AMERICAN INSTITUTE OF MINING AND METALLURGICAL ENGINEERS
Technical Publication No. 2179
Classes D and E, Metals Technology, June 1947

Laboratory Preparation of Lithium Metal by Vacuum Metallurgy*

BY W. J. KROLL† AND A. W. SCHLECHTEN,‡ MEMBER AIME

(New York Meeting, March 1947)

As this paper is written, the only method for the commercial production of lithium metal is by the fusion electrolysis of LiCl-KCl mixtures, as first proposed by Guntz.[2] The details of the industrial process have not been made public but Osborg[8] stated that an efficiency of more than 90 pct is obtained with a lithium metal recovery above 95 pct and that the metal is 99.5 pct pure. Pletenev[9] gave a power consumption of 66 kw-hr per kilogram of lithium metal produced with a salt consumption of 9 kg of LiCl and 0.4 kg of KCl. Pletenev's figures indicate a somewhat lower recovery than that given by Osborg. In a recent report on German lithium plants, Motock[7] gives figures that are also less favorable than those reported by Osborg. At the German plants the lithium recovery in electrolysis was only 83.4 pct, with a power consumption of 140 kw-hr per kilogram of lithium. The metal averaged only 97 pct pure, with sodium and potassium as the chief impurities. The presence of SO_2, SO_3, SiO_2, Ba, Ca, and appreciable amounts of Na and Fe_2O_3 were especially disturbing in the electrolysis, and it was necessary to run the cell for some time to eliminate most of these impurities and condition the bath. It may be noted here that most of these impurities do not interfere with a thermal reduction process.

These facts show that the present method of producing lithium is fairly efficient and would suggest that other methods could not compete. However, fusion electrolysis has certain drawbacks, such as the necessity of supplying costly, low-voltage direct current and of collecting and processing the anodic chlorine if it is not to be wasted. An even greater disadvantage is that lithium chloride must be used for an electrolyte. It is one of the most expensive salts of lithium, since it cannot be produced in anhydrous form by precipitation from aqueous solution, as is done with LiF or Li_2CO_3.

The reduction of lithium by a vacuum process similar to the ferrosilicon method for the production of magnesium would have certain advantages. Small units, such as Pidgeon retorts, would give flexibility of production to meet demand, and a small plant would require moderate capital outlay. There is a possibility of using idle Government-owned magnesium plants for such purposes. The raw materials needed for vacuum thermal reduction would not have to be extremely pure, especially with respect to the iron and calcium content.

This paper describes a series of experiments to determine the effectiveness of various agents for the reduction of lithium compounds. The investigation is part of a program of vacuum metallurgy con-

* Published by permission of the Director, Bureau of Mines, U. S. Department of the Interior. Manuscript received at the office of the Institute Dec. 19, 1946.

† Consulting Metallurgist, U. S. Bureau of Mines, Albany, Oregon.

‡ Professor of Metallurgical Engineering, Missouri School of Mines and Metallurgy, Rolla, Missouri.

[2] References are at the end of the paper.

ducted at the Northwest Electrodevelopment Laboratory of the Bureau of Mines, U. S. Department of the Interior, at Albany, Oregon, under the supervision of B. A. Rogers, former chief of the Albany Division, Metallurgical Branch.

Previous Work

Various proposals have been made for thermal reduction of lithium compounds. In Gmelin[1] it is stated that Warren reduced LiOH with magnesium, that Hackspill used calcium to reduce LiCl, and that Troost suggested sodium as a reducing agent for LiCl.

There are serious objections to all of these combinations. The reduction of LiOH with magnesium is violent, and the product is poor because hydrogen evolved by the reaction recombines with the lithium in the condenser. The volatility of magnesium is so nearly that of lithium that clean separation of the two metals appears to be impossible. The use of calcium as a reducing agent is hardly commercially feasible because of the high cost and high atomic weight of this metal. The reaction of lithium chloride and sodium rapidly reaches an equilibrium, with the production of very little lithium; high concentration of LiCl must be maintained, and the depleted salts must be reclaimed.

The reduction of LiCN with aluminum, iron, or magnesium has been proposed but does not seem promising because of the formation of the very stable lithium carbide. For the same reason, the reduction of lithium chloride, fluoride, or sulphide with CaC_2 or the reduction of lithium carbonate with carbon is likely to be ineffective.

General Considerations

Aluminum or silicon usually is taken as the reducing agent for the reduction of the alkaline earth metals according to Guntz process. The theory of the mechanism of reduction by these two metals has been stated in a previous paper.[4] The reaction with aluminum will not yield Al_2O_3, but a monoaluminate will be formed with whatever base is present. Likewise, silicon will end as an orthosilicate. Thus, to prevent consumption of the metal oxide being reduced by combination with alumina or silica, it is necessary to add some other base, such as CaO. The addition of the lime also has the effect of keeping the reaction mixture loose and facilitates the escape of the metal vapors.

Other reducing agents could be used but have objectionable features for various reasons. Beryllium, cerium, and most metals of the fourth, fifth, and sixth group would be costly. Iron-group metals are effective as reducing agents only at very high temperatures. Other commercial compounds, such as calcium silicide, zirconium silicide, or ferroalloys of aluminum, chromium, vanadium, and titanium, have no price advantage over aluminum, silicon, or ferrosilicon.

The choice of reducing agent is governed by the compound to be reduced; for example, the relative halide affinities of the alkaline earth metals compared with that of aluminum are not in the same order as the oxide or sulphide affinities. For this reason, aluminum cannot be used for the reduction of lithium chloride, although it effectively reduces the oxide. One other point to be considered is the relative volatility of the reducing agent and the compound to be reduced. In a vacuum-distillation process, magnesium cannot be used to reduce lithium fluoride to lithium metal, because the magnesium will distill over with the reduced lithium metal at the temperature required for reduction, and an alloy will be obtained.

With these theoretical considerations in mind, it was decided that the greatest chance of success would lie in the vacuum

reduction of Li_2O-CaO mixtures with Al and Si; of LiCl-CaO mixtures with Si; and of LiF-CaO mixtures with Si and Al. The production of Li-Mg alloys by reduction of Li_2O-CaO mixtures with magnesium was also considered.

The heats of formation of certain compounds that would be involved are given in Table 1. These data are not encouraging for most of the proposed reductions, nevertheless it was felt that the volatility of lithium metal was so great that it would be possible to promote such endothermic reactions.

Experimental Equipment and Procedure

The vacuum furnace used for the experiments described in this paper consisted of a porcelain tube 40 in. long with an inner diameter of 2⅜ in. (Fig 1). The tube was supported vertically with the closed end on top; a metal head was fastened by a wax seal to the lower end of the tube. Vacuum connections were made through the metal head, which also had a vacuum-tight cover with a conical ground joint that could be opened for the introduction of samples into the tube. A mechanical pump in series with an oil-diffusion pump gave a vacuum of less than one micron in the system. The vacuum was measured with a Stokes tilting McLeod gauge.

Only the top 12-in. section of the tube was heated. The heating element was made of Smith No. 10 alloy wire wound on an Alundum core embedded in Alundum cement and insulated with diatomite brick. The temperature was measured

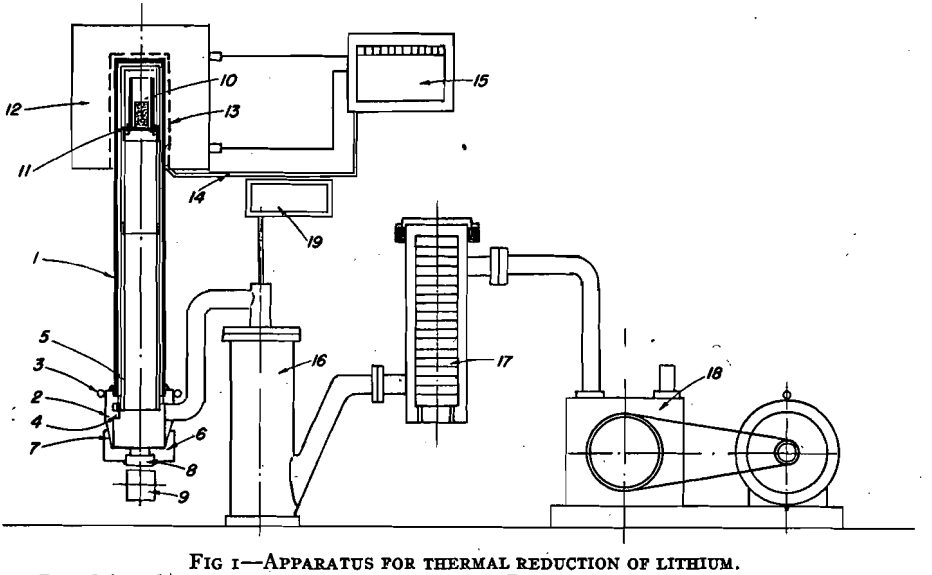

Fig 1—Apparatus for thermal reduction of lithium.

1. Porcelain tube.
2. Conical head.
3. Water cooling.
4. Bayonet.
5. Insert.
6. Conical cover.
7. Ground joint.
8. Glass window.
9. Mirror.
10. Crucible with batch.
11. Bayonet.
12. Metallic resistor furnace.
13. Smith No. 10 alloy coil.
14. Thermocouple leads.
15. Temperature controller.
16. Oil-diffusion pump.
17. P_2O_5 drying tower.
18. Mechanical pump.
19. McLeod tilting gauge.

TABLE 1—*Heat of Formation, in Kilogram-calories*

$2LiF = 289.4$	$MgF_2 = 264.2$	$\frac{2}{3}AlF_3 = 166.0$	$\frac{1}{2}SiF_4 = 119.9$
$2LiCl = 197.4$	$MgCl_2 = 151.0$	$\frac{2}{3}AlCl_3 = 111.2$	$\frac{1}{2}SiCl_4 = 75.1$
$Li_2O = 143.0$	$MgO = 145.8$	$\frac{1}{3}Al_2O_3 = 119.3$	$\frac{1}{2}SiO_2 = 97.4$

at the outside wall of the porcelain tube and controlled by means of a platinum platinum-rhodium thermocouple attached to a recording pyrometer controller. The use of the Smith No. 10 resistance wire made it possible to run at temperatures as high as 1300°C.

A sample to be heated was placed in a crucible, pushed up into the heated portion of the tube, and supported there on a small porcelain tube. If it was expected that there would be volatilization of some constituent or reaction product that would condense in the lower part of the furnace, the sample was placed in a crucible, which fitted inside a stainless-steel tube, which, in turn, slipped inside the furnace tube. With this arrangement, all condensate was caught inside the stainless-steel tube and was readily removed from the furnace.

The mixtures to be heated were first briquetted and then placed in a crucible in the furnace. The vacuum pumps were started and when a vacuum in the neighborhood of one micron was obtained the heating coils were turned on. The temperature was brought up slowly to the maximum desired and held there overnight. The operator could see the interior of the furnace through a small window in the metal head and observe whether or not a condensate was formed. After the run was completed, the furnace was allowed to cool, and was opened. Any condensate was scraped from the tube; the tube was washed, and the washing solution was analyzed for lithium. The residue of the charge was removed from the crucible and weighed.

PRODUCTION OF LITHIUM OXIDE

Lithium oxide is not commercially available, but it can be produced by thermal decomposition of the carbonate or the hydroxide. Johnston[3] gives dissociation pressures for the two compounds (Table 2).

The melting point of Li_2CO_3 is 732°C and that of LiOH is 455°C. They reach a dissociation pressure of 760 mm Hg at 1270°C and 924°C, respectively. Available data indicate that Li_2CO_3 is dissociated more easily than $BaCO_3$ but less readily than $CaCO_3$.

Few data are available on the physical and chemical properties of Li_2O. It is said to be slightly volatile at 1000°C and to melt above 1625°C.

To obtain lithium oxide for reduction experiments, it was decided to produce it by thermal dissociation of Li_2CO_3 in a vacuum. The use of a vacuum furnace makes it possible to eliminate most of the CO_2 at a temperature slightly lower than the melting point of Li_2CO_3. It would be possible to dissociate the Li_2CO_3 under an inert gas or with the addition of

TABLE 2—*Dissociation Pressures for* Li_2CO_3 *and* LiOH[a]

	Li_2CO_3					LiOH				
Temperature, deg C...	610	723	810	888	965	520	610	670	724	812
Pressure, mm Hg.....	1	4	15	32	63	2	23	62	121	322

[a] From Johnston.[3]

carbon or carbide, as is done with $BaCO_3$, but the temperature required would be much higher than that of the vacuum method.

Consideration was given to the possibility of using LiOH rather than Li_2CO_3, but the hydroxide is more expensive and melts at a lower temperature. Furthermore, the resultant moisture from the breakdown of the hydroxide would cause difficulty in the vacuum pumps.

As was mentioned before, if silicon or aluminum is to be used as a reducing agent for Li_2O, a strong base is required to combine with the SiO_2 or Al_2O_3. With this in mind, CaO was added to the Li_2CO_3 before calcination.

Li_2CO_3 was mixed with 1½ times as much CaO by weight; the mixture was briquetted and heated in the vacuum furnace. The first appreciable gas evolution was at 600°C. The temperature was maintained at 850°C until no more CO_2 was given off. After the furnace had cooled, the calcined material was removed and crushed to a powder. This product showed only a slight indication of melting.

In a subsequent test, Li_2CO_3 was calcined without the addition of CaO. The gas evolution started at 600°C and the charge had to be heated to 820°C to drive off the CO_2. At this temperature, which is above the melting point of the Li_2CO_3, the contents of the crucible fused and a small amount boiled over. The product obtained contained only 0.31 pct carbon dioxide. The addition of CaO facilitates the evolution of CO_2, the lime acting as a bulk material that keeps the passages open for the escape of the gases. The experiment shows that Li_2O can be obtained by thermal dissociation in vacuo more easily than BaO from its carbonate.

Reduction of Lithium Oxide

Reduction with Silicon

The reduction of mixtures of lithium oxide and calcium oxide with silicon, by analogy with the similar reduction of dolomite with ferrosilicon, probably proceeds according to the following equation:

$$2Li_2O + 2CaO + Si = SiO_2.2CaO + 4Li \quad [1]$$

The ground mixture of Li_2O-CaO from the calcination described in the previous section was thoroughly mixed with finely pulverized silicon (100-mesh). A 10 pct excess of silicon was added over that indicated by Eq 1. The mixture was briquetted and heated in the vacuum furnace under a residual pressure of one micron or less. The furnace was held for 15 hr at the maximum temperature. The deposition of lithium metal in a ring in the cooler part of the furnace immediately below the heated zone could be observed through the small window at the lower end of the tube.

The results obtained are given in Table 3. The recoveries increased with increased temperature. At 850°C the efficiency was only 52.5 pct while at 1300°C it had reached 92.7 pct. For comparison, some of the data obtained with aluminum and magnesium as reducing agents have been included in the table.

These data would indicate that a reasonable recovery of lithium is obtained in the temperature range 950° to 1000°C and that an increase above those temperatures only slightly improves the recovery. The residual gas pressure obtained in commercial magnesium units is generally of the order of 50 microns. The lithium recoveries probably would be slightly lower in commercial units than those obtained in the laboratory furnace with a residual gas pressure of one micron.

An average sample of lithium metal made by the silicon reduction of a mixture of lithium oxide and calcium oxide in four different runs contained: 0.01 Si, 0.01 pct Al, and 0.04 pct Ca. The metal

TABLE 3—*Reduction of* Li_2O-CaO *Mixtures*

No.	Grams Lithium			Percentage of Lithium			Temperature, Deg C
	Input	Output	Residue	Recovery	Residue	Not Accounted for	
Silicon as Reducing Agent							
1	6.1	5.66	0.85	92.7	13.9	+6.6	1300
2	3.2	2.7	0.55	84.2	17.2	+1.4	1100
3	3.7	3.0	0.46	81.0	12.4	−6.6	960
4	8.2	6.0	1.97	73.2	24.1	−2.7	950
5	4.0	2.1	1.45	52.5	36.4	−11.1	850
Aluminum as Reducing Agent							
6	3.84	3.1	0.44	80.6	11.5	−7.9	900
Magnesium as Reducing Agent							
7	6.7	4.83	0.6	72.2	8.9	−18.9	950

produced in this way is of outstanding purity and presumably was also free of chlorine.

Reduction with Aluminum

The reduction of lithium oxide with aluminum resembles very closely the reduction with silicon. The following equation represents the probable reaction:

$$3Li_2O + CaO + 2Al = CaO.Al_2O_3 + 6Li \quad [2]$$

The experimental procedure was the same as that used with silicon; a 10 pct excess of aluminum above the theoretical amount required was added to the Li_2O-CaO mixture.

At a temperature of 900°C and under a vacuum of one micron or less, 80 pct of the lithium in the charge was recovered as metallic lithium.

It appears that approximately the same recovery is obtained with aluminum for the reducing agent as with silicon, but slightly lower temperatures can be used.

Reduction with Magnesium

The reduction of Li_2O with magnesium does not seem promising, since the vapor pressure of magnesium is lower than that of lithium. The boiling point of lithium as given by Maucherat[6] is about 1257°C, as compared with 1100°C for magnesium. Despite this apparent difficulty it was thought worth while to attempt the reduction, as the production of metallic lithium would depend upon the relative stability of MgO and Li_2O at the temperature of the experiment.

A mixture of 15.8 grams Mg, 19.8 grams Li_2O and 55.2 grams CaO was briquetted as in the previous experiments. In this instance, the CaO had no chemical function. The briquette was heated 2½ hr at 1000°C under a helium atmosphere, to allow the Li_2O and the magnesium to react. The furnace was then cooled and reheated slowly to 950°C with a vacuum of one micron. This temperature was maintained overnight and a metal mixture was found to have distilled over, which contained 51.6 pct Li; the remainder was magnesium. Of the lithium in the charge, 72.2 pct was recovered in the condensed alloy.

This experiment indicates that while it is possible to reduce Li_2O with magnesium, sufficient magnesium is distilled over to contaminate the product badly.

However, magnesium-lithium alloys can be made in this manner.

Reduction of Lithium Carbonate

The conversion of Li_2CO_3 to Li_2O and the subsequent reduction of the oxide in a separate run has been described. Two experiments were made to determine whether the calcination and the reduction could be accomplished in one operation.

The Li_2CO_3, CaO, and the silicon were mixed in the same proportions as before, briquetted, and heated under vacuum at 750°C until all evolution of CO_2 ceased. The temperature was then raised to 950°C to promote the reduction reaction. A small amount of badly burned condensate was obtained, indicating that probably the lithium condensate had been oxidized by the CO_2 released from the Li_2CO_3. Most of the silicon reacted with CO_2 before reducing the free Li_2O.

Reduction of Lithium Chloride

A process has been developed by one of the authors[5] for producing metallic sodium from NaCl according to the following equation:

$$4NaCl + 4CaO + Si = SiO_2.2CaO + 4Na + 2CaCl_2 \quad [3]$$

In this operation sodium is evaporated because it is more volatile than its chloride; the boiling points are, respectively, 850° and 1685°C. The margin of operation with lithium is not nearly as great; the metal boils at 1257°C and LiCl at 1384°C. Silicon can be replaced by aluminum.

Two runs were made with LiCl plus CaO mixtures to which silicon had been added as a reducing agent. In the first experiment the briquettes were heated to 850°C under a vacuum, and in the second experiment the briquettes were heated to 1000°C under helium and then cooled and reheated to 850°C under a vacuum. In both instances a large condensate of LiCl was obtained, which contained no metallic lithium.

These experiments would indicate that LiCl is too volatile as compared with lithium to permit a successful reduction of the metal.

Reduction of Lithium Fluoride

The reduction of lithium fluoride by the same reaction as that proposed for lithium chloride has more chance for success because the vapor pressure of LiF is low. Van Laar[10] found that at 1390°C the vapor pressure was only 81 mm.

A run was made with LiF plus aluminum as the reducing agent; CaO was added, with the intention of tying up the fluorine of the lithium fluoride to make the formation of either AlF_3 or SiF_4 impossible. The probable reactions involved are:

$$6LiF + 4CaO + 2Al = Al_2O_3.CaO + 6Li + 3CaF_2 \quad [4]$$

$$4LiF + 4CaO + Si = SiO_2.2CaO + 2CaF_2 + 4Li \quad [5]$$

At 1000°C a condensate was obtained that contained approximately 90 pct of the lithium as metal and the other 10 pct as LiF. The lithium recovery was 44.2 pct of the input. A similar run with silicon as reducing agent gave at 1100°C a lithium recovery of 22.7 pct. There was no formation of SiF_4. In both cases lithium metal was produced, but it was contaminated with lithium fluoride. In Gmelin[1] a statement is credited to Speketer to the effect that LiF cannot be reduced in a vacuum with aluminum; the data given herein disprove that contention.

The boiling point of LiF is 1666°C, according to Gmelin, while, according to the same source, the boiling point of AlF_3 is 1294°C and the salt sublimts without melting. These data would indicate that aluminum fluoride would be found in the condensate rather than LiF. However, analyses of the condensate showed only a trace of aluminum. The appearance

of LiF in the condensate instead of the more volatile AlF_3 could be explained by the formation of the very stable lithium cryolite, which is not decomposed by CaO and in which the vapor pressure of AlF_3 is certainly reduced greatly, while excess LiF can evaporate. The true nature of the reaction would then be:

$$Al + 6LiF = AlF_3.3LiF + 3Li \quad [6]$$

It appears that while the reduction of LiF with aluminum or silicon is possible, the metal condensate contains some LiF.

Conclusions

Lithium metal was produced readily by the reduction of Li_2O-CaO mixtures with silicon or aluminum in a vacuum of less than one micron and at temperatures of 950° to 1000°C. Under these conditions, recoveries of better than 75 pct of the lithium content of the charge were obtained with silicon as a reducing agent and better than 80 pct with aluminum. The temperature required for the reduction with aluminum is lower than that needed with silicon. Lithium can be made by this process at a temperature that is substantially lower than that employed in the production of magnesium by the ferrosilicon process.

Lithium carbonate dissociates readily in a vacuum. The evolution of gas starts at 600°C and is complete at 850°C in a vacuum of one micron. Since the carbonate melts at 732°C, interference of the fusion with the degassing takes place, and it is advisable to add CaO to keep the mixture loose. Calcium oxide is needed in the reduction step to tie up the silica as an orthosilicate and the alumina as a monoaluminate.

Lithium carbonate-CaO mixtures could not be reduced efficiently with silicon, and the small amount of metal obtained was oxidized badly.

Lithium chloride could not be reduced with silicon in presence of CaO because the lithium chloride was too volatile. Lithium fluoride can be reduced in the presence of CaO with aluminum or silicon, but the product is contaminated with lithium fluoride. No SiF_4 was formed with silicon, and with aluminum, no AlF_3 was found in the condensate.

Magnesium-lithium alloys can be made by reducing Li_2O-CaO mixtures with magnesium at 950°C.

It appears that lithium is produced more easily by vacuum methods than is magnesium, barium, calcium, or strontium. The laboratory methods described for the production of lithium could be used with little modification for the commercial production of this metal.

The outstanding purity of the lithium metal made by thermal reduction of mixtures of lithium oxide and calcium oxide with silicon or aluminum may be emphasized. Only very minor amounts of silicon, aluminum or calcium could be found in the condensate.

Addendum

After this work had been completed and the article had been written, the National Defense Research Committee released reports PB24472 and PB24481, describing experiments done by the National Research Corporation on methods of producing lithium by the reduction of lithium compounds with ferrosilicon. Although the two entirely independent investigations do not concur in every respect, they both indicate the feasibility of producing lithium metal by such reactions.

References

1. Gmelin: Handbuch der anorganischen Chemie, 20. 8th Auflage, System No. 20, Verlag Chemie, Carl Winters. Heidelberg, 1927.
2. M. Guntz: Sur La préparation du Lithium métallique. *Compt. rend.* (1893) **117**, 732–734.

3. J. Johnston: Die Dissoziationsdrucke einiger Metallhydroxyde und Karbonate. *Ztsch. Physikal. Chem.* (1908) **62**, 339.
4. W. J. Kroll: Processes for Making Barium and its Alloys. U.S. Bur. Mines *I. C.* 7327 (1945).
5. W. J. Kroll: Process for Making Sodium Metal. Patent applied for.
6. M. Maucherat: Tension de vapeur du Lithium. *Compt. rend.* (1939) **208**, 499–501.
7. G. T. Motock: Extraction and Uses of Lithium in Germany. U.S. Bur. Mines *I. C.* 7361 (1946). 23 pp.
8. H. Osborg: Lithium. *Trans.* Electrochem Soc. (1934) **66**, 91. Monograph on Lithium. Electrochem. Soc., New York, 1935.
9. S. A. Pletenev, and A.N. Ivanova: Electrolytic Production of Lithium. *Redkie Metal* (1934) **3**, (3), 40–43; *Chem. Abst.* (1933) **27**, 4175; (1934) **28**, 7169.
   L. Wassilewski and J. E. Zaleski: Electrolytic Production of Lithium. *Prezemysl Chem.* (1934) **18**, 628–633.
10. J. A. Van Laar: Über die aus den Dampfspannungen berechneten Werte von a, etc. *Ztsch. anorg. Chem.* (1925) **148**, 240.