Effect of Pressure on the Refining of Lithium by Distillation[1]

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ABSTRACT

The experiments described show that lithium containing 0.5 per cent sodium can be refined by distillation in the presence of argon in a straight retort, the refined material containing as low as 0.002 per cent sodium. At gauge pressures up to 1 micron the sodium content differs very little from this value. In increasing the pressure from 1 to 740 microns the sodium content is quadrupled. In the presence of argon, nitrogen, oxygen, and hydrogen at different pressures in a slightly V-shaped retort, a sodium content of less than 0.01 per cent was not obtained. There was little or no evidence of oxide, nitride, or hydride formation at pressures of oxygen, nitrogen, or hydrogen below 35 microns.

Introduction

A great deal of interest has developed in regard to the metal lithium because of its low atomic weight (6.94), specific gravity (0.53), melting point (186°C), and boiling point (1336°C), and because of its high chemical activity and other important properties.

Due to the fact that there are important deposits of lithium-containing minerals in Canada, the Canadian Department of Mines and Technical Surveys has initiated a program of research in lithium metallurgy, and several papers have already been published (1–3).

In one phase of this general investigation it was found that lithium of high purity could be obtained by distillation of commercial metal containing about 0.5 per cent sodium. Since equipment for producing gauge pressures lower than 0.04 micron was available in the laboratory, the early work was done in this extremely low range. These experiments showed that lithium containing as low as 0.001 per cent sodium could be produced at a comparatively low rate when the charge was heated at a temperature of 600°C, and that metal containing 0.002 per cent sodium could be obtained at a much higher rate when a temperature of 800°C was used.

The effect of distilling crude lithium in the presence of the chemically inert gas argon and the chemically active gases, oxygen, nitrogen, and hydrogen, at different pressures was investigated, and the results are given in the present paper.

Covered first are results obtained in the presence of argon at various pressures in a straight, cylindrical retort. Although this type of retort was useful for certain kinds of experimental work, it could not be used for the large-scale refining of lithium without changes in design to permit the product to be collected more readily. So, the second part reports the results obtained when argon, oxygen, nitrogen, and hydrogen were used at different pressures in a slightly V-shaped retort equipped with a side arm to collect the refined lithium.

In the 21 experiments described the sodium content of the crude lithium varied between 0.41 and 0.60 per cent and the potassium content between 0.006 and 0.037 per cent.

Experimental

Equipment

The equipment used in the first part of the work consisted of a retort of low carbon steel, 61¼ in. (155 cm) long and 9¼ in. (23.5 cm) ID. One end of the retort was placed in a Globar-heated furnace and the other end was connected to a pumping system. This system included a vertical metal diffusion pump[2], a mechanical pump[3] to produce the primary vacuum, and an auxiliary mechanical pump[4] to maintain vacuum in the diffusion pump. A Pirani heat conductivity pressure gauge and a Philips ionization pressure gauge also were included in the unit. Details of the retort and contents are given in Fig. 1, which is drawn to scale. The condenser was water-cooled at the end which was outside the furnace. The surface of the condenser was divided into five different sections by means of circular ridges, numbered 1 to 5, 1 being nearest to the hot end of the retort and 5 being farthest from it. A steel pan was located directly underneath the condenser to collect the condensed lithium. This pan was divided into

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[2] MC-500, Distillation Products Industries, Rochester, New York.

[3] VSD 5-5-6, Kinney Manufacturing Company, Boston, Massachusetts.

[4] No. 1403, W. M. Welch Scientific Company, Chicago, Illinois.

sections, each one being located beneath one of the circular ridges on the condenser. The sections are numbered 1 to 5, 1 being nearest to the hot end of the retort and 5 being farthest from it. During the refining operation the temperature of the pan was above the melting point of lithium.

Procedure

Each of the individual experiments in this investigation was performed as follows. A piece of crude lithium, which had been stored in oil, was degreased in carbon tetrachloride. It was placed in a stainless steel beaker filled with argon, and as

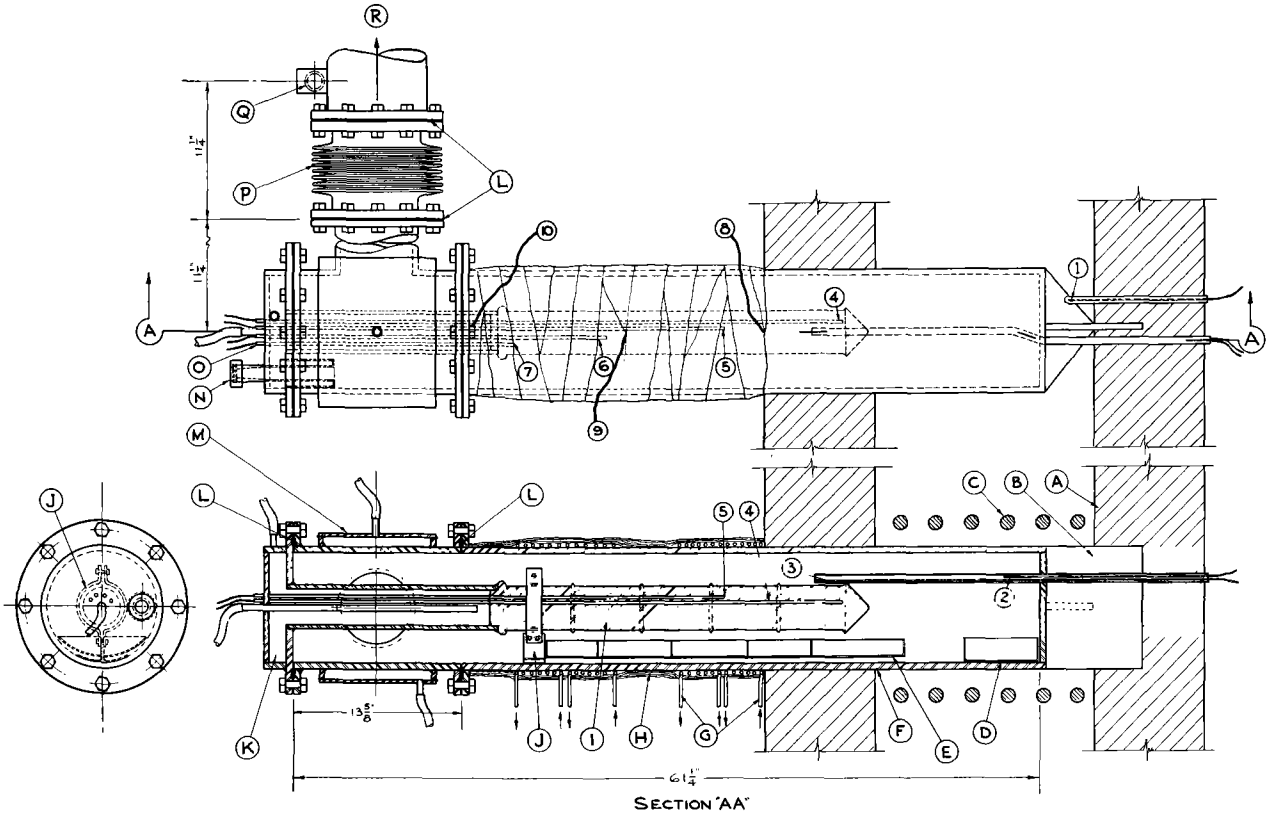

FIG. 1. Unit for refining lithium by distillation. A—furnace wall, B—support for hot end of retort, C—Globars, D—steel pan for charge, E—steel pan for collecting condensed lithium (Fig. 1 only), F—low carbon steel retort, 10 in. OD, G—copper coils for cooling with water, H—asbestos wrapping, I—steel condenser, water-cooled at one end, J—stool to support condenser, K—water-cooled retort head, L—gaskets, M—chamber for water-cooling T section, N—sight glass, O—thermocouple outlet, P—flexible connector, Q—Philips ionization pressure gauge tube (The accompanying indicator has the two scales, 0 to 25 microns and 0 to 0.2 micron.), R—to pumps, S—steel crucible for collecting condensed lithium (Fig. 2 only), T—side arm (Fig. 2 only), U—insulating brick (Fig. 2 only), 1—thermocouple in the interior of the furnace, 2—thermocouple located inside the retort above the charge in pan D, 3—thermocouple located inside the retort, 4, 5, 6, 7—thermocouples located inside the condenser, 8—thermocouple located on the outside of the retort, 9, 10—thermocouples located on the outside of the retort (Fig. 1 only), 11—thermocouple located on the outside of the retort (Fig. 2 only), 12—thermocouple located in the side arm (Fig. 2 only). All temperatures and pressures were recorded continuously on Minneapolis-Honeywell Electronik strip chart potentiometers.

The equipment used in the later work was the same as that just described, except that the retort was slightly V-shaped and the collecting pan was replaced by a side arm which extended downward from the tip of the V and contained a steel collecting crucible. The details of this retort are given in Fig. 2.

In both cases the distance between the Pirani gauge and the retort was slightly greater than that between the Philips gauge and the retort. There was a right-angle turn in the pipe between the two gauges.

much nonmetallic material as possible was removed from the surface. It was then placed in the steel pan D and weighed while still under argon. The pan containing the lithium was introduced into the retort, which previously had been cleaned by water washing and grit blasting and then filled with argon. Finally, head K, with the water-cooled steel condenser I attached, was bolted tightly into place. After the mixture of air and argon had been pumped from the retort down to a gauge pressure of less

than 0.04 micron, the power was turned on in the Globar furnace. (In the cases where the experiment was to be performed in an atmosphere of argon, nitrogen, oxygen, or hydrogen, the gas was permitted to enter the retort just before the power was turned on. In cases where absorption took place with the formation of lithium compounds the gas entered in a very slow continuous stream. It was difficult to regulate the rate of flow accurately and for that reason the retort remained connected to the pumping system. This insured that the desired pressure was maintained.) The retort was heated until the pan and its contents reached a temperature of 800°C as indicated by means of thermocouple 2. Without permitting the temperature of the pan to change materially from this value, slow heating was continued until the temperatures indicated by means of thermocouples 3 to 10 had become stationary. The pan was maintained at 800°C for approximately 270 minutes, at the end of which time, except in one case, all of the lithium had volatilized and condensed in the cooler parts of the retort. Then the power was turned off. When cool, the retort was filled with argon at about atmospheric pressure and the head and condenser were removed. A record was made of the conditions inside the retort and samples were taken for analysis.

In the first part of the investigation five experiments were performed in the straight retort. In Experiment 1 the lowest gauge pressure obtainable (<0.04 micron) was used. In Experiments 2, 3, 4, and 5, argon pressures of 0.1, 1.0, 360, and 740 microns, respectively, were used.

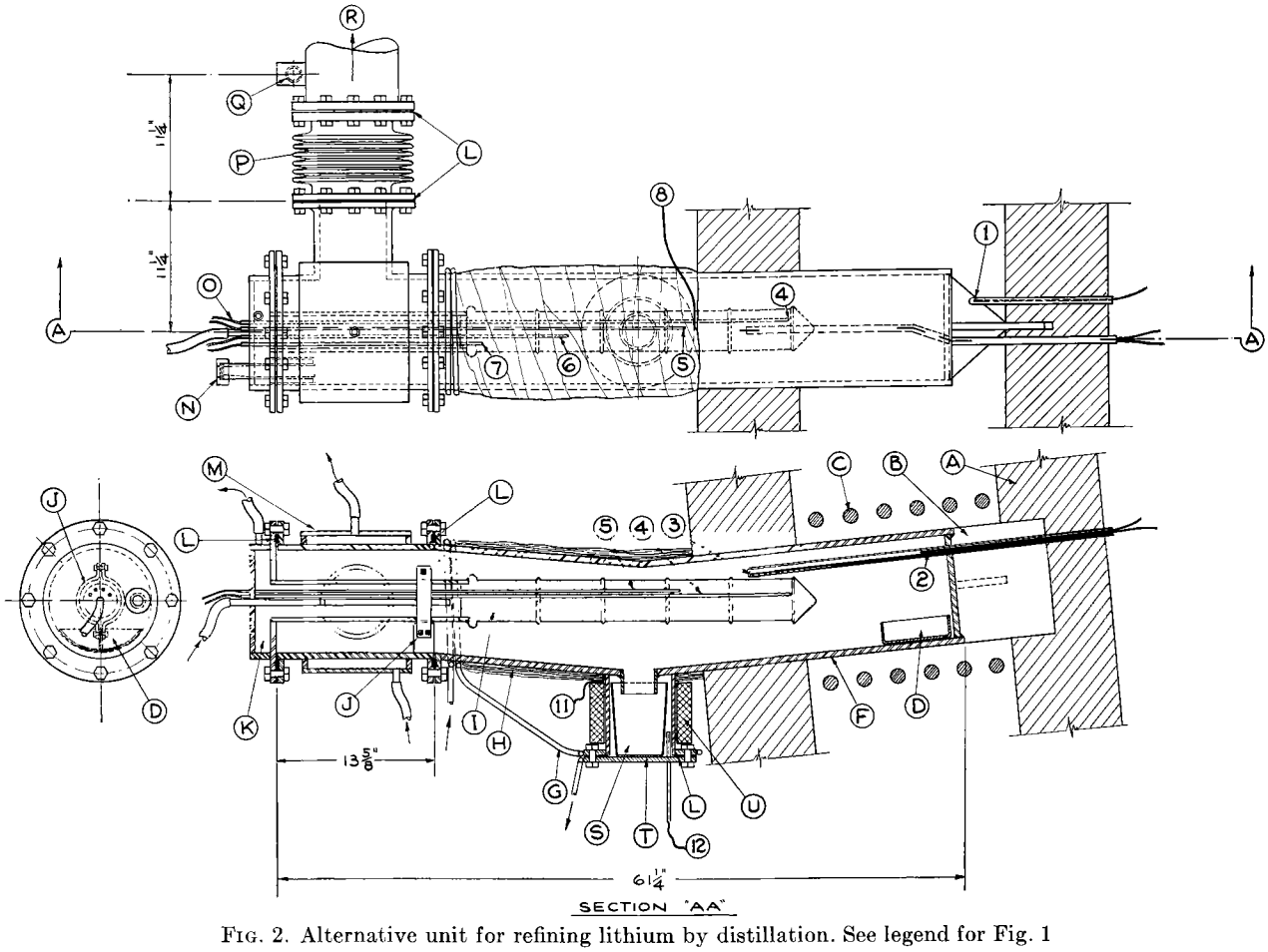

FIG. 2. Alternative unit for refining lithium by distillation. See legend for Fig. 1

In the second part, sixteen experiments were performed in the V-shaped retort. In Experiments 6 and 7, pressures of less than 0.04 micron were maintained. In Experiments 18 and 21, argon pressures of 80 and 450 microns, respectively, were used. In Experiments 9, 16, 19, and 20, nitrogen pressures of 30, 75, 125, and 250 microns, respectively, were used. In Experiments 10, 13, 14, and 17, oxygen pressures of 30, 35, 50, and 75 microns, respectively, were used. In Experiments 8, 11, 12, and 15, hydrogen pressures of 10, 30, 30, and 55 microns, respectively, were used.

Results

In the 21 experiments performed during this investigation the charges of crude lithium varied between 137 and 216 grams in weight. In all cases, with the exception of Experiment 21, the metal had completely disappeared from the pan by the end of the experiment. The nonmetallic residue remaining at the end of each experiment weighed approximately 1.5 grams and contained lithium, sodium, and potassium in the approximate proportions of 100:0.025:0.030. These metals probably were present mostly in the form of oxides. The metal which remained in the pan at the end of Experiment 21 weighed approximately 25 grams and contained 0.006 per cent sodium and 0.012 per cent potassium.

TABLE I. *Equilibrium temperatures in the water-cooled condenser*

Thermocouple No.*	Equilibrium temperature (°C)		
	Minimum	Maximum	Average
4 (above pan section 1).....	480	655	631
5 (above pan section 3).....	420	492	467
6 (above pan section 4)	225	275	251
7.....	27	75	45

* Thermocouple numbers are those given in Fig. 1.

TABLE II. *Location and sodium content of refined lithium in straight retort experiments*

Experiment No.	Argon pressure (microns)	Sodium content of refined lithium (%)			
		Pan section No. 1	Pan section No. 2	Pan section No. 3	Pan section No. 4
1	<0.04*	—	—	0.002	0.002
2	0.1*	—	0.002	0.002	0.003‡
3	1.0*	—	0.002	0.002	0.014‡
4	360	0.005	0.007	—	—
5	740	0.008	—	—	—

* Philips gauge reading. (The Pirani gauge was used for all other pressure readings.)

‡ Very small amount.

The equilibrium temperatures at thermocouples 4, 5, 6, and 7 (inside the water-cooled condenser) during the various experiments are shown in Table I. It would have been preferable to use exactly the same temperatures throughout the whole series but this proved to be impossible due to the fact that the cooling water was at different temperatures at different seasons.

Experiments with straight cylindrical retort.—During these experiments the refined lithium was condensed on the water-cooled condenser and on the cooler parts of the retort wall, and a considerable part of it accumulated in the various sections of the collecting pan. The sodium content and location in the collecting pan of the lithium produced in these experiments is given in Table II. At 740 microns practically all of the lithium was in the first section of the pan, indicating that it had condensed at a comparatively high temperature. At lower pressures the metal condensed at lower temperatures and the range of temperatures was wider. At <0.04 micron the largest proportion of the refined lithium was found in the third and fourth sections of the pan; however, a very thin film containing both metallic and nonmetallic constituents was found on all of the cooler surfaces right back to the water-cooled head K, including the sight glass N. In one experiment the combination of these materials, which was washed from the fourth and fifth divisions of the condenser, contained lithium, sodium, and potassium in the approximate proportions 100:530:10. In another experiment material washed from these same sections contained the metals in the approximate proportions 1:450:0.7. The metal in the collecting pan also showed refinement with regard to potassium but it was not nearly as marked as in the case of sodium. This was due, at least in part, to the fact that there was much less potassium than sodium in the crude metal.

Experiments with the V-shaped retort.—During these experiments the refined lithium which condensed on the condenser and the wall of the retort flowed down into the collecting crucible S in the side arm. At the end of each experiment the contents of the crucible were weighed and the per cent yield calculated. This plus the weight of the original charge and the sodium content of the refined lithium are given in Table III. A few of the data from Table II are included in order to permit a direct comparison to be made. In general the potassium content of the refined lithium varied between 0.006 and 0.01 per cent, indicating that a considerable amount of refinement had taken place in most cases. When the crude metal contained as low as 0.006 per cent of potassium no refinement with regard to potassium took place.

With argon, comparatively little nonmetallic material condensed on the various surfaces inside the retort. When any one of the chemically active gases, nitrogen, oxygen, and hydrogen, was present at a pressure below about 35 microns, comparatively little nonmetallic material condensed. However, an important amount of such material was produced at the higher pressures which were investigated. In the presence of oxygen a white material, probably lithium oxide, was formed, particularly on that part of the condenser where the temperature varied between about 450° and 500°C. In the presence of hydrogen a white material, probably lithium hydride, was formed, particularly on the zone where the tem-

perature varied between about 350° and 475°C. In the presence of nitrogen, red material was formed in the temperature range 400° to 470°C and black or gray material was formed in the range 470° to 550°C. Both of these compounds were believed to be lithium nitrides.

TABLE III. *Yield and sodium content of refined lithium in V-shaped retort experiments*

Experiment No.	Pressure (microns)	Charge (grams)	Yield (%)	Sodium content (%)			
				In argon	In nitrogen	In oxygen	In hydrogen
6	<0.04*	206	79	0.075			
7		176	63	0.080			
8	10*	142	90				0.031
9	30	137	63		0.064		
10		198	83			0.090	
11		208	89				0.100
12		200	86				0.100
13	35	196	90			0.111	
14	50	155	61			0.011	
15	55	194	83				0.061
16	75	185	—		0.085		
17		187	71			0.048	
18	80	181	—	0.080			
19	125	177	66		0.166		
20	250	160	41		0.530		
21	450	216	70	0.130			
Values from straight retort experiments for comparison							
1	<0.04*	209	—	0.002			
2	0.1*	214	—	0.002			
3	1*	208	—	0.002			
4	360	188	—	0.007			
5	740	201	—	0.008			

* Philips gauge reading. (The Pirani gauge was used for all other pressure readings.)

Discussion and Conclusions

In the first part of the investigation it was clearly demonstrated that crude lithium containing approximately 0.5 per cent sodium can be refined by distillation at 800°C in a straight retort at extremely low pressure and in the presence of argon, the refined metal containing as low as 0.002 per cent of sodium. At gauge pressures between <0.04 and 1 micron the sodium content remains at approximately that figure. However, as the pressure is increased from 1 to 740 microns the sodium content is quadrupled.

At first the low carbon steel of the retort was found to fail at welded areas due to lithium vapor attack. However, after a stress-relieving treatment was used, no further difficulty was experienced either in the retort or the steel pans.

It was found that the metal condenses at a temperature in the neighborhood of 300° to 400°C when the pressure is <0.04 micron. The boiling point of lithium at normal pressure is 1336°C.

In the second part of the work it was shown that crude lithium can be refined in a V-shaped retort of the design used in these experiments. However, the extent of the refinement is much less than that obtained in a straight retort, 0.011 per cent being the lowest sodium content obtained under these conditions. Here, again, the sodium content increases with pressure. This effect was masked to a considerable extent by the fact that the sodium content of the crude lithium and the weight of the original charge were far from constant throughout the series of experiments. The excellent quality of the analytical work is demonstrated by the fact that the sodium content of the refined metal was found to be the same (0.10%) in two similar experiments.

The potassium content of the lithium also was decreased by the distillation in the cases where the crude metal contained a comparatively high proportion of the impurity. However, no reduction in potassium content was obtained when that of the crude metal was 0.006 per cent or less.

As might be expected, the percentage yield was related fairly closely to the size of the original charge. It is worthy of note that, at a hydrogen gauge pressure of 10 microns, a comparatively high yield of 90 per cent was obtained in spite of the fact that the original charge was comparatively small.

In the presence of the chemically active gases, oxygen, hydrogen, and nitrogen, the oxide, hydride, and nitrides, respectively, were formed at the gauge pressures above 35 microns which were investigated.

Analytical Results

This investigation would have been impossible without the excellent work of the Analytical Laboratory of the Mines Branch in developing methods of determining very small amounts of sodium and potassium in lithium, and in analyzing a very large number of samples from the different experiments. The analytical procedures have been published in *Analytical Chemistry* (4). It was found that extreme care was necessary in procuring the samples for analysis, and a special procedure was developed for that purpose.

Any discussion of this paper will appear in a Discussion Section, to be published in the June 1952 issue of the Journal.

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