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Prepared for

3rd ANS Topical Meeting
on the Technology of Controlled Nuclear Fusion
May 9-11, 1978
Santa Fe, NM

MASTER

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EXPERIMENTAL STUDIES OF PROCESSING CONDITIONS FOR
LIQUID LITHIUM AND SOLID LITHIUM ALLOY FUSION BLANKETS*

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A 50-gallon-capacity liquid lithium loop (Lithium Processing Test Loop, LPTL) has been constructed and brought into operation at the Argonne National Laboratory. This system contains experimental assemblies to study (a) lithium processing technology based on molten salt extraction, cold trapping, and getter trapping and (b) on-line hydrogen monitoring. An efficient electrolytic method, employing a porous sparged electrode, has been developed to recover hydrogen isotopes from the types of molten salts (e.g., LiF-LiCl-LiBr) selected for use in the salt-processing system on the LPTL. This method, when tested under realistic conditions, has demonstrated the potential for recovering tritium (from lithium) at the sub-wppm level. Results of cold-trap tests on the LPTL and of getter-trap tests on both the LPTL and a much smaller lithium loop have provided some evidence that these types of processing methods can be used to control oxygen and nitrogen levels in lithium. Studies of the hydridation of solid Li-Al and Li-Pb alloys have provided data on activity coefficients and phase boundary locations for these binary systems as functions of temperature and composition. The Sieverts' constants for dilute hydrogen solutions in LiAl (in $wppm/Torr^{\frac{1}{2}}$) were found to be 10^3 to 10^4 times smaller than those for hydrogen in pure lithium at the same temperature.

I. INTRODUCTION

The Argonne National Laboratory (ANL) is engaged in a family of related studies to establish the technical basis for developing fusion reactor blanket-processing methodology. These studies include (a) the operation of several test facilities designed to develop materials and process-oriented information[1] and (b) a number of bench-scale experiments to obtain basic thermodynamic data (solubilities, phase relationships, etc.) on liquid lithium and lithium alloy systems.[2] This paper reviews the results of work in these areas over the past year. Considered in order are early results with the Lithium Processing Test Loop, development work on the salt extraction system, experiments with a miniture lithium loop, and basic research on hydrogen solutions in Li-Al and Li-Pb alloys.

II. THE LITHIUM PROCESSING TEST LOOP (LPTL)

The principal focus of work in the ANL blanket-processing program has been on the construction and operation of a large lithium test facility. This facility, the LPTL, is a 50-gallon-capacity, forced-circulation (EM-pumped) system, constructed almost exclusively of 300-series stainless steels (mostly 304L). The LPTL (shown schematically in Fig. 1) contains experimental assemblies to study (a) molten-salt extraction as a processing method, (b) cold-trapping, (c) getter-trapping, and (d) permeation-type (on-line) hydrogen monitoring. Operation of the LPTL began early in 1978 with the initiation of tests of the cold-trap/getter-trap system as a means of controlling nonmetallic element (e.g., O, H, N, C) concentrations in flowing lithium.

At the time of this writing, the LPTL had
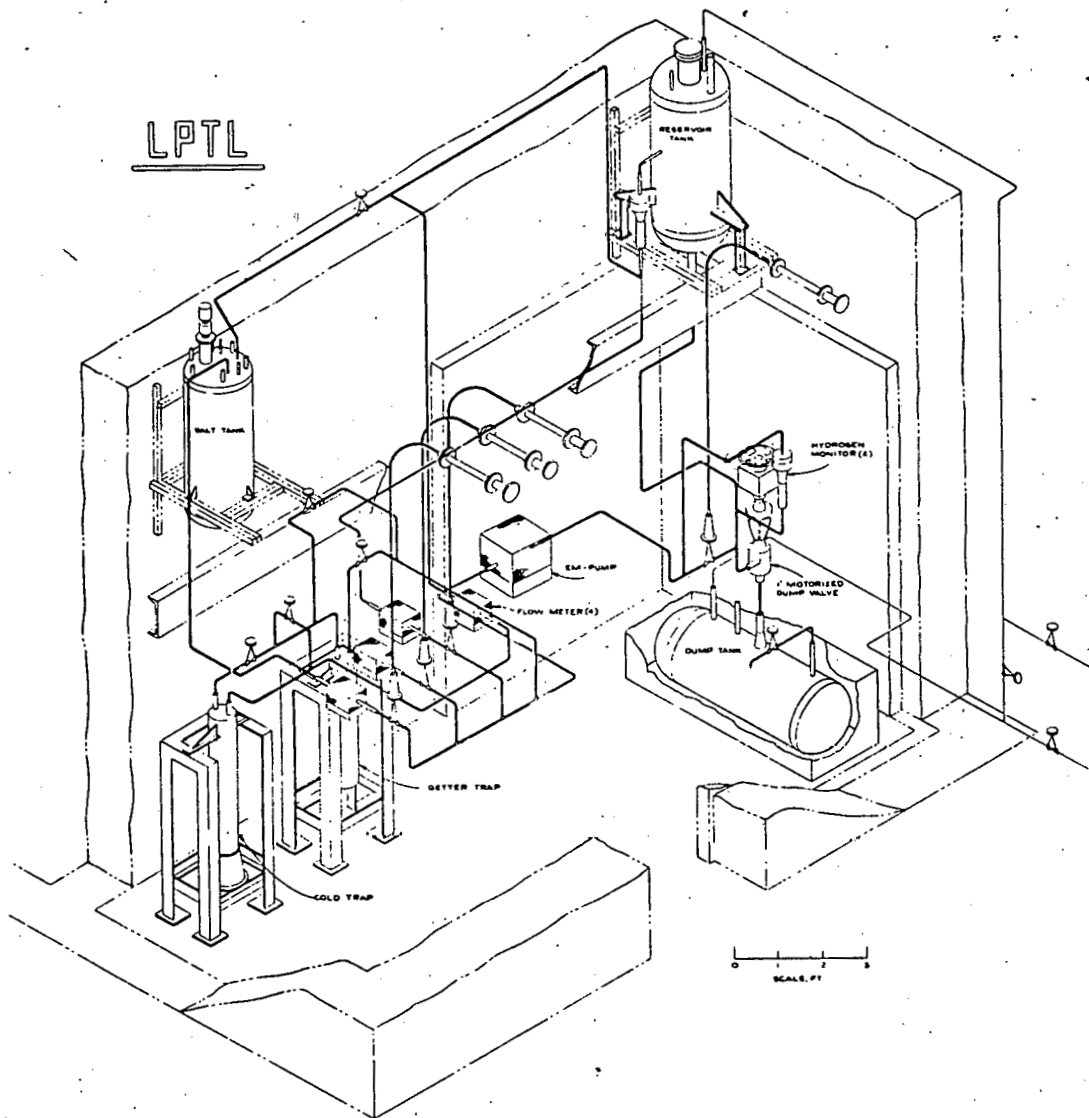
FIGURE 1. Schematic diagram of the Lithium Processing Test Loop.

operated continuously for 2000 hours. A graphical representation of the time-temperature histories for the reservoir tank, getter trap, and cold trap is shown in Fig. 2. This graph illustrates the controlled ramp-up of temperature during the first 400 hours and the gradual cool down of the cold-trap crystallizer section during the initial series of cold-trap/getter-trap tests. Also plotted in Fig. 2 are the concentration profiles for the impurities oxygen and nitrogen. The nitrogen level rose to ~2500 wppm during the first 500 hours, but thereafter showed a steady decline to ~700 wppm,

which is well below the saturation solubility of nitrogen[3] in lithium at the 200°C cold-trap temperature. It is not clear at this time how much of the apparent nitrogen control is due to the zirconium-packed getter trap and how much is due to a reequilibration of nitrogen between the lithium and the chromium in the stainless steel. This subject is discussed further in Section IV.

Although the available data for oxygen are limited to two points, the oxygen level also appears to be declining with time. While this decline seems to be correlated with cold-trap

temperature, the measured oxygen levels are approx-
imately ten times higher than the predicted satura-
tion solubility[4] at the corresponding cold trap
temperature. A series of experiments, wherein
oxygen samples are taken during controlled ramp-up
of the crystallizer temperature, is planned to
provide a more definitive test of oxygen level
sensitivity to cold-trap temperature. A discussion
of possible reasons for the disparity between cold
trap data and direct solubility studies is given in
reference 4. The problem with cold trapping ap-
pears to be break-through of finely precipitated
Li_2O which redissolves in the high temperature
sections of the loop. Subsequent tests of oxygen-
level control, planned for the LPTL, are expected
to aid in resolving the uncertainty connected with
oxygen solubility in lithium at low temperatures.

Nitrogen control in large liquid lithium
systems is considered to be important in that
nitrogen has been correlated with the corrosion of
austenitic and ferritic structural materials by
lithium.[5,6] Although oxygen in lithium does not
appear to exacerbate corrosion, it is one of the
less soluble of the normally occurring nonmetallic
elements in lithium, and its control is advisable
to prevent line-plugging in low-temperature legs of
circulating lithium systems.

The key experimental studies for which the LPTL
is intended are those associated with the proof-of-
principle test of the molten salt extraction con-
cept advanced in previous publications.[7,8] These
experiments are just getting underway and will be
reported on in future publications. The following
section contains a description of the process
development work that has been conducted to support
the design of the salt extraction system for the
LPTL.

III. DEVELOPMENT OF ELECTROCHEMICAL EXTRACTION
     SYSTEM.

The concept by which a molten salt is used
to extract tritium (as LiT) from liquid lithium
has been described in previous publications.[7,8]
A key step in this processing scheme is the
recovery of hydrogen isotopes from the molten
salt under conditions that would reflect the
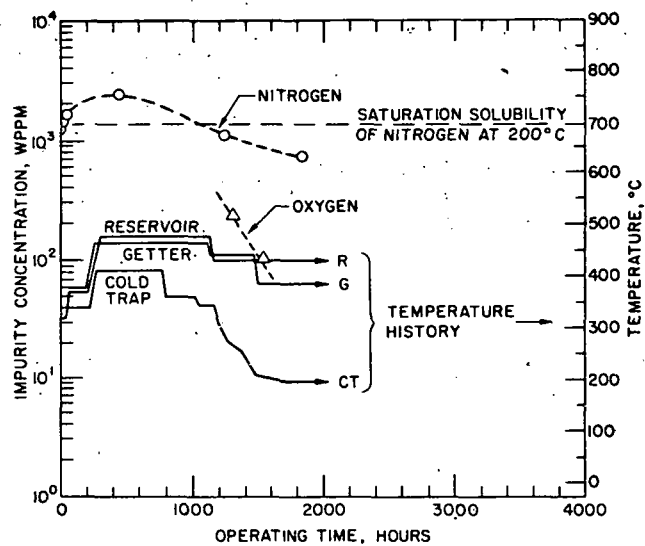

FIGURE 2.   Reservoir, getter, and cold trap
            temperature histories and nitrogen and
            oxygen concentration profiles during
            the first 2000 hours of operation of
            the LPTL.

achievement of sub-wppm levels of tritium in the
connected lithium circuit. (In essence, it is
necessary to achieve sub-wppm levels of hydrogen
or tritium in the molten salt during reprocessing.)
This aspect of the salt-process flow-sheet develop-
ment was designed to simulate as closely as
possible the conditions anticipated in an operating
fusion reactor. Details of the apparatus used in
these experiments have been reported.[8] Briefly,
the apparatus consists of a stainless steel gas-
handling system connected to a furnace well con-
taining a pot of molten salt (LiF-LiCl-LiBr, m,p.
∿440°C). An argon cover gas is circulated through
the apparatus in a closed loop by a stainless steel
bellows pump. The cover gas is dispersed as fine
bubbles through the salt by a porous stainless
steel filter which also serves as an electrode
for hydrogen evolution. After emerging from the
molten salt, the cover gas is circulated past a
controlled leak valve which couples the gas stream
to a mass spectrometer. In a typical experiment,
enough LiH or LiD is added to the salt pot to bring
the hydride ion concentration in the salt to
1-10 wppm. During electrolysis (at ∿1.0 V to avoid

decomposition of the salt) hydride ion is converted to molecular hydrogen (H_2) in the pores of the filter and the hydrogen gas is swept away by the circulating argon before it can back-react with the lithium metal dissolved in the salt. (All extraction experiments are done with lithium-saturated salt in anticipation of the condition of the salt when it returns from an actual extraction operation on a liquid lithium system.)

Results of a typical salt extraction test (using LiH) are shown in Fig. 3, where both the electrolysis current and the H_2 mass signal are followed as a function of time. As expected, no significant change is observed in the H_2 concentration of the gas stream (mass spectrometer trace) until the electrolyzing voltage is applied. The current rises sharply at the beginning of electrolysis, then drops off asymptotically as hydrogen is evolved from the salt. Note the effect on the H_2 mass signal and the current (in Fig. 3) when a titanium bed is inserted into the gas stream. As the H_2 is gettered from the gas stream, the current returns to the preelectrolysis background value. The small residual current observed when the titanium bed is not in use is believed to be due to back reaction of H_2 in the argon sweep gas with the lithium dissolved in the salt. When the titanium bed is left on line during the entire electrolysis experiment, the H_2 mass signal is not detected and the current shows a smooth return to the pre-electrolysis baseline. This effect is due to the continuous gettering of evolved hydrogen by the titanium.

By calibrating the magnitude of the H_2 signal against additions of know quantities of H_2 to the circulating gas stream, it is possible to determine the recovery efficiency for electrolysis, since the mass of LiH added to the salt prior to electrolysis is already known. The onset of the electrolysis of LiH in the salt occurs around 0.6 V and the efficiency for recovery of hydrogen as H_2 reaches 100% near 1.0 V. Above 1.0 V a slight decline in this efficiency is observed due to the initiation of other electrolysis reactions involving hydrogen, such as those leading to the formation of methane,
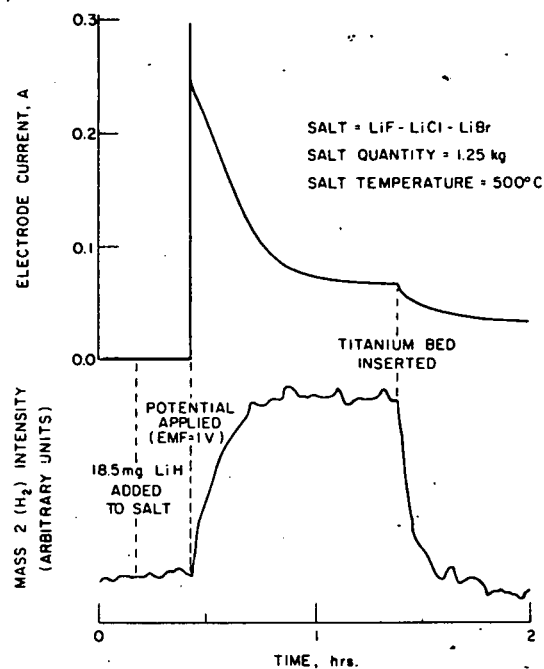

FIGURE 3. Results of a typical experiment to recovery hydrogen electrochemically from molten LiF-LiCl-LiBr.

which has been observed in the gas stream at the higher voltages. Similar results were obtained in experiments where LiD was added to the salt pot.

The results obtained with the porous sparged electrode represent a considerable improvement, in terms of both recovery efficiency and reduced complexity when compared to earlier work with chemical sparging agents[9] (e.g., HCl) and valve electrodes.[10] A processing system based on the sparged electrode has been assembled for the salt processing tank on the LPTL. This system will be tested extensively during 1978, to verify the compatibility of the salt extraction method with operation of a circulating lithium loop.

IV. DEVELOPMENT OF PROCEDURES AND TESTING OF COMPONENTS FOR LITHIUM SYSTEMS

A number of laboratory activities have been carried out in support of the design and operation of the LPTL. A 1-liter-capacity lithium mini-test loop (the LMTL) was fabricated (from 300-series stainless steels) for the purpose of testing (a) the type of valve selected for the LPTL, (b) the zirconium getter-trapping method employed on the

LPTL, (c) the sampling and analytical procedures developed for the LPTL, and (d) materials lifetime limits in circulating lithium loops. The LMTL, shown schematically in Fig. 4, has been operating with a flow rate >0.2 liter/min for over 7000 hours at temperatures up to 500°C. A thermally regenerative getter trap attached to the loop has been run at temperatures up to 600°C. One of the two valves has been cycled over 300 times without loss of bellows integrity. The steady-state analytical values for dissolved iron (∿150 wppm), zirconium (∿40 wppm) and chromium (∿50 wppm) are near the expected saturation solubilities of these elements at 500°C. Figure 5 shows the nitrogen level profile as a function of time for the LMTL together with the temperature history of the reservoir and the getter. During the first 1200 hours of loop operation with the getter at 500°C, the nitrogen concentration dropped from ∿700 to <200 wppm, presumably due to reaction with the zirconium. Thereafter, the nitrogen level showed a slow, steady increase indicating that mass-transfer (diffusion) rates into the bulk of the getter may be limiting getter effectiveness. Experiments to test higher getter temperatures are in progress.

The behavior of nitrogen in stainless steel lithium loops of the type under study at ANL and ORNL[11] is still not fully understood. There has been a general tendency in many of these loops for the nitrogen level to rise sharply at startup and then drop steadily. One possible explanation of the behavior observed in the LPTL and LMTL is that nitrogen is extracted from the surfaces of the steel during early operation, but then during extended operation it reequilibrates with the chromium in the steel (forming Cr_2N) and with the zirconium in the getter trap (forming ZrN). The relative amounts of nitrogen that associate with the chromium and with the zirconium cannot be reliably determined until the loops are sectioned for chemical analysis. Although chromium might be more active in controlling nitrogen during early operating phases, we suspect that over long periods of time most of the nitrogen will migrate to the zirconium. Another significant finding that bears
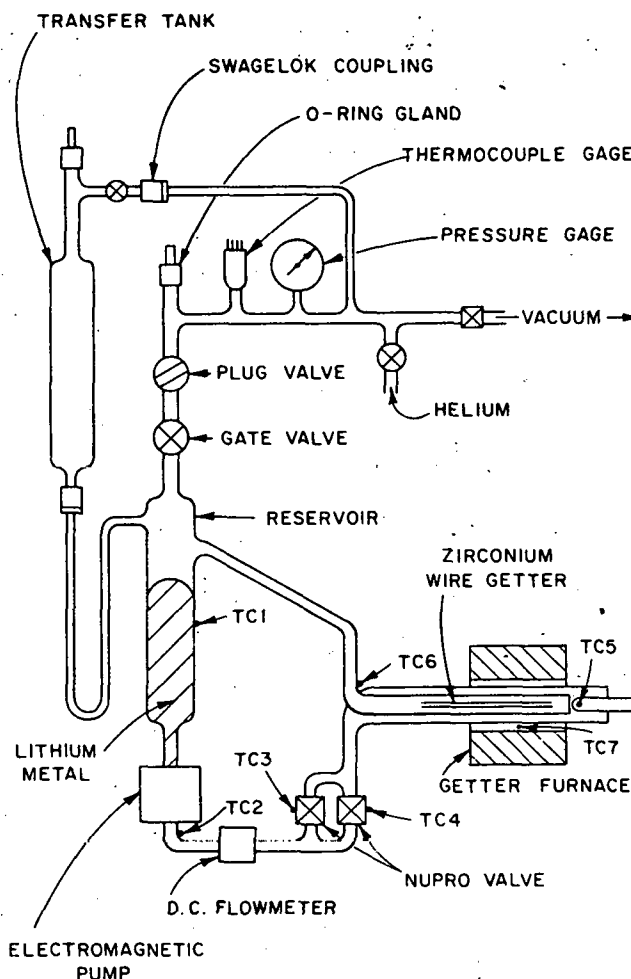

FIGURE 4. Schematic diagram of the Lithium Mini-Test Loop.

on the questions of nitrogen control and on the effects of nitrogen during corrosion, is the recently reported[12] identification and characterization of a stable lithium cyanamide (Li_2NCN) which was crystallized directly from lithium. This evidence of a concerted interaction between carbon and nitrogen in lithium could help to resolve the remaining uncertainities concerning intergranular attack of austenitic and ferritic steels by lithium.[13] Studies to investigate the specific nitrogen-gettering capacity per unit area and per unit weight for chromium and zirconium as a function of temperature are in progress. These studies are being done in the absence and presence of carbon.
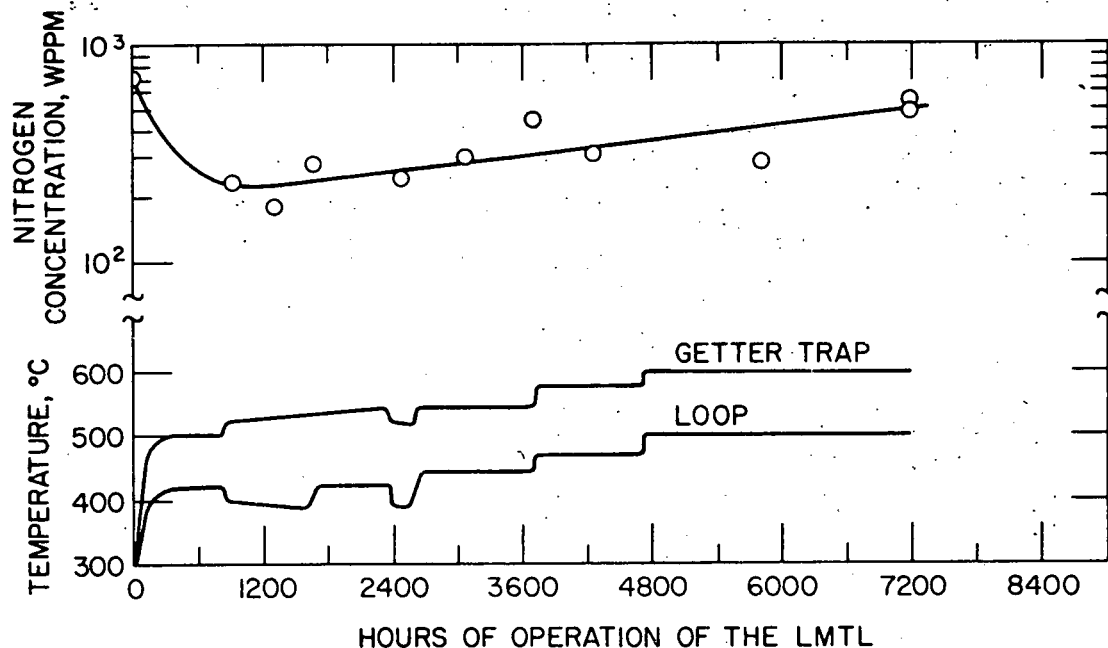
FIGURE 5. Nitrogen concentration profile and temperature histories of reservoir (loop) and getter for the first 7200 hours of operation of the LMTL.

V. THERMODYNAMIC STUDIES OF THE HYDRIDATION OF SOLID Li-Al AND Li-Pb ALLOYS

The proposed utilization of metallic lithium as a blanket medium in magnetic fusion reactors creates a number of problems which stem from the magnetohydrodynamic (MHD) interactions of a flowing conductor with the magnetic fields and the generally corrosive nature of liquid lithium itself. These problems can be mitigated by alloying lithium with another metal, e.g., Al, Pb, Sn, Bi, etc., while maintaining sufficiently high propor- tions of lithium in the alloys to provide the necessary tritium multiplication factors.[14] Many of these alloys form high melting intermediate phases that can be used in solid rather than liquid form, thereby relieving both the MHD and corrosion problems associated with liquid lithium. Knowledge of the thermodynamic properties of these alloys and their interactions with hydrogen isotopes is essential to a clear understanding of their suitability as blanket materials in fusion reactors.

In this laboratory, the thermodynamics of lithium-based alloys is being studied by a hydrogen titration method (HTM). The method is based on the reversible reaction between hydrogen* gas and alloyed lithium, the reaction product being solid LiH. Thus,

$$Li(alloy) + \tfrac{1}{2} H_2(g) \rightleftharpoons LiH(s) \qquad (1)$$
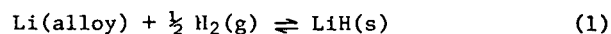
According to Eq.(1), as hydrogen is added stepwise to an alloy, LiM_x, the lithium in the alloy is precipatated out as LiH, leaving behind an alloy with a higher x-value. Equilibrium hydrogen pressures, measured after each consecutive addi- tion, produce a family of cascade-like isotherms of pressure versus alloy composition, from which one can deduce the phase relationships in the

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*Hydrogen serves as a stand-in for the hydrogen isotopes. As a first approximation, the decom- position pressures of deuterium and tritium can be given by $P_{D_2} = \sqrt{2}\, P_{H_2}$ and $P_{T_2} = \sqrt{3}\, P_{H_2}$. The D/H and T/H isotope effects on the phase boundaries are expected to be negligible.

corresponding Li-M phase diagrams--*i.e.*, the rising portions of the isotherms indicate the compositions of homogeneous phases and the plateau portions define two-phase coexistence regions.

Another important feature of the HTM lies in the simple relationship between measured hydrogen pressures and the activity coefficient of lithium, γ_{Li}, in the Li-M alloys. Thus, according to the equilibrium reaction in Eq. (1),

$$\gamma_{Li} = 1/\left(KN_{Li}\sqrt{P_{H_2}}\right) \qquad (2)$$

where K is the equilibrium constant for Eq. (1) in $atm^{-\frac{1}{2}}$, N_{Li} is the atom fraction of lithium in the LiM_x alloy, and P_{H_2} is the equilibrium hydrogen pressure in atm. (The activity of solid LiH is taken to be unity.)

Thermodynamic information yielded by HTM is comparable to that obtained using the more traditional coulometric titration method (CTM). An important advantage of HTM over CTM is its freedom from undesirable side reactions.

Two alloy systems are currently under study-- Li-Pb and Li-Al. The alloys were prepared by melting mixtures of the pure component metals in sealed, evacuated tantalum crucibles. HTM experiments were performed by (a) sealing *in vacuo* small quantities of alloys (powdered to -20 +80 mesh) in thin-walled Armco iron capsules, (b) placing the alloys in a Sieverts' apparatus, (c) heating them to the desired temperature, and then (d) adding hydrogen in small measured portions.

1. Li-Pb Alloys

The reported[15] Li-Pb phase diagram displays five intermediate phases: $Li_{22}Pb_5$, Li_7Pb_2, Li_3Pb, Li_8Pb_3, and LiPb. Figure 6 shows two HTM isotherms--one at 500°C (initial Pb/Li atom ratio = 0.286) the other at 550°C (Pb/Li = 0.261). Three of the rising segments of the isotherms match previously reported[15] stoichiometries (Li_7Pb_2, Li_3Pb, and Li_8Pb_3). The broad rising segment on the left of the 550°C isotherm appears to represent a previously unidentified phase with a range of homogenity, $Li_{3.7-3.8}Pb$. No HTM information was obtained for the $Li_{22}Pb_5$ and LiPb compounds because the hydrogen pressures at these stoichio-
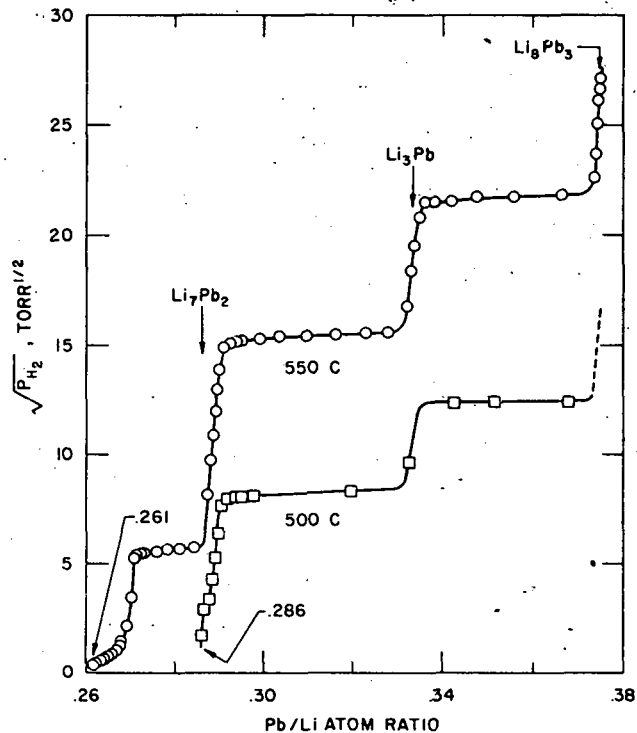

FIGURE 6. Hydridation data for Li-Pb alloys. The circles are data for Pb/Li = 0.261 and the squares are for Pb/Li = 0.286.

metries are above the measuring capabilities of the present apparatus (*i.e.*, ≤1 atm). In spite of the different initial alloy compositions, both isotherms identify the same intermediate phases. This agreement serves as a verification of the applicability of HTM to phase diagram investigations.

2. Li-Al Alloys

The recently reported Li-Al phase diagram[16] shows three intermediate phases. Only the highest melting phase (the β-phase), which has a wide homogeneity range (43 to 52 at. % Al), is of importance to fusion reactor applications. Three alloys were prepared for HTM investigations, all having compositions well within the β-phase boundaries (46.2, 47.7, and 51.5 at. % Al). Figure 7 shows five of the HTM isotherms that have been measured to date. Throughout the β-phase there is a monotonic increase in hydrogen pressure with alloy composition for each starting composition.
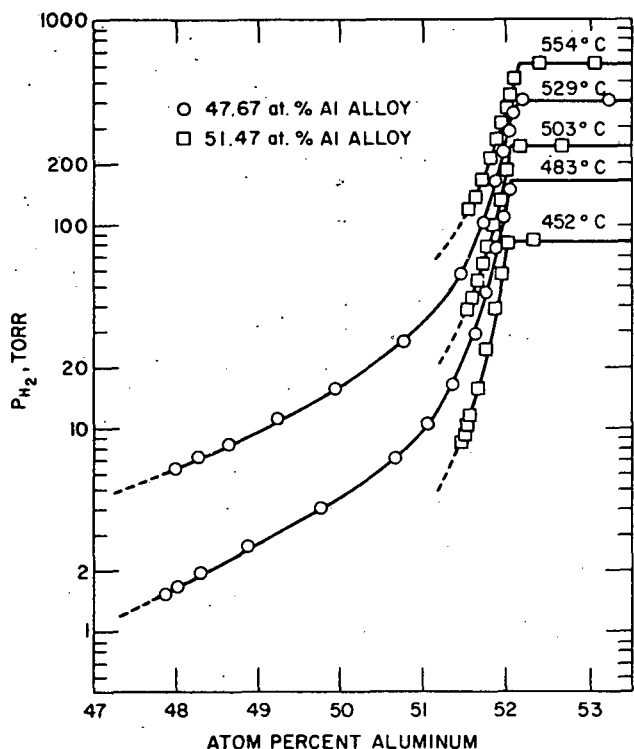
FIGURE 7. Comparison of the hydridation data for Li-Al alloys at three different starting alloy concentrations: 46.2, 47.7, and 51.5 atom % aluminum.

However, irrespective of starting composition, all isotherms exhibited a break (Al-rich β-phase boundary) at the same composition, 52 at. % Al, further illustrating the usefullness of HTM as a tool for determining phase boundary loactions.

The Sieverts' apparatus used in this work does not provide sufficient sensitivity for handling very small additions of hydrogen to the alloys. Nevertheless, the data collected on the 51.5 at. % Al alloy have shown that some hydrogen is being dissolved in the alloys prior to the precipitation of LiH (Eq. 1). The Sieverts' constants $\left(K_s = N_H / \sqrt{P_{H_2}}\right)$ estimated from these data are smaller by a factor of $\sim 10^3$ than the corresponding constants for solutions of hydrogen in pure lithium.[10] Small Sieverts' constants are beneficial in maintaining low tritium inventories in fusion reactor blankets, since they imply that much less hydrogen is dissolved in the alloy per unit of pressure than is dissolved in liquid lithium at the same temperature and equilibrium pressure.

VI. ACKNOWLEDGMENTS

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