THE VAPOR PRESSURE OF LITHIUM IN THE REDUCTION OF LITHIUM OXIDE BY SILICON[1]

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ABSTRACT

The vapor pressure of lithium over the system lithium oxide – calcium oxide – silicon has been measured using the gas entrainment method at temperatures between 970° C. and 1025° C. The experimental results are summarized in the form $4 \log P = 43.1 - (6.69/T) \times 10^4$, where P is in atmospheres and T in ° A. The reaction, as usually written,

$$2Li_2O + 2CaO + Si = 4Li(g) + 2CaO.SiO_2,$$

does not describe the process completely.

INTRODUCTION

The classical method of producing alkali metals involves electrolysis of fused chlorides, preferably a mixture of chlorides in order to utilize a low-melting-point eutectic. Lithium is so produced using LiCl–KCl mixtures. In this case, however, certain inherent disadvantages of electrolytic processes are intensified. Lithium is at the head of the electromotive series; hence, any metallic impurities present in the bath would be deposited at the cathode and find their way into the final product. The purity of the metal is dependent on the purity of the charge material.

These characteristics, together with the low electrochemical equivalent of lithium (6.94 lb. of Li per 500 amp-days of power) and the reactivity of the metal, justify the search for alternative methods in the form of thermal reduction techniques. The relative volatility of lithium metal should permit its evolution in the gaseous state from a reaction mixture consisting of the oxide and a suitable reducing agent.

Such a method has been successfully applied to magnesium, where calcined dolomite is reacted with silicon (as ferrosilicon) in the solid state, the reaction occurring being described as

$$2CaO.MgO(s) + Si(s) = 2Mg(g) + 2CaO.SiO_2(s). \quad [1]$$

Kroll and Schlechten (1) examined a number of reducing agents and decided that a reaction similar to that for magnesium was feasible and, in fact, preferable to others. For this purpose, these authors calcined mixtures of Li_2CO_3–CaO, which were subsequently briquetted with FeSi to provide the charge for their experiments. In a manner analogous to the magnesium-forming reaction, lime was added so that a calcium silicate rather than a lithium silicate would form according to the postulated reaction

$$2Li_2O(s) + 2CaO(s) + Si(s) = 4Li(g) + 2CaO.SiO_2(s). \quad [2]$$

These authors described the general procedures adopted and were not concerned with the measurement of the pressures of lithium over the system.

This paper describes measurements of the equilibrium pressures of lithium over a mixture of calcined $Li_2CO_3.CaO$ and silicon. The magnitude of this pressure is the effective driving force of the reaction, and directly controls the feasibility of a practical reduction process of this type.

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EXPERIMENTAL

From preliminary experiments, it was found that the reaction pressure of lithium in the reduction process was in the order of 5 mm. Hg at 1000° C. As a result, the entrainment method was adopted, similar to that used by Pidgeon and King (2) and later by Ellingsgaeter and Rosenqvist (3) in their examination of reaction [1].

Purified argon was employed as the carrier gas, which was saturated with lithium vapor. The metal vapors were carried downstream to a point where conditions were appropriate for condensation.

Owing to the reactivity of lithium metal, the reaction tube adopted was a clean 30-inch length of black iron pipe (1 inch diameter) enclosed by a heat-resisting nickel–chromium tube. Insert condensers were troublesome, and it was decided to utilize the downstream portion of the iron reaction tube itself as condenser. At the end of an experimental run the tube was cut in two, separating the condensing section from the charge zone. The condensed product could not be weighed directly because of the rapid formation of lithium nitride in the atmosphere. As a result, the deposit was dissolved in hot distilled water, and the amount of lithium collected determined by polarographic means (4).

Clean steel wool placed at the extreme downstream section of the charge prevented the contamination of the condensing section of the reaction tube by fine particles entrapped in the gas stream. Vapor-phase condensation of the lithium vapor similar to the formation of "blue powder" in the thermal reduction of ZnO was eliminated by inserting a second piece of clean steel wool slightly downstream from the point where the bulk of the condensation occurred. This vapor-phase condensation phenomenon is caused by the "cold blanket" of carrier gas on the walls of the condenser. Steel wool serves to eliminate this phenomenon and also acts as a dust trap.

The reaction zone was equipped with baffles which maintained a 3-inch zone constant to ±1° C.

CHARGE MATERIAL

Li_2O was produced by thermal dissociation of reagent grade Li_2CO_3–CaO mixtures in vacuum according to the procedures described by Kroll and Schlechten (1). The calcined product, originally containing 60% CaO and 40% Li_2CO_3, was mixed with a 20% addition of 100% −100 mesh ferrosilicon analyzing 79% Si, and subsequently briquetted to provide particles $\frac{1}{3}$ inch in average dimension. The mixture for reduction analyzed 7.0% Li and 16.9% Si.

PROCEDURE

Reduction briquettes were charged to the reaction tube and heated to the required temperature. After the passage of a given amount of argon, sufficient to bring about 5–10% reduction (i.e., approximately 0.3 g. Li collected), the reaction tube was removed from the furnace and cooled in argon. When the tube had cooled sufficiently, it was subsequently sectioned, and the product in the condensing section was dissolved and analyzed.

From the volume of argon used, corrected to N.T.P., and the amount of lithium collected, the reaction pressure of lithium over the system was calculated.

RESULTS

A series of experiments at a temperature of 993° C. and flow rates varying from 2.0 to 8.0 cc. per second was performed. The results are shown in Table I and plotted in Fig. 1.

From the graph (Fig. 1), it can be seen that the extrapolation to zero flow rate yields

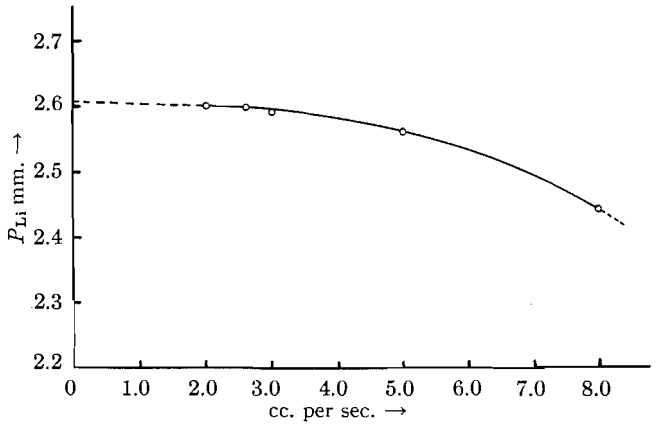

FIG. 1. Effect of flow rate on apparent vapor pressure.

TABLE I

Rate (cc./sec.)	P_{Li} mm. Hg)
2.0	2.60
2.6	2.60
3.0	2.59
5.0	2.56
8.0	2.44

a value of the vapor pressure essentially the same as the value at a flow rate of 2.6 cc. per second. At flow rates above 2.6 cc. per second saturation of the argon carrier gas was not established. This is shown by the lower values of the apparent vapor pressures at these higher rates.

The flow rate of 2.6 cc. per second is large enough to overcome thermal-diffusion effects, and small enough to establish saturation. At very low flow rates, it was observed that the iron reaction tube was bright-annealed by the lithium vapors upstream from the reaction zone, caused by the back-diffusion of lithium in the gas stream. At the saturation rates, this bright-annealing effect was not observed.

Saturation experiments were also performed at 972° C. and results similar to those at 993° C. were obtained.

EFFECT OF TEMPERATURE

At temperatures below 970° C., consistent results could not be obtained; at temperatures above 1025° C., the charge showed definite evidence of the formation of a liquid phase. Successful measurements were therefore restricted to this range of temperature.

TABLE II

P_{Li} (mm.)	log K_p (atm.)	° C.	° A.	$1/T$° K.
1.8	−10.5020	972	1245	8.032×10^{-4}
2.3	−10.0764	982	1255	7.968
2.6	− 9.8632	993	1266	7.899
2.9	− 9.6736	996	1269	7.880
3.5	− 9.3468	1005	1278	7.825
4.1	− 9.0720	1011	1284	7.788
4.5	− 8.9104	1012	1285	7.782
4.9	− 8.7624	1016	1289	7.758
6.6	− 8.2452	1025	1298	7.704

Table II summarizes the results obtained. The values quoted for the measured vapor pressure are estimated to have a probable error of 5% and represent the average of several determinations at the various temperatures.

Fig. 2 is a plot of $4 \log_{10} P_{Li}$ against $1/T°$ K.

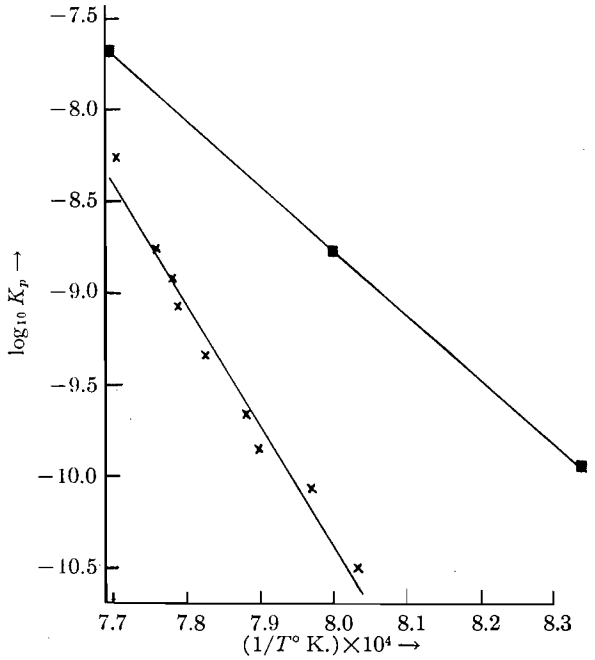

FIG. 2. Calculated and observed equilibrium constants plotted against reciprocal temperature.
■—Calculated. ×—Observed.

DISCUSSION

The reaction [2] as proposed by Kroll and Schlechten (1) served as a basis for the calculations. Experiments were performed in which the reaction was completed *in vacuo*. X-Ray diffractometer investigations on the solid residue revealed the presence of dicalcium silicate, excess CaO, and excess FeSi. The diffractometer traces also showed the presence of other compounds which could not be identified, suggesting that equation [2] is not the only reaction occurring.

The presence of the diatomic species of lithium vapor (Li_2), at a total pressure $P_{(Li+Li_2)}$ equal to 40 or 50 mm. Hg, would account for approximately 7% of the vapor phase at these temperatures (5). However, at the pressures of lithium involved in this research (in the order of 2–6 mm. Hg), the diatomic species can be shown to play a negligible role.

Assuming that the major reaction is reaction [2], equilibrium constants were computed and plotted against $1/T°$ K., both from the experimental values and from the calculated values for the reaction. The experimental values are shown in Table II and

TABLE III

P_{Li} (mm.)	log K_p (atm.)	° K.
2.46	−9.956	1200
4.94	−8.744	1250
9.25	−7.656	1300

plotted in Fig. 2. The calculated values are shown in Table III and are also plotted in Fig. 2.

For these calculations, the solids as predicted by reaction [2] were assumed to be present as pure, distinct phases; thus, their activities were equated to unity and the lithium vapors present were assumed ideal; hence, the equilibrium constant was written in the form

$$K_p = (P_{Li})^4.$$

The thermodynamic data used for the calculated values of the equilibrium constant were taken from Kubaschewski and Evans (6), Coughlin (7), and Kelley (8).

A statistical analysis of the experimental points gives the equation of the straight line in Fig. 2 in the form

$$\log_{10}K_p = 43.1 - (6.69\times10^4/T) \qquad [3]$$

corresponding to a heat of reaction of 306,000 cal. The calculated value for the heat of reaction utilizing the values shown in Table III is 164,000 cal.

The discrepancy between the calculated and the observed values is greater than either the experimental error or the uncertainty of the thermodynamic data used. The discrepancy must lie, then, in the assumption of unit activities or be due to the fact that the reaction cited (equation [2]) is an oversimplification.

It is quite probable that the formation of a lithium silicate should be accounted for, since in a series of experiments above 1025° C. the charge showed distinct evidence of the formation of a liquid phase. The melting point of pure Li_2SiO_4 is approximately 1025° C. A further possibility is the formation of the double silicate of Ca and Li.

In general, it can be stated that, if any side reaction occurs that effectively ties up any lithium, an increase in the heat of reaction would be observed.

CONCLUSIONS

1. The values of the pressure of lithium encountered in the reduction reaction are of sufficient magnitude to warrant a commercial thermal reduction process.

2. The experimental values are summarized in the form $\log_{10}P = 43.1 - (6.69/T)\times10^4$, where P is in atmospheres and T in ° K.

3. The reaction occurring, written in the form

$$2Li_2O + 2CaO + Si = 4Li + 2CaO.SiO_2,$$

is an oversimplification.

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