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THE CURRENT STATUS OF FUSION REACTOR BLANKET THERMODYNAMICS

by

E. Veleckis, R. M. Yonco, and V. A. Maroni

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Chemical Engineering Division

April 1979

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by

E. Veleckis, R. M. Yonco, and V. A. Maroni

ABSTRACT

The available thermodynamic information is reviewed for three categories of materials that meet essential criteria for use as breeding blankets in deuterium-tritium (D-T) fueled fusion reactors: liquid lithium, solid lithium alloys, and lithium-containing ceramics. The leading candidate, liquid lithium, which also has potential for use as a coolant, has been studied more extensively than have the solid alloys or ceramics. Recent studies of liquid lithium have concentrated on its sorption characteristics for hydrogen isotopes and its interaction with common impurity elements. Hydrogen isotope sorption data (P-C-T relations, activity coefficients, Sieverts' constants, plateau pressures, isotope effects, free energies of formation, phase boundaries etc.) are presented in a tabular form that can be conveniently used to extract thermodynamic information for the α -phase of the Li-LiH, Li-LiD, and Li-LiT systems and to construct complete phase diagrams. Recent solubility data for Li₃N, Li₂O, and Li₂C₂ in liquid lithium are discussed with emphasis on the prospects for removing these species by cold-trapping methods. Current studies on the sorption of hydrogen in solid lithium alloys (e.g., Li-Al and Li-Pb), made using a new technique (the hydrogen titration method), have shown that these alloys should lead to smaller blanket-tritium inventories than are attainable with liquid lithium and that the P-C-T relationships for hydrogen in Li-M alloys can be estimated from lithium activity data for these alloys. There is essentially no refined thermodynamic information on the prospective ceramic blanket materials. The kinetics of tritium release from these materials is briefly discussed. Research areas are pointed out where additional thermodynamic information is needed for all three material categories.

I. INTRODUCTION

Of all the potentially useful thermonuclear fuel cycles, the deuterium-tritium reaction,

remains the leading candidate for near-term fusion reactor applications because of its relatively low ignition temperature (about 10^8 K) and because most of the thermonuclear energy appears in the form of energetic neutrons which can be converted to thermal energy using the same principles that are

employed in present-day fission reactors.¹ The deuterium required for fueling a D-T reactor is in sufficient natural abundance to last for many hundreds of years. The tritium, however, does not occur naturally in significant quantities and must be produced by some other means. While the prospects for supplying tritium by external manufacture appear to be severely constrained from an economic viewpoint,² breeding tritium within the reactor is well recognized as a practically achievable solution.³ This breeding can be accomplished via the ${}^6\text{Li}(n,\alpha)\text{T}$ and ${}^7\text{Li}(n,n'\alpha)\text{T}$ nuclear reactions, and in some designs it must be further augmented by the addition of materials with large $(n,2n)$ cross sections (e.g., Be, Pb).

The basic features of a D-T fusion reactor consist of a magnetically confined D-T plasma (or an inertially confined D-T pellet) contained in an evacuated chamber. The chamber is surrounded by a blanket material that is interspersed with some type of coolant/heat-transfer medium. The tritium breeding and neutron thermalization occur in the blanket from which the thermal energy is carried off by the coolant in much the same way as in a fission reactor.

Although the technology required to effect the utilization of fusion energy must still be considered to be in the very early stages of development, a significant amount of encouraging information has been generated in recent years.^{1,4,5} The availability of the thermodynamic data to support work in many areas of fusion technology will be pivotal to the development of workable concepts for fusion reactors. We have limited the scope of this paper to recent work on the thermodynamic characteristics of plausible blanket material options for D-T fueled fusion reactors. There are, of course, other areas of fusion technology where thermodynamic considerations are important, e.g., cryogenics, fluid/structure interactions, fuel purification, isotopic enrichment, and surface chemistry. The future expansion of the supportive research base for fusion technology will, no doubt, spur the preparation of separate treatises in these areas.

This review will summarize the pertinent data on three basic classes of prospective blanket materials: liquid lithium, solid lithium alloys, and ceramics. Emphasis will be placed on dilute solutions of hydrogen isotopes and other non-metallic elements in these materials and on the contribution of such data to the development of blanket processing technology.

II. STATUS REPORT

In developing generic criteria for the selection of potential breeding materials, the following factors are important: (1) the lithium atom density must be high enough to yield a positive breeding gain in a reasonable thickness (<1 m) of material; (2) the constituents present with the lithium must not have parasitic effects on the neutron flux and energy distribution; and (3) the material must be chemically stable in the blanket environment. Other considerations³ which relate to tritium recovery, hydraulic and mechanical performance of the blanket, availability of resources, and blanket system maintainability are highly concept-dependent and must be weighed against one another in evaluating alternative design choices.

A. Liquid Lithium

Liquid lithium is regarded as a leading candidate for the breeding medium. Its major attributes are its high atomic density which results in a favorable tritium breeding gain, low melting point which makes it possible to circulate lithium into and out of the blanket for processing, and excellent heat-transfer characteristics which make it potentially useful as a primary reactor coolant. The drawbacks of liquid lithium stem from its high reactivity with air and water, its corrosivity, and its large magnetohydrodynamic interactions with the confining fields of magnetic fusion reactors.⁶

B. Solid Lithium Alloys

A large number of the fusion reactor design concepts advanced to date have incorporated solid lithium-containing alloys as the breeding material.³ A number of binary lithium alloy systems are known to have at least one Li-rich, high-melting compound (e.g., LiAl, Li₇Pb₂, Li₄Si, Li₄Sn, and Li₃Bi) that has the capability of yielding an adequate breeding gain. cursory thermal hydraulic analyses³ have indicated that the nuclear heat generated in appropriately sized pebbles of these alloys can be removed without running into meltdown problems or compromising overall reactor power cycle efficiency. Bench-scale studies^{7,8} on selected alloys have shown that, under steady-state tritium production conditions, it is possible to reduce their tritium concentrations to acceptable levels for fusion reactor blankets [<1 weight parts per million (wppm) T] by extracting tritium into a stream of helium.

One design study has appeared⁹ that employs a liquid Li-Pb alloy (about 38 at. % Pb) as the coolant and breeding medium. During the refueling phase of the reactor operating cycle, the alloy is allowed to freeze ($fp = 450^{\circ}\text{C}$) in the heat exchangers so that the heat of fusion of the alloy can sustain the energy conversion cycle. This design tends to facilitate tritium removal but may create materials compatibility problems that are more severe than those with lithium alone.

C. Ceramic Materials

Numerous fusion reactor conceptual designs have employed solid lithium-containing ceramics as the breeding material.³ With the exception of Li₂O which has adequate lithium atom density, most of the materials considered have marginal breeding gains and would require utilization of neutron multiplication schemes. Although tritium recovery from the ceramics appears to be straightforward,^{7,8,10} the adequacy of their thermal hydraulic performance, their stability in the radiation field, and their compatibility with structural materials at elevated temperatures remains to be demonstrated.

III. THERMODYNAMIC STUDIES RELATED TO LIQUID LITHIUM BLANKETS

Of all the candidate blanket materials discussed in the preceding section, liquid lithium has been subjected to the most extensive study from a thermodynamic viewpoint. This section contains a comprehensive review of recent work on the thermodynamics of the systems comprised of lithium with selected non-metallic elements and the implications of the results to fusion reactor technology.

A. The Li-LiH, Li-LiD, and Li-LiT Systems

Until recently, information on the thermodynamics of the systems of lithium with hydrogen isotopes was sparse. Early work on the Li-LiH system was summarized in a 1960 review article by Messer¹¹ and in a 1972 book, Lithium Hydride, by Shpilrain and Yakimovich.¹² The 1968 book, Metal Hydrides, also contains a chapter on saline hydrides.¹³ In this section we will discuss the more recent work on the Li-LiH, Li-LiD, and Li-LiT systems that was not covered by the above reviews.

1. Isothermal Studies

The measurement of the pressure-composition-temperature (P-C-T) relationships under isothermal conditions constitutes perhaps the most widely accepted technique used in investigating the metal-hydrogen systems. The data produced by this technique form a family of $\sqrt{P}$ vs. C isotherms whose shapes reflect the phase relationships in the system under investigation. In the lithium systems, each isotherm is comprised of two rising portions that are separated by a horizontal plateau.^{14,15} The composition ranges of the first and second rising portions correspond to homogeneous α - and β -phases. The constant pressure plateau defines a two-phase ($\alpha + \beta$) coexistence region.

The isothermal reaction between gaseous hydrogen* and liquid lithium, and the corresponding equilibrium constant K can be written as

$$K = N_2 \gamma_2 / (N_1 \gamma_1 \sqrt{P}) \quad (3)$$

where the subscripts 1 and 2 refer to Li and LiH, respectively, N is the mole fraction, γ is the activity coefficient, P is the equilibrium hydrogen pressure, and the hydrogen is assumed to be dissolved in lithium as a monohydride species.¹³ It is customary to express γ as a power series in N according to Margules' equations,¹⁶ i.e.,

$$\ln \gamma_1 = \alpha N_2^2 + \beta N_2^3 \quad (4)$$

and

$$\ln \gamma_2 = (\alpha + 3/2 \beta) N_1^2 - \beta N_1^3 \quad (5)$$

Substitution of Eqs. 4 and 5 in Eq. 3 and rearrangement gives a second-order power series in N_2

$$\ln (\sqrt{P} \cdot N_1 / N_2) = -\ln K + \alpha(1 - 2N_2) + 1/2 \beta(1 - 3N_2^2) \quad (6)$$

in which experimentally measured quantities appear on the left-hand side and the unknown, temperature-dependent constants (K, α , and β) are on the right-hand side.

* In order to simplify notation, the hydrogen symbol serves as a stand in for all three hydrogen isotopes.

Experimental $\sqrt{P}$ vs. N_2 data can be subjected to iterative least-squares procedures to give numerical expressions for the parameters $\ln K$, α , and β as linear functions of $1/T$. These data-fitting procedures have been described in detail elsewhere.^{14,15} The resulting thermodynamic expressions for the lithium-rich (α) phases of the Li-LiH, and Li-LiD systems are given in Table 1. They are based on work carried out at the Argonne National Laboratory (ANL).^{14,15,17} Sieverts' law constants reported at the Oak Ridge National Laboratory (ORNL)^{18,19} are also listed in Table 1.

Table 1. Thermodynamic Data for the α -Fields of the Li-LiH, Li-LiD, and Li-LiT Systems

P-C-T Relations^{14,15}

$$\ln (P_{H_2}, \text{ atm})^{1/2} = \ln (N_{LiH}/N_{Li}) + 6.498 + 0.4589 N_{LiH} + 0.1558 N_{LiH}^2 - (1/T)(6182 + 1973 N_{LiH} + 3462 N_{LiH}^2)$$

$$\ln (P_{D_2}, \text{ atm})^{1/2} = \ln (N_{LiD}/N_{Li}) + 6.138 + 1.8516 N_{LiD} - 1.3010 N_{LiD}^2 - (1/T)(5599 + 3492 N_{LiD} + 1951 N_{LiD}^2)$$

Activity Coefficients of the Solute Species¹⁷

$$\ln \gamma_{LiH} = 1.135 N_{Li}^2 - 2.690 N_{Li}^3 + (1/T)(3118 N_{Li}^2 + 211.4 N_{Li}^3)$$

$$\ln \gamma_{LiD} = 1.124 N_{Li}^2 - 2.776 N_{Li}^3 + (1/T)(3285 N_{Li}^2 + 143.8 N_{Li}^3)$$

Sieverts' Law Constants^a Reported at ANL^{14,15}

$$\text{Li-LiH: } \ln (K_S, \text{ atm}^{-1/2}) = -6.498 + 6182/T$$

$$\text{Li-LiD: } \ln (K_S, \text{ atm}^{-1/2}) = -6.138 + 5599/T$$

Sieverts' Law Constants^a Reported at ORNL^{18,19}

$$\text{Li-LiH: } \ln (K_S, \text{ atm}^{-1/2}) = -6.525 + 6242/T$$

$$\text{Li-LiD: } \ln (K_S, \text{ atm}^{-1/2}) = -6.198 + 5644/T$$

$$\text{Li-LiT: } \ln (K_S, \text{ atm}^{-1/2}) = -5.909 + 5085/T$$

^a

The Sieverts' law constant is defined by $K_S = N_2/\sqrt{P}$, where N_2 is the mole fraction of LiH, LiD, or LiT in lithium and P is the pressure of H_2 , D_2 , or T_2 in atmospheres.

In liquid lithium blankets, hydrogen isotopes are expected to be present at very low concentrations. Thus, for the condition $N_2 \rightarrow 0$, Eq. 6 becomes

$$\ln K_S = \ln K - \alpha - 1/2 \beta \quad (7)$$

where $K_S = N_2/\sqrt{P}$ is the Sieverts' law constant corresponding, in this case, to the change in state $RT \ln K_S = \mu_{Li}^o(l, T, P) + \mu_{H_2}^o(g, T, 1 \text{ atm}) - \mu_{LiH}^*(T, P)$, where μ_{LiH}^* , μ_{Li}^o , and $\mu_{H_2}^o$ are the standard chemical potentials for the species indicated defined in terms of an infinitely dilute solution, a pure liquid, and a pure ideal gas, respectively.

The analytical form of the results in Table 1 permits an extrapolation into dilute-solution regions where the data are important for fusion reactor applications. The reliability of such an extrapolation was tested by comparisons with the data that had been obtained experimentally for the Li-LiD system by Smith *et al.*,¹⁸ by Goodall and McCracken,^{15,20} and by Ihle and Wu.²¹ The latter two studies were made at very low deuterium concentrations using mass-spectrometric techniques. As shown in Fig. 1, the agreement among the four studies is very good, thus verifying the accuracy of the equations in Table 1.

Fig. 1. Comparison of the Calculated P vs. N Isotherm with the Literature Data at 700°C for the Li-LiD System.

2. Solubility Studies

Above the monotectic temperatures the solubility of hydrides in the α -phases can be deduced from the points of intersection of the first rising portion and plateau portion of the isotherms. Below the monotectic temperature, where the precipitating phases are solid hydrides, this technique

is ineffective¹⁴ and more direct experimental methods have been sought. At the University of Nottingham the solubilities of LiH²² and LiD²³ in lithium have been determined using a resistometric technique; at ANL the solubility of LiD in lithium was measured by a direct melt-sampling technique.¹⁷ The results of these investigations are shown in Fig. 2 on a plot of $1000\text{ K}/T$ vs.

Fig. 2. Phase Diagrams for the Li-LiH and Li-LiD Systems Projected on $1000\text{ K}/T$ vs. $\log$ (Composition) Plane.

the logarithm of the mole fraction of hydride. In this particular type of plot the data are presented as a conventional phase diagram but with an expanded scale towards low temperatures where the solubility data are more important for fusion reactor applications.

The solubility data in Fig. 2 do not lie on straight lines. Smooth liquidus curves, best representing the observed data, can be determined as follows.¹⁷ Consider a solution having a composition that corresponds to the liquidus curve at the monotectic temperature. At this point the activity of hydride is near unity and, therefore, the monotectic temperature may be looked upon as the freezing point of the pure hydride (solvent). As

more lithium (solute) is added, the freezing point of the solution will be lowered as shown by the descending solubility curves in Fig. 2. The activity of saturated solvent, a_{LiH} , may be related to the freezing point lowering by the equation²⁴

$$\begin{aligned} \ln a_{\text{LiH}} &= \ln \gamma_{\text{LiH}} N_{\text{LiH}} \\ &= \ln a_{\text{LiH}}^{\circ} - \frac{\Delta H_m}{R} \frac{\theta}{TT_m} + \frac{\Delta a}{R} \left[\frac{\theta}{T} + \ln \left(1 - \frac{\theta}{T_m} \right) \right] + \frac{\Delta b}{R} \frac{\theta^2}{2T} \end{aligned} \quad (8)$$

where γ_{LiH} and N_{LiH} are the activity coefficient and mole fraction of LiH at the liquidus line, $\Delta H_m = 5307$ cal/mol is the latent heat of fusion of LiH,²⁵ T_m is the monotectic temperature, $\theta = (T_m - T)$ is the freezing point lowering, ΔC_p , cal/(deg·mol) = $\Delta a + \Delta bT = 20.61 - 0.0192 T$ is the difference in the heat capacities between liquid and solid LiH,²⁵ and a_{LiH}° (about equal to 0.98) is the activity of LiH at the monotectic temperature, serving here as the standard state for liquid LiH. Equation 8 can be taken to be valid also for LiD, assuming identical values for ΔC_p and ΔH_m .

Substitution of equations given in Table 1 for γ_{LiH} and γ_{LiD} into Eq. 8 yields expressions for the solubility of LiH and LiD in lithium between the eutectic and monotectic temperatures. These expressions and the miscibility gap boundary data for temperatures above the monotectic are presented in Table 2.

Extrapolation of the liquidus curves to the eutectic temperature yields the eutectic compositions and the freezing point depressions for Li-LiH and Li-LiD. Since the isotope effects along the liquidus lines are small, approximately the same eutectic composition would apply also to the Li-LiT system. The lowest tritium concentration achievable by direct cold-trapping of lithium would be well in excess of 100 wppm--a level that would be intolerably high for a fusion reactor blanket system.

Table 2. Miscibility Gap Boundaries of the Li-LiH and Li-LiD Systems.^a

Between the Eutectic and Monotectic Temperatures^{b,17,22,23}

$$\ln N_{\text{LiH}}' - 10.372 \ln T + 4.8314 \times 10^{-3}T + (68.024 + 487.77/T) \\ + (5.8000 - 6870.2/T)N_{\text{LiH}}' - (6.9350 - 3752.2/T)N_{\text{LiH}}'^2 \\ + (2.6900 - 211.40/T)N_{\text{LiH}}'^3 = 0$$

$$\ln N_{\text{LiD}}' - 10.372 \ln T + 4.8314 \times 10^{-3}T + (67.917 + 591.35/T) \\ + (6.0800 - 7001.4/T)N_{\text{LiD}}' - (7.2040 - 3716.4/T)N_{\text{LiD}}'^2 \\ + (2.7760 - 143.80/T)N_{\text{LiD}}'^3 = 0$$

Above the Monotectic Temperature^{14,15}

$$\ln N_{\text{LiH}}'' = 2.235 - 3576/T^c$$

$$\ln N_{\text{LiD}}'' = 2.604 - 3992/T^c$$

$$N_{\text{LiH}}'' = 0.984(\text{at } 710^\circ\text{C}), 0.971(759^\circ\text{C}), 0.957(803^\circ\text{C}), \\ 0.923(847^\circ\text{C}), 0.888(878^\circ\text{C}), \text{ and } 0.855(903^\circ\text{C})$$

$$N_{\text{LiD}}'' = 0.980(\text{at } 705^\circ\text{C}), 0.972(756^\circ\text{C}), 0.953(805^\circ\text{C}), \\ 0.931(840^\circ\text{C}), \text{ and } 0.905(871^\circ\text{C})$$

^aThe prime and double prime refer to the lithium-rich and hydride-rich limits of the miscibility gap, respectively.

^bIn the temperature range 200-600°C these expressions can be approximated by the linear equations: $\ln N_{\text{LiH}}' = 3.769 - 5472/T$ and $\ln N_{\text{LiD}}' = 3.165 - 5117/T$.

^cThese equations are valid up to about 900°C.

3. Decomposition Pressures in the ($\alpha + \beta$) Fields

Within the ($\alpha + \beta$) fields of the Li-LiH phase diagrams, the decomposition pressures do not vary with the composition of the corresponding condensed phases. This property tends to simplify experimental procedures to allow the inclusion of tritium and the determination of precise H/D/T isotope effects.

Several recent studies on the plateau pressures have been reported. For temperatures above the monotectic, measurements have been made by Smith and Land,²⁶ and by Shpilrain et al.²⁷ using the customary equilibration techniques. Below the monotectic, measurements were made for the Li-LiH system by Ihle and Wu,²⁸ using a combined mass spectrometric-Knudsen effusion technique and by Katsuta et al.,²⁹ using gas chromatography. For temperatures on both sides of the monotectic, plateau pressure studies were made by Smith and Webb³⁰ for the Li-LiH and Li-LiD systems; at ANL we used an equilibration technique to make comprehensive plateau-pressure measurements for all three hydrogen isotope systems.³¹ The results reported in this section are based mainly on this latter study.

Figure 3 shows the plateau-pressure plots. For a given temperature the pressures are in the order $P_{T_2} > P_{D_2} > P_{H_2}$. Each plot has two distinct linear segments. The point at which the segments intersect defines the monotectic temperature. Linear $\ln P = A + B/T$ equations derived for each segment are listed in Table 3. Above the monotectic temperature these equations represent least-squares fits of the data in Fig. 3. Below the monotectic the plateau-pressure data were collectively fitted to individual equations (shown in Table 3) in which the parameter B was constrained to a value common to all three systems. These equations yield temperature-independent isotope effects, $P_{D_2}/P_{H_2} = 1.492$ and $P_{T_2}/P_{H_2} = 1.751$, that are only slightly different from $\sqrt{2}$ and $\sqrt{3}$ as predicted from the D/H and T/H mass ratios.

Fig. 3. Plateau-pressure Data for the Li-LiH, Li-LiD, and Li-LiT Systems.

Table 3. Decomposition Pressures in the ($\alpha + \beta$) Fields of the Li-LiH, Li-LiD, and Li-LiT Systems.³¹

	$\ln (P, \text{ atm}) = A + B/T$			
	Below Monotectic		Above Monotectic	
	A	B	A	B
Li-LiH	20.79	-23,310	14.71	-17,420
Li-LiD	21.19	-23,310	14.52	-16,870
Li-LiT	21.35	-23,310	14.29	-16,530

4. Species Characterization in the Gas Phase

In addition to hydrogen molecules, the gas phase over very dilute solutions of hydrogen in lithium is expected to include molecular species containing lithium atoms. The complexity of the gas phase has been recently revealed by Ihle and Wu.³² Employing the combined mass spectrometric-Knudsen effusion method, they observed the following molecular species in the gas phase over dilute solutions of deuterium in lithium: Li_2 , Li_3 , LiD , LiD_2 , Li_2D , Li_2D_2 and D_2 . From the data they evaluated the partial pressures of each species as functions of liquid-phase composition ($10^{-7} < N_D < 10^{-4}$) and temperature (800 to 1600 K), their atomization and binding energies, and the equilibrium constants for the exchange reactions among the species.

Although the existence of gaseous hydrides does not affect the Sieverts' law relationships,³² it leads to an increased density of hydrogen isotopes in the saturated vapors over the liquid lithium blanket. Ihle and Wu³³ have pointed out that, owing to this enrichment, it is feasible, in principle, to separate hydrogen isotopes from lithium by fractional distillation performed at temperatures above 1240 K.

5. Summary of Thermodynamic Data

The general features of the Li-LiH phase diagrams have been known for many years.^{11,12} There is a wide monotectic horizontal along which two liquid phases, one rich in lithium (α) the other rich in hydride (β), are in equilibrium with essentially stoichiometric LiH. Above the monotectic temperature there is a miscibility gap [$\alpha(\ell) + \beta(\ell)$] that closes at the consolute point. Below the monotectic temperature there is a coexistence region [$\alpha(\ell) + \text{LiH}(s)$] that terminates at the eutectic temperature. The data presented in Section III-A permit an accurate construction of the phase diagrams for the Li-LiH and Li-LiD systems and a good approximation for the Li-LiT system, owing to the small effect of isotopic substitution on the phase-boundary compositions. The liquidus lines can be drawn by solving the equations in Table 2. Other phase-boundary data required for phase diagram construction are given in Figs. 2 and 3.

In addition to phase-boundary information the relations in Tables 1-3 can be used to derive various properties pertaining to the solution thermodynamics of the Li-LiH systems. For example, they have been used to estimate the standard free energies of formation of the liquid^{14,15} and solid³¹ hydrides (see Table 4).

Table 4. Standard Free Energy of Formation of Solid and Liquid Hydrides

Above the Monotectic Temperature^{a,14,15}

$$\text{LiH(l)}: \Delta G_f^\circ, \text{ kcal/mol} = 13.47 \times 10^{-3}T - 16.55$$

$$\text{LiD(l)}: \Delta G_f^\circ, \text{ kcal/mol} = 13.17 \times 10^{-3}T - 15.87$$

Below the Monotectic Temperature³¹

$$\text{LiH(s)}: \Delta G_f^\circ, \text{ kcal/mol} = 19.76 \times 10^{-3}T - 22.63$$

$$\text{LiD(s)}: \Delta G_f^\circ, \text{ kcal/mol} = 20.30 \times 10^{-3}T - 22.73$$

$$\text{LiT(s)}: \Delta G_f^\circ, \text{ kcal/mol} = 20.64 \times 10^{-3}T - 22.82$$

^aSmith et al.^{18b} have recently reported the following expressions for liquid hydrides:

$$\text{LiH(l)}: \Delta G_f^\circ, \text{ kcal/mol} = 12.83 \times 10^{-3}T - 15.71$$

$$\text{LiD(l)}: \Delta G_f^\circ, \text{ kcal/mol} = 11.86 \times 10^{-3}T - 14.18$$

$$\text{LiT(l)}: \Delta G_f^\circ, \text{ kcal/mol} = 10.94 \times 10^{-3}T - 12.72$$

B. Interaction of Non-hydrogenous Elements with Liquid Lithium

The binary systems of lithium with non-metals other than hydrogen isotopes are of interest to the fusion program primarily from the standpoint of materials compatibility. These systems have been reviewed by Messer,³⁴ by Cairns et al.,³⁵ by Adams et al.,³⁶ and by Smith and Moser.³⁷ Because of the limited scope of this presentation, we will concentrate on published work related to the systems Li-N, Li-O, and Li-C which has appeared since the earlier reviews.

1. The Li-N System

Nitrogen gas reacts with lithium to form Li_3N which exists in liquid lithium solutions probably as an ionic species since the phase in equilibrium with the saturated solutions is solid Li_3N and since ammonia is evolved upon hydrolysis of these solutions.

The system Li- Li_3N was first investigated by Bolshakov et al.³⁸ who employed thermal analysis techniques to determine the liquidus line between the eutectic temperature and the melting point of Li_3N . Adams et al.²² determined the solubility of Li_3N in lithium from 200 to 450°C using a resistometric technique in which the saturation concentrations are detected by corresponding breaks in the resistivity curves. Yonco et al.³⁹ determined the solubility of Li_3N in lithium from 195 to 441°C by taking filtered samples of

saturated solutions and assaying them for nitrogen using the micro-Kjeldahl method. They also measured the equilibrium nitrogen pressure over solid Li_3N between 660 and 778°C and the melting point of Li_3N ($813 \pm 1^\circ\text{C}$).

Figure 4 shows a plot of $\ln (\text{mol } \% \text{ Li}_3\text{N})$ vs. $1/T$ constructed from the composite results of these three studies. Below 450°C the combined data of the latter two studies were statistically fitted to the linear equation

$$\ln N_{\text{Li}_3\text{N}} = 3.086 - 4878/T \quad (9)$$

with 4% uncertainty in the mean value of $N_{\text{Li}_3\text{N}}$, the mole fraction of Li_3N in lithium. Above 450°C the solubility can be represented by the curve that is formed by extrapolation of Eq. 9 to a point where the line joins smoothly with the data of Bolshakov *et al.*, although the exact shape of the curve at the melting point of Li_3N is subject to question.³⁹

Fig. 4. Comparison of Data for the Solubility of Li_3N in Liquid Lithium.

A eutectic point of 0.047 mol % Li_3N (940 wppm N) and 180.2°C , inferred from Eq. 9 and from the freezing point depression of lithium, is in good agreement with the values of 0.068 mol % Li_3N and 180.24°C reported by Hubberstey *et al.*⁴⁰ who determined the hypoeutectic liquidus by thermal analysis. The high eutectic concentration precludes cold-trapping as an effective way to remove nitrogen from lithium.

The solubility information in Fig. 4, when used in conjunction with the Li_3N decomposition pressures,³⁹ permits the evaluation of the thermodynamic properties of the Li- Li_3N system. The equilibrium reaction between gaseous nitrogen and liquid lithium to form a liquid solution of Li_3N in lithium and the corresponding equilibrium constant K may be written as

$$K = N_2 \gamma_2 / (N_1^3 \gamma_1^3 \sqrt{P}) \quad (11)$$

where N_1 and N_2 are the mole fractions of Li and Li_3N , γ_1 and γ_2 are their activity coefficients, P is the nitrogen pressure, and the standard states of Li and Li_3N are the pure liquid phases.

A reasonable estimate of the γ 's can be made from the Margules' equations¹⁶ truncated at the quadratic term. For the solvent lithium this would give

$$\ln \gamma_1 = (\omega/RT) N_2^2 \quad (12)$$

where ω is a temperature-independent constant. By application of the Gibbs-Duhem relationship to Eq. 12 one obtains for the activity coefficient of the solute Li_3N

$$\ln \gamma_2 = (\omega/RT)(N_1^2 - N_1'^2) - \ln N_2' \quad (13)$$

where the primed symbols refer to the values at the liquidus boundary. The constant ω was evaluated³⁹ by substituting Eq. 12 into Eq. 11, selecting values of P and N_2 existing at the liquidus boundary, defining solid Li_3N as the standard state (i.e., $N_2 \gamma_2' = 1$), and choosing a value for ω such that a plot of $\ln K$ vs. $1/T$ would give a statistically best straight line. The resulting linear relationship at $\omega = 3.14 \text{ kcal/mol}$ for $\ln K$ vs. $1/T$ yielded the following standard free energy of formation of solid Li_3N

$$\Delta G_f^\circ, \text{ kcal/mol} = 33.2 \times 10^{-3} T - 39.1 \quad (14)$$

In the temperature range from 600 to 1000 K, ΔG_f° values calculated from Eq. 14 are 1.5 to 2.1 kcal/mol less negative than those listed in the JANAF tables for solid Li_3N ,⁴¹ based on the recent calorimetric work of O'Hare and Johnson⁴² and of Osborne and Flotow.⁴³ The discrepancy can be considered to be small when one takes into account the approximations made by Yonco *et al.*³⁹ in deriving the expression for ΔG_f° . The coefficients in Eq. 14 also compare favorably with those reported in the recent emf studies by Bonomi *et al.*,⁴⁴ namely, $\Delta G_f^\circ, \text{ kcal mol}^{-1} = 35.2 \times 10^{-3} T - 40.65$.

Dilute solutions of Li_3N in lithium are important in the use of lithium as the blanket material. For the condition $N_2 \rightarrow 0$ and $N_1 \gamma_1 \rightarrow 1$, Eq. 11 may be rewritten to define the Sieverts' law constant, K_S . Thus,

$$\lim_{N_2 \rightarrow 0} N_2 / \sqrt{P} = K_S = K / \gamma_2^* \quad (15)$$

where γ_2^* is the activity coefficient of Li_3N at infinite dilution, calculated by applying the condition $N_1 \rightarrow 1$ to Eq. 13. For the temperature range 661–778°C, the Sieverts' law constant can be represented by

$$\ln (K_S, \text{atm}^{-1/2}) = -13.80 - 14,590/T \quad (16)$$

2. The Li-O System

The compounds Li_2O and Li_2O_2 are known to exist in the lithium-oxygen system, although only the normal oxide is formed by the direct reaction of oxygen with lithium.³⁴ Available thermochemical information for Li_2O and Li_2O_2 has been reviewed elsewhere.³⁷ Yonco *et al.*⁴⁵ determined the solubility of Li_2O in lithium for temperatures between 195 and 734°C by taking equilibrated melt samples filtered through 2- μm -pore-size filters. The samples were assayed for oxygen by a fast neutron activation method. The data can be represented by

$$\ln N_{\text{Li}_2\text{O}} = 1.449 - 6669/T \quad (17)$$

with a correlation coefficient of 0.997, where $N_{\text{Li}_2\text{O}}$ is the mole fraction of Li_2O in a saturated solution in lithium.

The solubilities calculated from Eq. 17 are considerably lower than those reported previously by Hoffman⁴⁶ and by Konovalov *et al.*⁴⁷ who used similar experimental techniques but coarser filters (20 μm ⁴⁶ and 30–40 μm ⁴⁷). Since undissolved Li_2O may pass through coarse pore filters,³⁵ the lower solubility values reported in the ANL work are preferred over those of the earlier studies.

The solubility of oxygen at the melting point of lithium (180.49°C) is 1.76×10^{-4} mol % Li_2O (4 wppm O). This concentration defines a theoretical limit for oxygen removal from liquid lithium that can be reached by cold-trapping in conjunction with the use of fine pore size (<2 μm) filters.

3. The Li-C System

This system appears to have a single intermediate phase, Li_2C_2 , which dissolves in lithium as an acetylide ion. Carbon added to lithium in any form will ultimately be converted to acetylide if heated to 600°C.⁴⁸

The solubility of acetylide in liquid lithium is being measured at ANL by Yonco *et al.*⁴⁹ by taking filtered samples (2- μm pore size filters) of saturated solutions of Li_2C_2 in lithium and analyzing for carbon by the acetylene-evolution method.⁴⁸ The data collected thus far vary between

9.0×10^{-5} mol % Li_2C_2 at 200°C and 2.7×10^{-2} mol % Li_2C_2 at 600°C . The indicated solubility at the melting point of lithium is 5×10^{-5} mol % Li_2C_2 (2 wppm C) which strongly implies that carbon elimination by cold-trapping methods should be feasible in liquid-lithium systems. Thermal analysis studies of Fedorov and Su⁵⁰ yield acetylide solubilities that are at least ten times higher than those of Yonco *et al.* and are believed to be in error.⁴⁰ The available thermochemical data for Li_2C_2 have been summarized elsewhere.³⁷

Recently Down *et al.*⁵¹ reported the synthesis of dilithium cyanamide by reaction of lithium nitride with dilithium acetylide in excess lithium

This is the first observation of a complex salt whose stability in liquid lithium is greater than that of the binary reactants; this information could contribute significantly to an understanding of lithium corrosion phenomena and nitrogen/carbon chemistry in liquid lithium.

IV. THERMODYNAMIC STUDIES RELATED TO SOLID BLANKETS

The sorption characteristics of solid lithium-containing alloys toward the hydrogen isotopes constitute important considerations in evaluating the suitability of the alloys as fusion reactor blanket materials. There is very little information available on this subject in the literature. Early work, devoted mainly to the thermal decomposition of higher hydrides (e.g. LiAlH_4 ⁵²), has contributed little to the understanding of the dilute solutions of hydrogen in Li-M alloys. The dissolution of hydrogen in aluminum-rich solid Li-Al alloys has been analyzed by Owen and Randall.⁵³ The sorption of hydrogen in solid Li-Al and Li-Pb is currently under a thorough investigation at ANL using the hydrogen titration method (HTM).⁵⁴ The latter studies have shown that hydrogen sorption characteristics in solid Li-M alloys can also be determined indirectly from the lithium activity data in binary Li-M alloys. Such data are available for a number of solid alloys from studies in which the traditional coulometric titration method (CTM) was employed.

A. Hydrogen Titration Studies

During the early stages of work at ANL it became apparent that lithium-based alloys react with hydrogen in a different manner than do the alloys of the transition metals. Instead of forming stable ternary solutions, hydrogen reacts with the lithium in the alloy to form solid LiH, according to the following reversible reaction

for which the equilibrium constant is given by

$$K = a_{\text{LiH}} / (a_{\text{Li}} \sqrt{P}) \quad (20)$$

where a is the activity of the subscripted component and P is the equilibrium hydrogen pressure in atmospheres.

According to Eq. 19, when small quantities of hydrogen are added to an alloy LiM_x , the composition of the alloy will change from $x = n_M/n_{\text{Li}}$ to a new composition $x = n_M/(n_{\text{Li}} - n_{\text{H}})$. Equilibrium hydrogen pressures, measured after each consecutive hydrogen addition, produce isothermal $\sqrt{P}$ vs. x traces whose cascade-like shapes reflect the phase relationships in the binary Li-M systems--the homogeneous intermediate phases reveal themselves as rising segments and the two-phase coexistence fields appear as constant pressure plateaus. The process leading to the equilibrium in Eq. 19 is equivalent to a titration in which hydrogen is the titrant, LiH the titration product, and the equivalence points are identifiable from the shape of the isotherms. Hence, this method of investigating binary alloys is referred to as the hydrogen titration method (HTM).

Another important feature of HTM arises from the simple relationship between the measured decomposition pressures and the lithium activity in the binary Li-M alloy. Below the monotectic temperature of the Li-LiH system the LiH-rich phase is solid LiH. Therefore, the LiH precipitating out of LiM_x alloy may be taken to have unit activity and Eq. 20 becomes

$$a_{\text{Li}} = 1/(K\sqrt{P}) \quad (21)$$

The proportionality factor in Eq. 21 is the inverse of the equilibrium constant for the reaction in Eq. 19 which can be evaluated from the standard free energy of formation of solid LiH, given in Table 4. HTM thus provides a powerful new technique for investigating both the phase relationships and the lithium activities in Li-M alloys. The technique has been applied to two alloy systems: Li-Al-H and Li-Pb-H.⁵⁴

1. The Li-Al-H System

According to a recent phase diagram,⁵⁵ the Li-Al system has four homogeneous solid phases: α (dilute solution of lithium in aluminum), β ("LiAl"), γ ("Li₃Al₂"), and δ ("Li₉Al₄"). The latter two phases are believed to be line compounds, but the highest melting β -phase has a wide homogeneity range (46-52 at. % Al). Since the β -phase has been emphasized for fusion reactor applications, we have prepared two Li-Al alloys having compositions within this phase.

The results are shown in Fig. 5 as $\log P$ vs. at % Al isotherms. The fact that both alloys have produced essentially the same Al-rich β -phase boundary (about 52 at. % Al) serves as a verification for the reaction in Eq. 19. On the left side of this boundary the rising isothermal segments correspond to the homogeneity ranges of the β -phase. Constant pressure plateaus on the right side indicate the onset of a wide ($\alpha + \beta$) two-phase region. Yao et al.⁵⁶ have determined lithium activities from emf measurements on the 50 at. % Al alloy at three temperatures (314, 343, and 380°C). The corresponding hydrogen pressure values, extrapolated from their data to the temperatures of the HTM study, are in excellent agreement. Further agreement is indicated by comparisons in the ($\alpha + \beta$) region, where the data produced by either technique are more reliable because of their insensitivity to variations in alloy composition.

Fig. 5. Hydrogen Pressure vs. Alloy Composition Isotherms for the Li-Al System.

2. The Li-Pb-H System

The reliability of HTM is also being tested on the more complex Li-Pb alloy system. the reported phase diagram⁵⁷ reveals several intermediate phases: $\text{Li}_{22}\text{Pb}_5$, Li_7Pb_2 , Li_3Pb , Li_8Pb_3 , and LiPb . HTM results are shown in Fig. 6. Three of the isotherms (at 500, 549, and 598°C) were obtained with an alloy having an initial Pb/Li ratio of 0.2610. The fourth isotherm (also at 500°C) had an initial Pb/Li ratio of 0.2858.

Fig. 6. Square Root of Hydrogen Pressure vs. Alloy Composition Isotherms for the Li-Pb System.

The isotherms have the expected cascade-like shapes with four rising portions separated by three pressure plateaus. Each of the rising portions was assigned a band (β , γ , δ , and ϵ) representing the maximum limits of homogeneity for that phase. The bands γ , δ , and ϵ include the stoichiometries of the phases Li_7Pb_2 , Li_3Pb , and Li_8Pb_3 , respectively. For concentrations below $\text{Pb/Li} = 2/7$, the shape of the isotherms suggest the existence of a wide homogeneous phase (β), whose lead-rich boundary may correspond to $\text{Li}_{11}\text{Pb}_3$.

Lithium activities, calculated for each two-phase plateau portion from the corresponding hydrogen pressure using Eq. 21 show an excellent agreement with those recently determined by the coulometric titration technique.⁵⁸ This agreement and the superimposition of the two isotherms at 500°C in Fig. 6, despite their different starting compositions, lends further credence to the applicability of HTM in investigating the thermodynamic properties and phase relations of binary lithium-containing alloys.

B. Coulometric Titration Studies

According to Eq. 21, if isothermal a_{Li} vs. C data were available for a Li-M alloy, one could construct a corresponding set of $\sqrt{P}$ vs. C isotherms that represent hydrogen sorption characteristics of that alloy. Electromotive force measurements provide a convenient means of determining activities in binary alloys. For Li-M systems these measurements can be carried out in cells of the type [Li(l)/Li-salt/Li-M(alloy)] in which the isothermal cell emfs are continuously recorded as functions of the alloy concentration which is varied by the coulometric titration method (CTM).

CTM studies on the Li-Al^{56,59} and Li-Pb⁵⁸ systems and their agreement with the HTM data were mentioned above. Other solid alloy systems, for which CTM data are available, are: Li-Bi,⁶⁰ Li-Sb,⁶⁰ and Li-Si.^{61,62} Lithium activities and the corresponding hydrogen decomposition pressures, calculated using data of these studies at 500°C, are given in Table 5 for selected intermetallic compounds that show promise in fusion reactor applications.

Table 5. Maximum Hydrogen Pressures (or minimum lithium activities) at 500°C that can be Reached in Solutions of Hydrogen in Selected Intermetallic Compounds Containing Lithium.

Compound	mp, °C	a_{Li}	P_{max} , atm
Li ₃ Sb	~1200	2.5×10^{-6}	1.0×10^7
Li ₃ Bi	1145	2.5×10^{-5}	1.1×10^5
Li ₈ Pb ₃	642 ^b	4.8×10^{-3}	3.0
Li ₃ Pb	658 ^b	2.0×10^{-2}	1.6×10^{-1}
Li ₇ Pb ₂	726	3.2×10^{-2}	6.8×10^{-2}
β -LiAl ^a	700	7.5×10^{-2}	1.2×10^{-2}
Li ₂ Si	703	1.7×10^{-2}	2.4×10^{-1}
Li ₄ Si	635 ^b	5.9×10^{-1}	1.9×10^{-4}
Lithium	liquid	1.0	$5.0 \times 10^{-10^c}$

^aAt 50 at. % Al.

^bIncongruent melting.

^cAt $N_{\text{H}} = 10^{-4}$.

C. Solubility of Hydrogen in Solid Lithium Alloys

The slight inclination in the initial vertical portions of the isotherms in Fig. 5 implies that there is some dissolution of hydrogen in Li-M alloys. Only when the hydrogen solubility limit is exceeded, can the precipitation of LiH occur, according to Eq. 19. This information is important in fusion reactor applications because it relates to the concentration of tritium present in the blanket medium under steady-state operating conditions.

Very little information is available on these solutions. Talbot *et al.* have determined the Sieverts' law constants ($K_S = N_H/\sqrt{P}$) for tritium in LiAl and LiBi_{5.6} alloys⁶³ and for hydrogen in LiAl alloy.⁶⁴ Current work at ANL on the dissolution of hydrogen in Li-Al and Li-Pb alloys,⁵⁴ however, indicates considerably lower K_S values.

Lacking exact hydrogen solubility data, one can attempt to estimate the magnitude of K_S from CTM data, such as those listed in Table 5. The estimates are made by assuming that the same hydrogen solubility limit (e.g., $N_H = 10^{-4}$) exists for all alloys and that Sieverts' law is obeyed throughout the solution range, i.e., $K_S \propto 1/\sqrt{P_{\max}}$.

Materials possessing large $P_{\max}$ values are more desirable for blanket applications because of the increased tendency of hydrogen isotopes to favor the gas phase, thereby facilitating tritium removal and reducing tritium inventory in the condensed blanket phase. The compounds listed in Table 5 show large variations in $P_{\max}$ which could be useful as a criterion in selecting an appropriate alloy. In all cases the $P_{\max}$ values are much larger than the equivalent value for liquid lithium, which is also shown in Table 5 for comparison.

V. STUDIES RELATED TO CERAMIC BLANKETS

There is little thermodynamic information that pertains to the use of ceramics as breeder blanket materials. This section will be devoted to a brief discussion of available literature studies on the lithium-containing ceramics,^{7,8,10,53,65} which describe the kinetics of tritium extraction from these materials. In these studies tritium is introduced into the ceramic specimens by neutron irradiation via the $(n, {}^6\text{Li})$ and $(n, {}^7\text{Li})$ transmutations. Since this procedure is analogous to the mode of tritium production in fusion reactor blankets, the experience gained should readily extrapolate to fusion reactor operating conditions.

Powell *et al.*⁷ and Wiswall and Wirsing⁸ have reported that temperatures in excess of 600°C were necessary to recover >99% of the tritium from Li₂O, LiAlO₂, and Li₂SiO₃ granules in one hour or less. Johnson *et al.*¹⁰ have observed that, during the neutron irradiation itself, >80 % of helium and from 9 to 90 % of tritium was released from the ceramic targets, the amount of tritium released being inversely proportional to the bulk density of the target material. The tritium appeared mostly in a noncondensable form (HT or T₂) but

the fraction of the condensible form (HTO or T₂O) increased with increasing temperature of the target. Release of tritium from LiAlO₂ targets was also investigated by Yunker.⁶⁵ His data have shown that essentially all of the tritium can be recovered by vacuum outgassing at 850°C with a large fraction of tritium appearing in a condensible form.

It can be concluded from the results of these studies that thermal extraction can be an effective method of removing tritium from the oxide-type ceramics. A small fraction of tritium bred in a ceramic blanket will be ejected in situ into the gas space by direct recoil. The remaining tritium will diffuse to the surface of the hot ceramic granules where it can be swept away by a purge gas. Lower tritium inventory in the blanket can be effected by increasing its steady-state operating temperature and/or by decreasing the mean size of the granules.

VI. RECOMMENDATIONS FOR FUTURE RESEARCH

The impetus of the fusion energy program has already stimulated a significant amount of thermodynamic research on the candidate blanket materials. Nevertheless, more work is required for full evaluation of the in-reactor performance of these materials. In this section we will attempt to point out some areas where thermodynamic data are either lacking or are in need of verification.

As was shown above, the existing thermodynamic data on lithium are quite substantive. There still are, however, areas where additional information would be beneficial. The uncertainty remaining in the Sieverts' law constants for tritium would be clarified by additional experiments on very dilute solutions of tritium in lithium. The stability and precipitation of oxide species in liquid lithium and conditions for their removal by cold-trapping need further investigation. Identification and characterization of the carbon/nitrogen species formed in dilute solutions in lithium should be undertaken. Correlation of these latter studies with lithium corrosion data could provide a clearer understanding of the compatibility of lithium with structural materials.

Considerably more work is needed to complete the thermodynamic data base for solid lithium alloy systems. Accurate measurements of Sieverts' law constants for tritium in these alloys would provide a firmer basis for evaluating blanket inventories. Thermodynamic properties of the systems formed between the alloys and non-metallic impurity elements may be important in determining long-term tritium release characteristics. Thermochemical data for many of the candidate alloys are needed in evaluating thermal hydraulic response, safety aspects related to accidental melt-down, and possible uses as thermal storage sinks to sustain pulsed thermonuclear power production. Pressure-composition-temperature data on solutions of hydrogen isotopes in the alloys that are on the lithium-rich ends of the corresponding phase diagrams would contribute insight on the potential utility of "slightly-alloyed" liquid lithium as a blanket material.

From the standpoint of thermodynamic data, ceramics are the least-studied category of the blanket materials. There are essentially no data available on the sorption of hydrogen isotopes in the prospective ceramic materials

under anticipated fusion reactor operating conditions. The effects of impurity elements on the performance of these materials need to be investigated. Thermochemical and sintering information are also needed for the same reasons as were mentioned in the preceding paragraph for the solid lithium alloys.

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REFERENCES

1. F. L. Ribe, Rev. Mod. Phys. 47, 7 (1975).
2. T. B. Rhinehammer and L. J. Wittenberg, An Evaluation of Fuel Resources and Requirements for the Magnetic Fusion Program, Mound Laboratory, Monsanto Research Corporation, Report MLM-2419 (1978).
3. Proc. Magnetic Fusion Energy Blanket and Shield Workshop, J. R. Powell, J. A. Fillo, B. G. Twining, and J. J. Dorning, Eds., U. S. Dept. of Energy Report CONF-760343 (1975).
4. Proc. 2nd Topical Meeting, on Technology of CTR, J. L. Kulcinski, Ed., U.S. Dept. of Energy Report CONF-760935 (1976).
5. Proc. 7th Symp. on Engineering Problems of Fusion Research, M. S. Lubell and C. Whitmore, Eds., IEEE Publication No. 77CH1267-4-NPS (1977).
6. G. A. Carlson, Magnetohydrodynamic Pressure Drop in Lithium Flowing in Conducting Wall Pipe in a Transverse Magnetic Field--Theory and Experiment, Lawrence Livermore Laboratory Report UCRL-75307 (1974).
7. J. R. Powell, R. H. Wiswall, and E. Wirsing, Tritium Recovery from Fusion Blankets Using Solid Lithium Compounds, Brookhaven National Laboratory Report BNL-20563 (1975).
8. R. H. Wiswall and E. Wirsing, The Removal of Tritium from Fusion Reactor Blankets, Brookhaven National Laboratory Report BNL-50748 (1977).
9. D. K. Sze and D. C. Schluderberg, Trans. Am. Nucl. Soc. 30, 68 (1978).
10. A. B. Johnson, T. J. Kabele, and W. E. Gurwell, Tritium Production from Ceramic Targets: A Summary of the Hanford Coproduct Program, Battelle Pacific Northwest Laboratories Report BNWL-2097 (1976).
11. C. E. Messer, A Survey Report on Lithium Hydride, AEC Research and Development Report NYO-9470 (1960).
12. E. E. Shpilrain and K. A. Yakimovich, Lithium Hydride. Physicochemical and Thermophysical Properties, State Service of Standard and Reference Data. Monograph Series No. 10, Moscow (1972).
13. C. B. Magee, Metal Hydrides, W. M. Mueller, J. P. Blackledge, and G. G. Libowitz, Eds., Academic Press, New York, Chapt. 6 (1968).
14. E. Veleckis, E. H. Van Deventer, and M. Blander, J. Phys. Chem. 78, 1933 (1974).
15. E. Veleckis, J. Phys. Chem. 81, 526 (1977).
16. J. H. Hildebrand and R. L. Scott, The Solubility of Nonelectrolytes, 3rd Ed., Reinhold, New York, p.34 (1950).

17. E. Veleckis, R. M. Yonco, and V. A. Maroni, J. Less-Common Met. 55, 85 (1977).
18. F. J. Smith, A. M. Batistoni, G. M. Begun, and J. F. Land, (a) Proc. 9th Symp. Fusion Technology, Pergamon Press, New York, 325 (1976); (b) submitted for publication in J. Inorg. Nucl. Chem.
19. F. J. Smith, J. D. Redman, R. A. Strehlow, and J. T. Bell, Proc. Symp. Tritium Technology Related to Fusion Reactor Systems, W. H. Smith, W. R. Wilkes, and L. J. Wittenberg, Eds., ERDA-50, p. 41 (1975).
20. G. M. McCracken, D. H. J. Goodall, and G. Long, The Extraction of Tritium from Liquid Lithium, IAEA Workshop on Fusion Reactor Design Problems, Culham, U. K. (1974).
21. H. R. Ihle and C. H. Wu, Proc. 8th Symp. on Fusion Technology, Noordwijkerhout, The Netherlands, EUR-5182C, p. 787 (1974)
22. P. F. Adams, M. G. Down, P. Hubberstey, and R. J. Pulham, J. Less-Common Met. 42, 325 (1975).
23. P. F. Adams, P. Hubberstey, R. J. Pulham, and A. E. Thunder, J. Less-Common Met. 46, 285 (1976).
24. G. N. Lewis and M. Randall, Thermodynamics, revised by K.S. Pitzer and L. Brewer, 2nd Ed., McGraw-Hill, New York, p. 404 (1961).
25. E. E. Shpilrain, K. A. Yakimovich, D. N. Kagan, and V. G. Shvalb, Fluid Mech.-Sov. Res. 3, 3 (1974).
26. F. J. Smith and J. F. Land, Trans. Am. Nucl. Soc., Annual Meeting, p. 167 (1975).
27. E. E. Shpilrain, K. A. Yakimovich, and V. A. Shereshevskii, Teplofiz. Vys. Temp. 15, 661 (1977).
28. H. R. Ihle and C. H. Wu, J. Inorg. Nucl. Chem. 36, 2167 (1974).
29. H. Katsuta, T. Ishigai, and K. Furukawa, Nucl. Technol. 32, 297 (1977).
30. H. M. Smith and R. E. Webb, Equilibrium Dissociation Pressures of Lithium Hydride and Lithium Deuteride, Oak Ridge V-12 Plant, Oak Ridge, TN, Y-2095 (1977).
31. E. Veleckis, J. Nucl. Mater. 79, 20 (1979).
32. H. R. Ihle and C. H. Wu, Proc. 2nd Int. Congress on Hydrogen in Metals, Pergamon Press, New York, paper 1D8 (1977).
33. H. R. Ihle and C. H. Wu, J. Phys. Chem. 79, 2386 (1975).
34. C. E. Messer, The Alkali Metals, The Chem. Soc. (London) Spec. Bull. No. 22, p. 183, (1966).

35. E. J. Cairns, F. A. Cafasso, and V. A. Maroni, The Chemistry of Fusion Technology, D. M. Gruen, Ed., Plenum Press, New York, pp. 91-160 (1972).
36. P. F. Adams, P. Hubberstey, and R. J. Pulham, *J. Less-Common Met.* 42, 1 (1975).
37. J. F. Smith and Z. Moser, *J. Nucl. Mater.* 59, 158 (1976).
38. K. A. Bolshakov, P. I. Fedorov, and F. A. Stepina, *Izv. Vyssh. Uchebn. Zaved. Tsvetn. Metall.* 2, 52 (1959).
39. R. M. Yonco, E. Veleckis, and V. A. Maroni, *J. Nucl. Mater.* 57, 317 (1975).
40. P. Hubberstey, R. J. Pulham, and A. E. Thunder, *J. Chem. Soc., Faraday Trans.* 1, 431 (1976).
41. JANAF Thermochemical Tables, Dow Chemical Co., Midland, MI (March 31, 1978).
42. P. A. G. O'Hare and G. K. Johnson, *J. Chem Thermodyn.* 7, 13 (1975).
43. D. W. Osborne and H. E. Flotow, *J. Chem. Thermodyn.* 10, 675 (1978).
44. A. Bonomi, M. Hadate, and C. Gentaz, Proc. Int. Symp. on Molten Salts, J. P. Pemsler, J. Braunstein, D. R. Morris, K. Nobe, and N. E. Richards, Eds., The Electrochemical Society, Princeton, NJ, 1976, p. 78.
45. R. M. Yonco, V. A. Maroni, J. E. Strain, and J. H. DeVan, *J. Nucl. Mater.* 79, 354 (1979).
46. E. E. Hoffman, Newer Metals, Am. Soc. Test. Mater., Spec. Tech. Publ. 272, p. 195 (1960).
47. E. E. Konovalov, N. E. Seliverstov, and V. P. Emelyanov, *Russ. Metall.* 3, 77 (1969).
48. E. M. Hobart and R. G. Bjork, *Anal. Chem.* 39, 202 (1967).
49. R. M. Yonco and M. I. Homa, accepted for presentation at the ANS Annual Meeting, Atlanta, GA, June 3-7, 1979.
50. P. I. Fedorov and M. T. Su, *Acta Chim. Sinica* 23, 30 (1957).
51. M. G. Down, M. J. Haley, P. Hubberstey, R. J. Pulham, and A. E. Thunder *J. Chem. Soc. Chem. Comm.*, 52 (1978).
52. S. Aronson and F. J. Salzano, *Inorg. Chem.* 8, 1541 (1969).
53. J. H. Owen and D. Randall, Proc. Int. Conf. on Radiation Effects and Tritium Technology for Fusion Reactors, J. S. Watson and F. W. Wiffen, Eds., Rep. CONF-750989 (1976), III-433.
54. E. Veleckis, Argonne National Laboratory, work in progress.

55. K. M. Myles, F. C. Mrazek, J. A. Smaga, and J. C. Settle, Proc. Symp. and Workshop on Advanced Battery Research and Design, Argonne National Laboratory Report ANL-76-8, 50B (1976).
56. N. P. Yao, L. A. Heredy, and R. C. Saunders, J. Electrochem. Soc. 118, 1039 (1971).
57. R. Hultgren, P. D. Desai, D. T. Hawkins, M. Gleiser, and K. K. Kelley, Selected Values of the Thermodynamic Properties of Binary Alloys, Am. Soc. Metals, Metals Park, OH, p. 1078 (1973).
58. M. L. Saboungi and J. Marr, Argonne National Laboratory, personal communication.
59. C. J. Wen, B. A. Baukamp, and R. A. Huggins, Extended Abstracts, The Electrochem. Soc. 78-1, Abstract No. 171 (1978).
60. W. Weppner and R. A. Huggins, J. Electrochem. Soc. 125, 7 (1978).
61. R. A. Sharma and R. N. Seeforth, J. Electrochem. Soc. 123, 1763 (1976).
62. S. Lai and L. R. McCoy, Extended Abstracts, The Electrochem. Soc., 75-2, Abstract No. 21 (1975).
63. J. B. Talbot, A Study of Tritium Removal from Fusion Reactor Blankets of Molten Salt and Lithium-Aluminium, Oak Ridge National Laboratory Report ORNL/TM-5104 (1976).
64. J. B. Talbot, F. J. Smith, J. F. Land, and P. Barton, J. Less-Common Met. 50, 23 (1976).
65. W. Yunker, Extraction of Tritium from Lithium Aluminate, Hanford Engineering Development Laboratory Report HEDL-TME 76-81 (1976).

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