. Chupka, G. D. Blue, and J. L. Margrave, "Mass Spectrometric Study of the Sublimation of Lithium Oxide," J. Phy. Chem., 63(5), 644 (May 1959).

²¹Horsley, G., The Purification of Commercial Lithium, Atomic Energy Research Establishment, Harwell, England, Report No. AERE-M/R-1251, p 9 (Sept. 26, 1953).

²²Jackson, C. B. (ed), Liquid Metals Handbook, Sodium-NaK Supplement, Atomic Energy Commission, Department of Navy, Washington, D. C. (1955) p 146.

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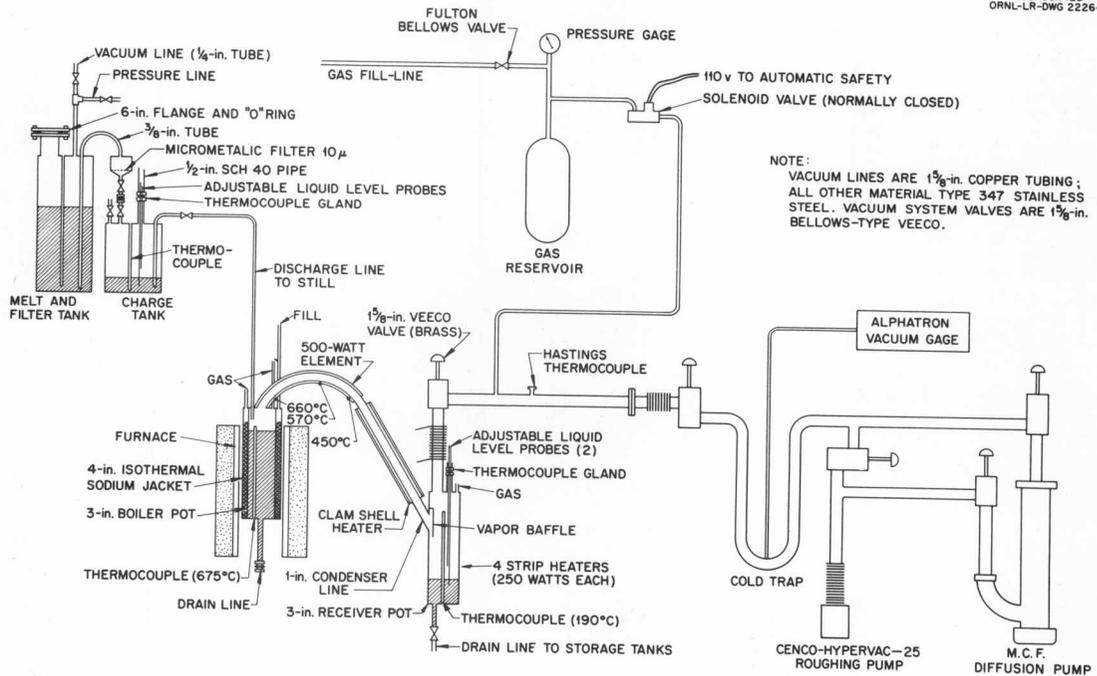


Fig. 4. Lithium Distillation System.

TABLE I

EFFECT OF VACUUM DISTILLATION^a AT 1202°F (650°C) ON THE NITROGEN AND OXYGEN CONTENT OF LITHIUM

Distillation No.	Nitrogen (ppm)		Oxygen ^b (ppm)		Remarks
	Separate Analyses ^b	Average	Separate Analyses	Average	
Charge to still (1100 g)	1170, 1250	1210	226	(226)	As-received and filtered at 300°C through a 5-micron filter
1	1400, 1300	1350	370, 285	330	
2	1260, 1150, 885, 1010	1080	700, 389, 376, 533	500	
3	3000, 1900	2450	375	(375)	Condenser leaked near end of run
4	4200, 5300	4750	1120, 1210	1170	Some contamination of system occurred during repair of leak following Distillation No. 3
5	1600, 1600, 2000	1730	203, 198	200	
6	1800, 2100 2700, 3100	2430	701, 758 688, 630	690	

^a80% of each charge was distilled and the remaining 20% was discharged through the drain line.

^bAll samples obtained at end of 80% distillation.

at 250°C, filtration at this temperature is not an effective method of reducing the nitrogen concentration to less than 100 ppm.

Cold-Trapping

The effectiveness of cold-trapping as a method of purification is also dependent on the solubility of the impurities at the cold-trap temperature. The procedure used in these experiments consisted of holding a relatively large volume (500 g) of lithium at 400°C in a container of the type illustrated in Fig. 5. A temperature gradient from 400 to 150°C was maintained in the lower section of this system. If the solubilities of the impurities, nitrogen and oxygen, are low near the melting point of lithium (179°C), then continual purification should result when the system is held under these conditions. The results of two cold-trap purification experiments are listed in Table II. Lithium samples were taken at 24-hr intervals.

Despite several anomalous results, a definite decrease in oxygen content was apparent as a result of cold-trapping. The nitrogen content decreased during cold-trapping, but purification to nitrogen levels of less than 100 ppm appears to be difficult, if not impossible, by this procedure. These results were consistent with the oxygen and nitrogen solubility values reported above.

Gettering of Oxygen and Nitrogen with Active Metals

The addition to lithium of metals whose oxides and nitrides are more stable than those of lithium was found to be the most practical and effective purification method investigated. Standard free energies of reaction of various metals with lithium nitride and lithium oxide calculated from standard free energies of formation were used as guides in the selection of metals for the gettering studies. On the basis of the possible reduction reactions for lithium nitride²³ listed in Table III, titanium, zirconium, and yttrium were selected for study as potential purifying agents for nitrogen. Both titanium and zirconium were found to be very effective gettering agents in removing nitrogen from lithium at 816°C, but were not effective in

²³Quill, L. L., The Chemistry and Metallurgy of Miscellaneous Materials (McGraw-Hill, New York, 1950), p 42.

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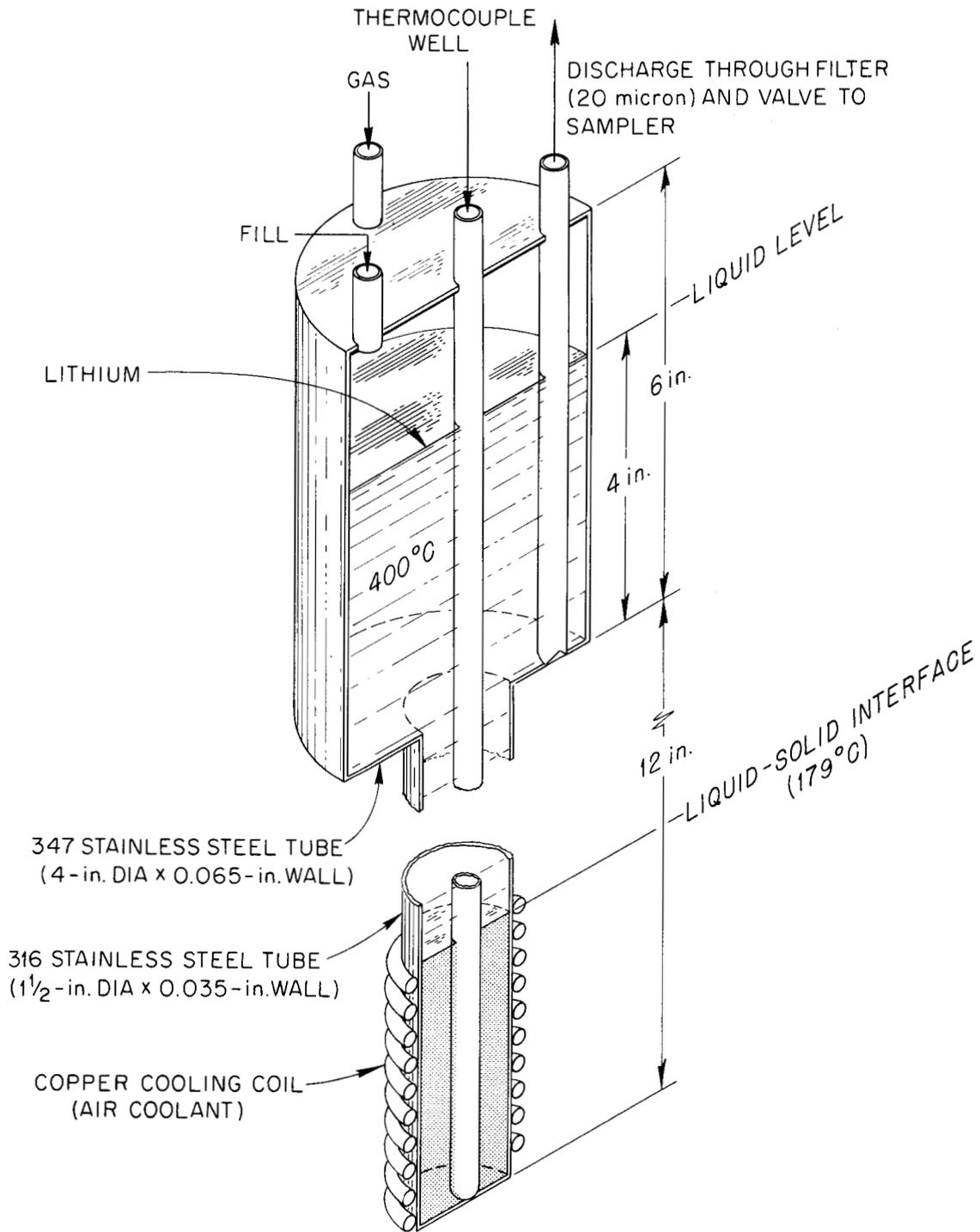


Fig. 5. Cold-Trap Purification System.

TABLE II
RESULTS OF EXPERIMENTS TO PURIFY LITHIUM OF LITHIUM
OXIDE AND LITHIUM NITRIDE BY COLD-TRAPPING

Container Temperature: 400°C (752°F)
Minimum Cold-Trap Temperature: 150°C (302°F)

	Sampling Time (hr)	Oxygen Content ^a (ppm)	Nitrogen Content ^b (ppm)
Test No. 1	0	810	965
	24	10	710
	48	270	680
	96	162	675
Test No. 2	0	607	420
	24	17	---
	48	---	195
	72	222	---
	96	29	220

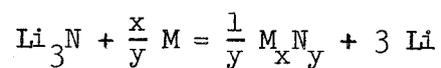
^aOxygen contents are average of three determinations.

^bNitrogen contents are average of two determinations.

TABLE III

STANDARD FREE ENERGY CHANGES FOR REACTIONS BETWEEN

Li_3N AND VARIOUS METALS



$\frac{\text{M}_x\text{N}_y}{x \ y}$	ΔF_{298}° Kcal/g-atom of N
ZrN	- 38.0
UN	- 37.7
TiN	- 36.2
Th_3N_4	- 33.6
YN	- 26.7
Be_3N_2	- 23.4
CbN	- 15.7
TaN	- 14.9
Mg_3N_2	- 10.8
Ca_3N_2	- 9.3
Ba_3N_2	+ 0.6

reducing the oxygen content. This was expected from the oxide free energy data²⁴ shown in Fig. 6. Typical test results are shown in Table IV which gives the data obtained for titanium. In these tests, flat titanium specimens having measurable surface areas were used so that the gettering rate as a function of the surface area could be determined. The metallographic appearance of the titanium before and after the gettering experiment is illustrated in Fig. 7.

Titanium sponge was used in subsequent purification experiments in order to obtain the benefit of a very high surface area-to-weight ratio. These tests were conducted at 816°C for 24 hr on 40-lb batches of commercial lithium that were held in stainless steel containers to which 5 lb of titanium sponge had been added. This procedure reduced the nitrogen content of lithium to less than 10 ppm and was subsequently used routinely to produce low-nitrogen lithium.

The results of experiments in which zirconium sheet specimens were used indicated that zirconium was slightly less effective than titanium as a nitrogen getter under similar test conditions. Since it was clear that no significant improvement could be achieved using zirconium, which is more expensive than titanium, no further testing on zirconium was undertaken.

The results of preliminary studies using yttrium indicated that this metal is more effective than either titanium or zirconium in reducing the oxygen content of molten lithium. The lithium which was purified by exposure to yttrium turnings at 816°C for 100 hr contained less than 100 ppm each of oxygen and nitrogen. Chemical analyses obtained on yttrium metal specimens exposed to impure lithium for various time periods are listed in Table V and are indicative of the relative effectiveness of yttrium as a gettering agent for these impurities. Additional tests will be required to confirm the results of these preliminary studies.

²⁴Glassner, A., The Thermochemical Properties of the Oxides, Fluorides, and Chlorides to 2500°K, U. S. Government Printing Office, Washington, D. C. (1957).

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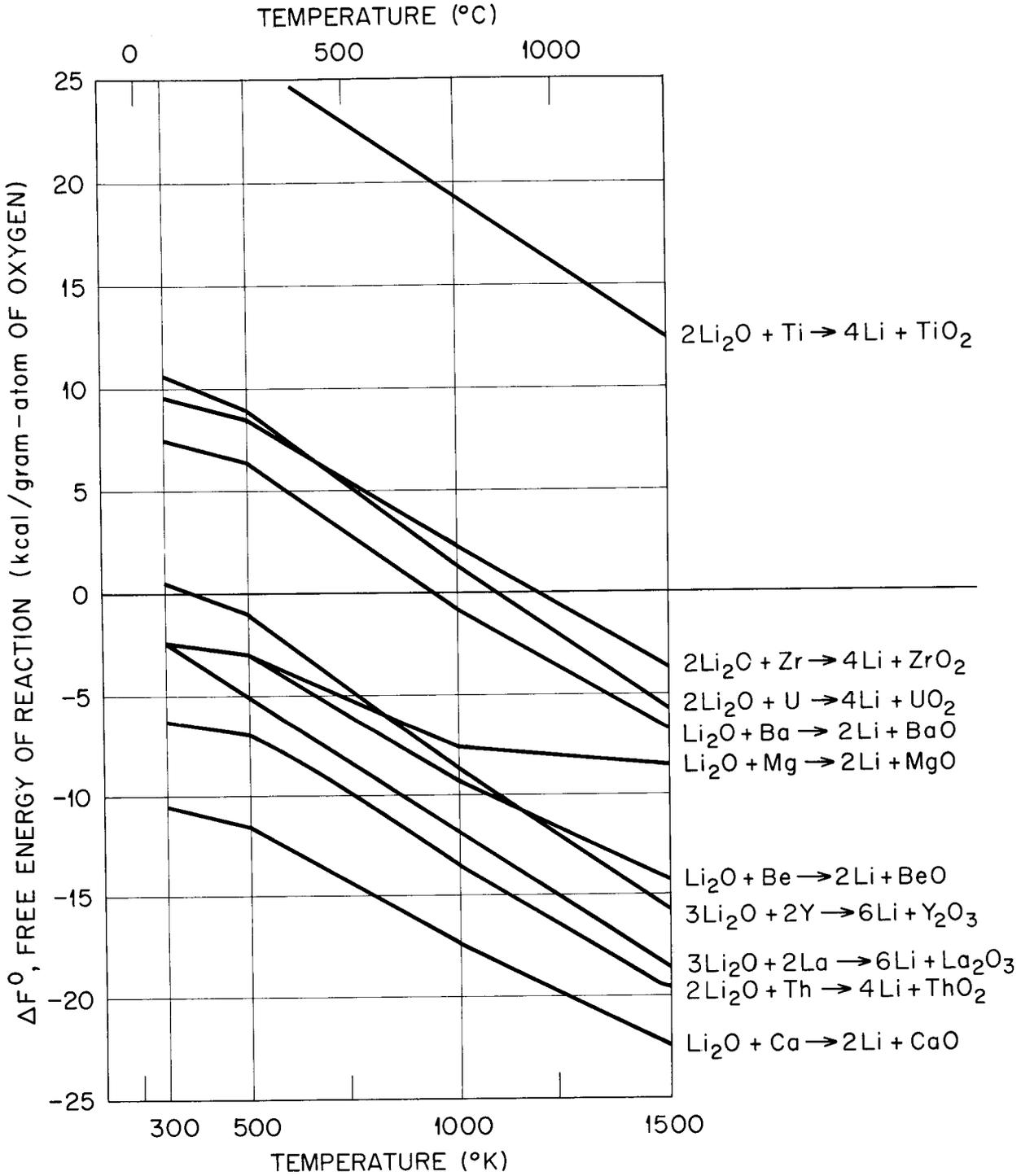


Fig. 6. Standard Free Energy Changes for Lithium Oxide Reduction Reactions.

TABLE IV

RESULTS OF LITHIUM PURIFICATION EXPERIMENT UTILIZING
TITANIUM SHEET AS THE GETTERING METAL

Test Conditions:
 Temperature: 1500°F (816°C)
 Container: Type 347 Stainless Steel
 Weight of Lithium: 730 g
 Volume of Lithium: 94.8 in.³
 Dimensions of Titanium Sheets: 8.0 x 1.75 x 0.012 in.
 Number of Titanium Sheets: 10
 Total Weight of Titanium Sheets:^a 130 g
 Ratio of Total Surface Area of Titanium to Lithium Volume: 2.98 in.²/in.³

Material Analyzed	Impurity Content (ppm)		Remarks
	N ₂	O ₂	
Lithium			
Before test	2450	370	
After 24 hr	740	910	Rate of N ₂ loss (0-24 hr), 71 ppm/hr.
After 48 hr	380	730	Rate of N ₂ loss (24-48 hr), 15 ppm/hr.
Titanium Sheet			
Before test	74	1500	
After 24 hr	1600	1000	X-ray examination of surface showed TiN; metallographic examination showed 0.0004-in. layer of TiN.
After 48 hr	3200	1400	X-ray examination of surface showed TiN; metallographic examination showed 0.0006-in. layer of TiN.

^aWeight change of titanium specimens during 48-hr test: 1.0 g (3.55 mg/in.²).

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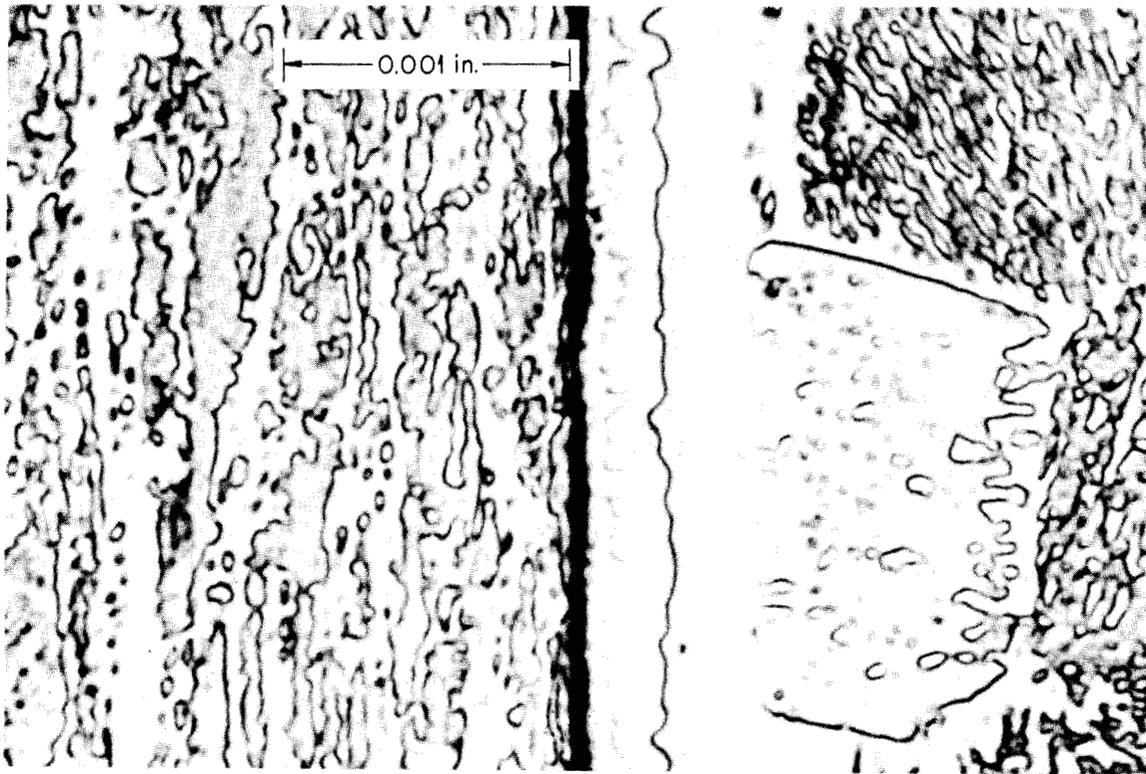


Fig. 7 Surface of Titanium Gettering Specimen: (a) Specimen Before and (b) Specimen Following Exposure to Lithium. Gettering Test Conditions: 816°C (1500°F), 100 hr; Ratio of Titanium Surface Area to Lithium Volume - 2.98 in.²/in.³; Specimen Thickness - 0.012 in. Nitrogen Content of Lithium: Before Test - 2450 ppm. After Test - 380 ppm. Etchant: HF, HNO₃, Glyceria (25-25-50 vol %).

TABLE V
COMPOSITIONS^a OF YTTRIUM GETTER SPECIMENS^b BEFORE AND AFTER
EXPOSURE TO LITHIUM CONTAINING NITROGEN AND OXYGEN

Test Temperature: 1500°F (816°C)
 Total Time of Test: 72 hr

Yttrium Specimen Number	Time Period of Exposure, (hr)	Oxygen Content of Yttrium (ppm)			Nitrogen Content of Yttrium (ppm)		
		Before Test	After Test	Change	Before Test	After Test	Change
1	0-72	1300	3800	+ 2500	450	1100	+ 650
2	24-72	1400	3900	+ 2500	570	850	+ 280
3	48-72	940	1800	+ 860	110	170	+ 60

^aAs determined by vacuum-fusion analysis.

^bDimensions of cylindrical specimens: Diameter, 0.3 in. - Length, 1.0 in.

VI. CONCLUSIONS

The results of determinations of the solubilities of nitrogen and oxygen in lithium indicate that nitrogen has an appreciably higher solubility in the temperature range studied.

Vacuum distillation was found to be ineffective in reducing the nitrogen and oxygen content of lithium.

Low-temperature filtration was effective in reducing the oxygen concentration of contaminated lithium to levels of approximately 100 ppm but did not reduce the nitrogen concentration to this level.

The results of cold-trapping experiments indicate that this technique of purification reduces the oxygen concentration to acceptable levels but does not reduce the nitrogen concentration to the desired level.

Gettering with an active metal, such as titanium, is the most practical and efficient, as well as the cheapest method of decreasing the nitrogen concentration of lithium to less than 50 ppm. Reduction of the oxygen concentration of lithium by gettering was found to be quite difficult compared to the relative ease with which the nitrogen content can be lowered. This is attributed to the thermodynamic stability of lithium oxide.

The purification procedure recommended as a result of these experiments is as follows:

1. Filtration of the gas-packed, commercial lithium at 250°C to remove gross amounts of nitrogen and oxygen contamination generally found in commercial-grade lithium.
2. Gettering by an active material, such as titanium sponge, at 800°C for 24 hr or more to reduce the nitrogen concentration to less than 100 ppm.
3. Cold-trapping for approximately 100 hr to reduce the oxygen concentration to less than 100 ppm.

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