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**A REVIEW OF THE CHEMICAL, PHYSICAL,
AND THERMAL PROPERTIES OF LITHIUM
THAT ARE RELATED TO ITS USE
IN FUSION REACTORS**

MASTER

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and F. A. Cafasso**

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Chemical Engineering Division

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ABSTRACT

Herein, we review a number of important properties of lithium that are pertinent to its use as a blanket and/or coolant in a D-T fusion-power plant. Among the topics we cover are natural abundance; thermodynamic and transport properties; characterization, analysis, and control of species in lithium; and corrosion of materials (including electronic insulators) by molten lithium. Throughout this review we have attempted to indicate the importance of the individual properties as they would affect the overall design considerations of an operating reactor and to point out areas where information is lacking and where additional work is needed.

I. INTRODUCTION

There are numerous options open with regard to the path to controlled fusion as a source of energy based on the thermonuclear reactions:

At this time, the most promising confinement concepts for these reactions are either magnetic or inertial (laser ignition), with various configurational differences. The status and outlook for controlled fusion have been reviewed recently in several places,¹⁻⁴ and a number of technological assessments have appeared.⁵⁻⁸

A majority of the fusion-technology studies conducted to date have focused on the D-T reactor concept, because of the lower temperature necessary for ignition of the D-T reaction.⁴ Since tritium is not abundant in nature and not easily manufactured in the quantities needed, D-T power reactors (even those of the first generation) will most certainly be required to breed tritium. The use of pure lithium or lithium-containing substance as a blanket material has been a central idea in virtually all D-T reactor-design studies advanced thus far because advantage can be taken of the $^6\text{Li}(n,\alpha)\text{T}$ and $^7\text{Li}(n,n'\alpha)\text{T}$ reactions to breed tritium, if a reasonable neutron economy is achieved. In addition, liquid lithium, and some molten lithium salts which have favorable heat-transfer characteristics, offer the possibility of combining the blanket and coolant functions. The technological aspects of using lithium-containing molten salts in these applications have been considered elsewhere.⁸⁻¹⁰

An excellent review of the properties of lithium by Cowles and Pasternak¹¹ appeared in 1969. In it are compiled references to work published prior to 1968. Our review covers mostly the work that has been reported since 1968, but overlaps somewhat the review by Cowles and Pasternak to give perspective in certain areas.

II. NATURAL ABUNDANCE OF LITHIUM RELATIVE TO POTENTIAL CTR NEEDS

Since the fuel cycle for the D-T concept actually requires consumption of deuterium and lithium, it is important to consider the natural reserves of these materials in terms of the total energy which could be produced. In this regard, reserves of deuterium appear to be inexhaustible, with deuterium making up about 0.016% of the world's total hydrogen isotope inventory. As Gough and Eastlund¹ point out, deuterium used in this way would provide a natural energy source which could meet the world's power demands for billions of years. The energy available from lithium-blanketed D-T reactors is, in fact, limited by the extent of natural lithium resources. The nature and lithium content of the free world's landbound lithium reserves are listed in the first two columns of Table 1. These figures do not include lithium reserves in the ocean.

Blanket neutronic calculations¹²⁻¹⁴ have shown that tritium-breeding ratios in excess of 2.1 (tritons produced per fusion neutron from each D-T reaction) could conceivably be obtained in lithium-blanketed D-T reactors. However, breeding ratios that high require enhancement of the ⁶Li concentration above the value in natural lithium (7.42%). Even with natural lithium in the blanket, the total ⁶Li cross section for thermal-neutron capture is so much greater than the total ⁷Li cross section that ⁶Li will be consumed

Table 1. Free World Lithium Reserves^a (Landbound) and Corresponding Energy Reserves for D-T Fusion Reactors with Lithium Blankets

Nature of Reserve	Lithium Content, kg	Available Electrical Energy, ^b MW-hr
Measured & Indicated	0.43×10^{10}	0.54×10^{14}
Inferred	0.07×10^{10}	0.09×10^{14}
Potential	1.69×10^{10}	2.14×10^{14}
Total	2.19×10^{10}	2.77×10^{14}

^aThese data were obtained from H. R. Grady (Foote Mineral Co.) in a private communication to M. L. Kyle (Argonne National Laboratory). In this communication, Mr. Grady pointed out that appropriate incentive has led to the mapping of new resources for virtually every mineral, and lithium should be no exception.

^bAssuming optimized lithium utilization [25.3 MW-hr(t)/gram]¹³ and a thermal-to-electrical conversion efficiency of 50%.

at a greater rate than ${}^7\text{Li}$. Lithium utilization studies¹³ have indicated that the amount of energy per gram of natural lithium can be maximized to a value of ~ 25 MW-hr (thermal) by appropriately diminishing the ${}^6\text{Li}/{}^7\text{Li}$ ratio in the blanket so that the reactor operates at a breeding ratio only slightly greater than 1.0. Using the value 25 MW-hr(t)/gram of natural lithium and assuming a 50% thermal-to-electrical conversion efficiency,* we have calculated the amounts of available electrical energy to which the quantities of lithium listed in the second column of Table 1 correspond. These amounts are listed in the third column of Table 1. In order to make an estimate of the amount of time that these reserves will last, we note that 1.3×10^9 MW-hr of electricity were purchased in the USA in 1969. If, at the time D-T-fueled fusion plants come into operation, the annual electrical energy consumption rate in the USA has increased by a factor of ten over the 1969 figure, and the USA is permitted to burn only 10% of the lithium resources indicated in Table 1, there would still be over 2,000 years' worth of electrical energy available from these reserves. If we assume that methods can eventually be developed for recovery of lithium from the ocean in an economically competitive manner, the quantity of energy corresponding to the total world's supply of lithium would then be expected to meet electricity demands for millions of years.¹

The estimated total lithium inventories and required lithium per MW(t) for three reference design studies,^{9,15,16} which have appeared for D-T power reactors, are listed in Table 2. Each of these designs calls for about 10^5 kg of lithium and is based on a reactor system for which the heat

Table 2. Lithium Inventory Estimates for D-T Fusion Reactors^a

Reference Design	Blanket Material	Estimated Lithium Inventory, kg	Power Output, MW(t)	Lithium, kg/MW(t)
Mirror (Ref. 15)	Lithium	1.5×10^5	5,000	30
Astron (Ref. 16)	Lithium	0.9×10^5	15,000	6
Stellarator (Ref. 9)	Li_2BeF_4	1.0×10^5	5,000	20

^aTotal free world reserves $\approx 2.2 \times 10^{10}$ kg.

load on the first wall (vacuum wall) is ≥ 10 MW(t)/m². This inventory corresponds to only 10^7 kg of lithium for enough reactors to generate all of the electricity consumed in the USA in 1969, and is only 0.2% of the measured and inferred reserves shown in Table 1. Current thinking, however, is that materials considerations may force the heat loadings on the first wall to be considerably lower [of the order of 1 MW(t)/m²], thus increasing the size of the reactor for a given power level. These latter systems [~ 1 MW(t)/m²]

*It is anticipated that power-generation systems of the future will be operated at higher temperatures than those now used; hence thermal conversion systems with topping cycles can be expected to have conversion efficiencies higher than the 35-40% currently achieved.

may require in the neighborhood of 200 kg Li/MW(t) or up to 10^6 kg of lithium for a 5000-MW(t) plant. Even so, only about 2% of the measured and inferred reserves would be required as inventory at the 1969 power-generation level. At the current market price for high-purity lithium (\$15/kg), it would cost 15 million dollars to provide a 1-million-kg inventory, a small fraction of the total cost of the plant. These estimates indicate that the supply and cost of lithium are not likely to be a problem for fusion reactors unless competing demands develop.

III. THERMODYNAMIC AND TRANSPORT PROPERTIES OF LITHIUM

A. Thermodynamic Properties

It is beyond the scope of this report to provide an exhaustive critical review of each of the thermodynamic properties of lithium. Instead, the values considered to be most reliable (in some cases, the only values) by the authors of this report and their colleagues are cited. It was not feasible to check the cited values from various sources for thermodynamic consistency with one another. This should be done by the user in situations where consistency is important.

Data on the thermodynamic and transport properties of lithium published through 1967 have been compiled by Cowles and Pasternak¹¹ (C & P). Herein, we summarize results which have appeared since 1967 and compare them with some of the earlier work reviewed by C & P. In many cases, more extensive reviews of earlier work on a particular subject are contained in the references we cite.

The values of the melting and boiling points, heats of fusion and vaporization, critical properties, and triple point for lithium are given in Table 3. The value for the volume change on melting is presented with some reservation because it is rather old (1914) and has not been verified. One of the most notable properties of lithium is its wide liquid range, spanning more than 1160 centigrade degrees at one atmosphere pressure. The high boiling point of lithium makes it attractive as a blanket and/or coolant for CTR use.

Table 3. Some Thermodynamic Properties of Lithium

Property	Value	Reference
Melting point	180.6°C	17
Boiling point	1342°C	17
Heat of fusion	717 cal/(gm)(atom)	17
Heat of vaporization	37.7 kcal/(gm)(atom)	17
Volume change on melting	1.5% of solid volume	18
Critical properties		
Temperature	3223°K	19
Pressure	680 atm	19
Volume	66 ± 19 cm ³ /mol	19
Density	0.120 ± 0.33 gm/cm ³	19
Triple point		
Temperature	453.70°K	20
Pressure	1.4×10^{-10} Torr	20

Density. The density of liquid lithium, as determined by Novikov *et al.*,²¹ Goltsova,²² and Shpil'rain *et al.*,²³ can be expressed by Eqs. 1, 2, and 3, respectively, in Table 4. In the temperature range from 600 to 1000°C, the density values determined from these equations are within 1% of one another, as shown by the entries in Table 5. The specific volume of lithium increases by about 20% from 25 to 1000°C. This expansion will have to be accommodated in the design of fusion-reactor blankets that employ liquid lithium.

Compressibility. The speed of sound in molten lithium has been measured by Novikov *et al.*²⁴ from the melting point to 1100°K. Their results are plotted in Fig. 1 and described by Eq. 4 in Table 4. Values for the isothermal compressibility, β_T , determined from these ultrasound data are given in Table 5 for 600, 800, and 1000°C. Pasternak²⁵ has attempted to predict the compressibility of lithium from a correlation of reduced compressibility and reduced temperature for the other alkali metals. Approximate values for the isothermal compressibility, β_T , of lithium estimated from the curves given by Pasternak are compared with the results of Novikov *et al.*²⁴ in Table 5. The compressibility of lithium is particularly important to the inertial confinement concept,⁷ where lithium is expected to absorb some of the blast wave created by detonation of the fuel pellets. It may also be important in pulsed magnetic confinement systems, where shock waves are generated. In this light, the ultrasound measurements of lithium should probably be extended to temperatures well above 1100°K.

Fig. 1. Speed of Sound vs. Temperature for Liquid Lithium (Ref. 24)

Table 4. Empirical Equations for Some Physical and Thermal Properties of Lithium as a Function of Temperature

Property	Equation Number	Equations ($t = ^\circ\text{C}$, $T = ^\circ\text{K}$)	Reference
Density, d , gm/cm ³	1	$d = 0.5082 - 1.0336 \times 10^{-4} (t - 271.7)$ $- 4.8279 \times 10^{-10} (t - 271.7)^2$ $- 5.2853 \times 10^{-12} (t - 271.7)^3$ (300-1000°C)	21
	2	$d = 0.515 - 1.01 \times 10^{-4} (t - 200)$ (200-1600°C)	22
	3	$d = 0.5368 - 1.0208 \times 10^{-4} t$ (400-1125°C)	23
Speed of sound, v , m/sec	4	$v = 4784.5 - 0.591 T$ (458.16 to 1100°K)	24
Enthalpy, H_f , cal/gm	5	$H_f = 270.4 + C_p (T - 453.6)$ (190-650°C) ($C_p = 0.995$ from 600 to 1000°C)	21
	6	$H_f = -5.075 + 1.0008 t - 5.173/t$ (500-1300°C)	23
Vapor pressure, P , torr	7	$\log_{10} P = 10.2788 - 8283.1/t$ $- 0.7081 \log_{10} T$ (800-1400°C)	26
	8	$\log_{10} P = 7.7639 - 7877.9/T$ (1000-1500°C)	27
	9	$\log_{10} P = 7.67 - 7740/T$ (1100-1700°C)	28
Surface tension, σ , dyne/cm	10	$\sigma = 0.16 (3550 - t) - 95$ (200-1300°C)	29
	11	$\sigma = \frac{3530}{d^2} \exp \left(- \frac{1.815}{d} \right)$ (range not given)	31
Viscosity, η , centipoise	12	$\log_{10} \eta = 1.4936 - 0.7368 \log_{10} T + 109.95/T$ (185-1000°C)	23
	13	$\log_{10} \eta = 726.07/T - 1.3380$ (600-1200°C)	33
Thermal conductivity, λ , cal/(sec)(m)(°C)	14	$\lambda = 10.1 + 2.94 \times 10^{-3} t$ (250-950°C)	35
	15	$\lambda = 17.46 + 4.98 \times 10^{-3} (t - 180.6)$ $- 0.58 \times 10^{-6} (t - 180.6)^2$ (300-1100°C)	21
	16	$\lambda = 8.24 + 7.46 \times 10^{-3} t$ (320-830°C)	36
Electrical resistivity, ρ , $\mu\text{ohm-cm}$	17	$\rho = 18.33 + 3.339 \times 10^{-2} t - 6.795 \times 10^{-6} t^2$ (200-1000°C)	38
	18	$\rho = 21.934 + 2.598 \times 10^{-2} t + 2.581 \times 10^{-6} t^2$ $- 1.819 \times 10^{-9} t^3$ (200-1430°C)	39
Self-diffusion coefficient, D , cm ² /sec	19	$D = 0.94 (\pm 0.4) \times 10^{-3} \exp \left(- \frac{2300 \pm 300 \text{ cal}}{RT} \right)$ (190-250°C)	45
	20	$D = 1.41 (\pm 0.12) \times 10^{-3} \exp \left(- \frac{2825 \pm 90 \text{ cal}}{RT} \right)$ (195-450°C)	43

Table 5. Values for Some Thermodynamic Properties of Lithium at 600, 800, and 1000°C

Temp., °C	Density, gm/cc			Isothermal Compressibility, 10 ⁻¹² cm ² /dyne		Heat Capacity, cal/(gm)(°C)	
	Eq. 1	Eq. 2	Eq. 3	Ref. 24	Ref. 25	Ref. 21	
600	0.474	0.474	0.476	11.3	~9	0.996	
800	0.453	0.454	0.455	13.0	~10	0.993 ^a	
1000	0.431	0.434	0.434	15.1	~13	0.992 ^a	

Temp., °C	Standard Enthalpy, cal/gm		Vapor Pressure, Torr			Surface Tension, dyne/cm	
	Eq. 5	Eq. 6	Eq. 7	Eq. 8	Eq. 9	Eq. 10	Eq. 11
600	688	595	~0.05 ^a	0.06 ^a	0.06 ^a	333	~341
800	887 ^a	795	2.6	2.6 ^a	2.9 ^a	301	~313
1000	1086 ^a	996	38	38	39 ^a	269	~282

^aDetermined by extrapolating the indicated equation or graph beyond the range of experimental data.

Heat Capacity and Enthalpy. The heat-capacity values of lithium, as measured by Douglas *et al.*,²⁰ Novikov *et al.*,²¹ and Shpil'rain *et al.*,²³ vary from the value 0.995 cal/(gm)(°C) by less than 1% from 600 to 1000°C. Values for the heat capacity at lower temperatures have been tabulated by Hultgren *et al.*¹⁷ The enthalpy, H_T , as determined by Novikov *et al.*,²¹ and Shpil'rain *et al.*,²³ can be estimated by Eqs. 5 and 6, respectively, in Table 4. Values for H_T at 600, 800, and 1000°C determined by Eqs. 5 and 6 are listed in Table 5. Lithium has the highest heat-carrying capacity per unit volume of all the alkali metals.

Vapor Pressure. Experimental results on the vapor pressure of lithium as a function of temperature have been summarized by Hultgren *et al.*¹⁷ Anisimov and Volyak²⁶ measured the pressure of saturated lithium vapor from 800 to 1400°C and fitted their results to the expression given as Eq. 7 in Table 4, which has been used to calculate the saturated vapor pressures at 600, 800, and 1000°C listed in Table 5. Equation 8 (Rigney *et al.*,²⁷) and Eq. 9 (Bohdansky and Schins²⁸) listed in Table 4 are both based on vapor pressure data collected above 1000°C, but are in good agreement with Eq. 7 at 1000°C. Fusion reactors with static lithium blankets must be designed so as to avoid condensation of lithium in (1) the ducts required to vent helium formed by the tritium-producing reactions involving lithium and (2) other penetrations that may serve diagnostic and decontamination functions.

Surface Tension. Bohdansky and Schins²⁹ have measured the surface tension of lithium from 900 to 1300°C, and have fitted their data to the expression given as Eq. 10 in Table 4. This expression is also accurate in reproducing results obtained by Taylor^{30a} and Achener^{30b} in the range from 200 to 600°C and is probably reliable from the melting point up to at least 1300°C. Volyak and Os'minin³¹ have attempted to correlate the surface tension of lithium with its density via Eq. 11 in Table 4. Values obtained

with this expression differ from those of Eq. 10 by about 10%. The surface tension data obtained in these studies are plotted in Fig. 2, along with the curve which results from Eq. 10. Above 600°C, lithium can be expected to wet virtually all materials (metallic and insulating) and to thoroughly penetrate any porous substance with which it is in contact. Potential problems resulting from wetting and penetration by lithium are discussed in the section on materials compatibility.

B. Transport Properties

Viscosity. Kalakutskaya³² has measured the kinematic viscosity, ν , of liquid lithium up to 1500°C by the method of damped torsional oscillations. Absolute viscosities, η , at 600, 800, and 1000°C determined from his data using the densities given by Eq. 1 in Table 4 ($\eta = \nu \cdot d$) are listed in Table 6. These values are in reasonably good agreement with the results of Shpil'rain *et al.*²³ and Rigney *et al.*³³ (see Table 6) which are represented by Eqs. 12 and 13, respectively, in Table 4. Figure 3 shows the results of these studies on a plot of η vs. $1/T$ (T in °K). (Also included in this plot are some earlier results of Novikov *et al.*^{34a} and some low temperature data of Andrade^{34b}.) This plot indicates that the equation $\eta T = \text{constant}$ gives an adequate representation of the data over the temperature range of 180 to 1600°C. A value for the constant is given in Fig. 3. The low viscosity of lithium adds to its attractiveness as a heat-transfer fluid. Also, because of its low viscosity, the diffusion rates for species (*e.g.*, tritium, helium) in liquid lithium would probably be relatively high, but this remains to be investigated in greater detail.

Fig. 2. Surface Tension vs. Temperature for Liquid Lithium (Refs. 29 and 30)

Table 6. Values of Some Transport Properties of Lithium at 600, 800, and 1000°C

Temp., °C	Viscosity, centipoise			Thermal Conductivity, cal/(sec)(m)(°C)			Electrical Resistivity, μohm-cm		Self- Diffusion, 10 ⁻⁴ cm ² /sec	
	Ref. 32	Eq. 12	Eq. 13	Eq. 14	Eq. 15	Eq. 16	Eq. 17	Eq. 18	Eq. 19	Eq. 20
600	0.284	0.312	0.299	11.8	12.5	12.7	35.9	38.1	2.5 ^a	2.8 ^a
800	0.231	0.218	0.248	12.4	13.4	14.2	40.7	43.4	3.2 ^a	3.8 ^a
1000	0.196	0.171	0.216	13.0 ^a	14.2	15.7 ^a	44.9	48.7	3.8 ^a	4.6 ^a

^aDetermined by extrapolating the indicated equation or graph beyond the range of experimental data.

Thermal Conductivity. Inspection of the results of thermal conductivity studies that have been reported for liquid lithium from 200 to 1100°C shows a range of uncertainty as high as ±10% at the higher temperatures. This is illustrated in Fig. 4 for the work of Shpil'rain and Krainova,³⁵ Novikov *et al.*,²¹ and Cooke.³⁶ Empirical equations for λ as a function of temperature determined by these investigators are given in Eqs. 14, 15, and 16 in Table 4. Values obtained with these equations for 600, 800, and 1000°C are listed in Table 6.

The dashed line in Fig. 4 represents the result of a linear least-squares refinement of 95 data points from the three studies mentioned above. The equation for this line, $\lambda = 9.59 + 4.55 \times 10^{-3}t$, yields values that are in best agreement with Eq. 15 in Table 4.

Conductive heat transfer will predominate in lithium blankets that are

Fig. 3. Viscosity vs. $1/T$ (°K) for Liquid Lithium (Refs. 32, 33, 34)

static or in slow laminar flow. Hence designers will probably require more precise data on λ for lithium in the range from 600 to 1000°C than are currently available.

Electrical Resistivity. Arnol'dov *et al.*³⁷ have measured the effect of both dissociating and thermally stable gaseous impurities on the electrical resistivity of lithium at 300°C. Of the elements tested (N, O, C, and H), nitrogen had the greatest effect (on an atom % basis), raising the resistivity of lithium 0.7 $\mu\text{ohm-cm}$ for each 0.1 at. % nitrogen in the lithium. Shpil'rain and Savchenko³⁸ applied impurity corrections to their resistivity data for liquid lithium and obtained the expression for ρ given as Eq. 17 in Table 4. Values of resistivity at 600, 800, and 1000°C determined from Eq. 17 are listed in Table 6, together with values calculated from Eq. 18 in Table 4, which is due to Rigney *et al.*³⁹

Freedman and Robertson⁴⁰ measured the resistivity of lithium below 600°C. Their results are plotted in Fig. 5, together with the results of Rigney *et al.*³⁹ and Tepper *et al.*⁴¹ (Other investigators^{37,38} have failed to list the actual experimental data and have given only empirical relations.) Based on the results in Fig. 5 it appears unwarranted to extend the power series in temperature beyond the first power, *i.e.*, $\rho = A + Bt(^{\circ}\text{C})$ is adequate. Values for A and B determined by least-squares refinement of the data of Refs. 39, 40, and 41 are given in Fig. 5.

Because of lithium's low resistivity, magnetohydrodynamic effects will make it difficult to pump the lithium across magnetic field lines.⁴² If lithium is employed as a circulating heat-transfer medium, it will probably have to be pumped into and out of the reactor with the direction of flow being mostly parallel to the field lines in order to avoid large pumping power requirements. This poses a significant difficulty to closed magnetic confinement schemes, where the core of the reactor is completely enclosed by magnetic field lines.

Diffusion. The work of Ott and Lodding⁴³ and Ott, Lunden, and Lodding⁴⁴ on the self-diffusion coefficient for ^6Li and ^7Li and the relative thermal

Fig. 4. Thermal Conductivity vs. Temperature for Liquid Lithium (Refs. 21, 35 and 36)

diffusion of isotopes in liquid lithium has been reviewed by C & P.¹¹ More recently, Murry and Cotts⁴⁵ have measured the self-diffusion rate for ^7Li in lithium by magnetic resonance techniques. Their data and the data of Ott and Lodding⁴³ are represented by Eqs. 19 and 20, respectively, in Table 4. The minor differences in these expressions may result from the neglect of ^6Li diffusion by Murry and Cotts.⁴⁵

C. Nuclear Properties

The curves shown in Fig. 6 give a general indication of the relationship between cross section and incident neutron energy for the $^6\text{Li}(n,\alpha)\text{T}$ and $^7\text{Li}(n,n'\alpha)\text{T}$ reactions. Inspection of the experimental data⁴⁶ shows that there is a considerable uncertainty in the cross section for the latter reaction. Additional data for the nonelastic scattering of neutrons by ^6Li and ^7Li are given in Ref. 46. The implications of these data, in connection with the neutronic behavior of fusion reactor blankets, have been reviewed elsewhere.¹²⁻¹⁴

IV. MATERIALS COMPATIBILITY AND CHEMISTRY

The compatibility of various metals and ceramics with liquid lithium at elevated temperatures depends to a significant extent on the concentrations of various impurities in the lithium and in the metal or ceramic. The magnitude of the effect of a given concentration of a given impurity on the corrosion rate depends upon the thermodynamics and phase relationships for the impurity-lithium, the impurity-metal, or impurity-ceramic system, and

Fig. 5. Electrical Resistivity vs. Temperature for Liquid Lithium (Refs. 39, 40, and 41)

upon the ternary interactions. For this reason, it is important to have phase-diagram and thermodynamic data for the various impurities in lithium and in the metals and ceramics of interest. In this connection, the most important "impurities" are hydrogen, deuterium, and tritium.

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

The paucity of literature data on phase equilibria in the Li-LiH, Li-LiD, and Li-LiT systems has been indicated elsewhere.⁴⁷ For the Li-LiH system, there are several studies dealing with the dissociation pressure of hydrogen as a function of temperature and composition. Hill^{48,49} obtained a pressure-composition isotherm at 700°C, Perlow^{49,50} measured two isotherms at 770 and 825°C, and Heumann and Salmon^{49,51} redetermined Hill's isotherm at 700°C. The data of these investigations lack consistency, particularly in the dilute (in hydrogen) region, where the disagreements result in the crossing of isotherms as shown in Fig. 7. Because of these inconsistencies, it is not possible to make a reliable estimate of pressure-composition relationships in the region of dilute solutions of hydrogen in lithium using the data in Fig. 7. More recently, Veleckis and Van Deventer⁵² have measured pressure-composition isotherms in the Li-LiH systems at temperatures in the range from 700 to 900°C. Their results, some of which are shown in Fig. 8, represent the most consistent set of isotherms yet obtained for the Li-LiH system, and have permitted the estimation of Sieverts' law constants, K_S , for dilute solutions of hydrogen in lithium. Values of K_S , where

$$\sqrt{P_{H_2}} = K_S \cdot N$$

P_{H_2} = H_2 partial pressure

N = mole fraction of H in Li

Fig. 6. Cross Section vs. Neutron Energy for the ${}^6\text{Li}(n, \alpha)\text{T}$ and ${}^7\text{Li}(n, n'\alpha)\text{T}$ Reactions (Ref. 46)

Fig. 7. Pressure-Composition Isotherms for the Lithium-Hydrogen System (Refs. 48-51)

Fig. 8. Recent Pressure-Composition Data for the Lithium-Hydrogen System (Ref. 52)

were determined by Veleckis and Van Deventer⁵² for 700, 800, and 900 °C and estimated for 1000°C; these values are listed in Table 7.

Heumann and Salmon⁵¹ have also measured pressure-composition isotherms in the Li-LiD and Li-LiT systems. Their results at 700°C, shown in Fig. 9, indicate a significant isotope effect on the partial pressure at a given mole fraction. For instance, the deuterium pressure over lithium is consistently a factor of two higher than the hydrogen pressure at concentrations

Table 7. Estimated Sieverts' Constants, K_S , for Dilute Solutions of Hydrogen, Deuterium, and Tritium in Lithium

Temp., °C	K_S , Torr ^{1/2} /Atom Fraction H, D, or T		
	H in Li	D in Li	T in Li
1000	148	209	243
900	96	136	157
800	57	81	93
700	31	44	51

Fig. 9. Isotopic Dependence of the Hydrogen Pressure vs. Composition Curves for the Lithium-Hydrogen System at 700°C (Ref. 51)

in the single-phase region (<20 mol% H in Li). The results for the Li-LiT system at 700°C are inconsistent with those for the Li-LiH and Li-LiD systems, in that the pressure-composition curve for tritium in lithium at 700°C should lie parallel to and slightly above that for deuterium in lithium on the log-log plot in Fig. 9. As a result of this discrepancy, it is not possible to determine the tritium-to-protium partial-pressure ratio at 700°C from the work of Heumann and Salmon.

Swain *et al.*⁵³ have derived the following equation

$$\frac{Q_H}{Q_T} = \alpha \left(\frac{Q_H}{Q_D} \right)^{1.442}$$

to describe the relationship between the isotope effects of tritium and deuterium on a thermodynamic quantity, Q , as measured for hydrogen. The value of α has been shown to lie in the range from 0.907 to 1.157 for a variety of properties over a wide temperature range. Using this equation with $\alpha = 1.0$ and assuming $P_D/P_H \approx 2.0$ as indicated in Fig. 9 ($Q = P =$ partial pressure), we estimate that $P_T/P_H \approx 2.7$ for H in Li and T in Li solutions having the same mole fraction of H or T and the same temperature. Using these values for the P_D/P_H and P_T/P_H ratios and Veleckis and Van

Fig. 10. Schematic Drawing of Lithium-Lithium Hydride Phase Diagram Based on Existing Data (Dashed Lines Represent Boundaries Not Investigated Experimentally)

Deventer's results for the Li-LiH system, we have estimated Sieverts' constants for the dilute (in hydrogen isotope) regions of the Li-LiD and Li-LiT systems. The values for these constants, given in Table 7 for 700, 800, 900, and 1000°C, represent the best estimates that can be extracted from existing data at this time. Further experiments are definitely needed to confirm or refine the accuracy of these values.

A schematic representation of the Li-LiH phase diagram based on existing experimental data is shown in Fig. 10. The monotectic at 685°C, which extends from ~26 to ~98 mol % LiH (indicated by the squares), was measured by Messer *et al.*⁵⁴ The circles are from the pressure-composition data of Veleckis and Van Deventer.⁵² Also included are the known melting points (indicated by the triangles) of the terminal phases, lithium (180.6°C) and LiH (685°C). The solubility of LiH in Li below the monotectic was determined from the following equation as given by Messer *et al.*⁵⁴

$$\log_{10} \frac{n}{1+n} = 2.835 - 3381/T$$

where n is the H/Li atom ratio and T is in °K. The extent of freezing-point depression of lithium by LiH, the consolute temperature of the miscibility gap, and the behavior at compositions >98% LiH remain to be determined, as indicated by the dashed lines.

The solution chemistry and thermodynamics of the hydrogen isotopes in

liquid lithium (particularly in the region of dilute solutions of hydrogen in lithium) are of fundamental importance to D-T reactor systems with lithium blankets. In addition to the tritium generated by the ${}^6\text{Li}(n,\alpha)\text{T}$ and ${}^7\text{Li}(n,\alpha)\text{T}$ reactions, there will also be some amount of both protium and deuterium in the blanket. The latter isotopes will, in the main, arrive in the blanket by permeation through the structural materials. Deuterium, of course, is present in the system as part of the fuel cycle. The protium enters the system (1) via its formation in one branch of the D-D reaction (which will take place to a certain extent even in D-T reactors), (2) from (n,p) reactions involving the structural materials, and (3) by back permeation of hydrogen from steam heat exchangers.

The effects of hydrogen isotopes on the interactions of liquid lithium with candidate structural materials remain to be thoroughly investigated. One report⁵⁵ has appeared on the formation of ternary hydride phases between lithium hydride and selected metals. Results of this study for niobium and molybdenum at temperatures up to 700°C indicated that no ternary hydride phases were formed. Measurements of other physical, chemical, thermodynamic, and electrochemical properties of lithium hydride and lithium-lithium hydride mixtures have been presented and reviewed elsewhere.^{49, 56-58}

B. Solubilities of Various Nonmetals in Lithium

Solubility of Oxygen and Nitrogen in Lithium. The solubilities of oxygen and nitrogen in lithium were determined in the range of 250-450°C by Hoffman.^{59a} The oxygen and nitrogen data are shown in Fig. 11 and Table 8, respectively.

The oxygen data were fitted by the method of least squares to the following equation

$$\log S(\text{ppm}) = 5.85 - 2038/T$$

where S is the solubility of oxygen in lithium in parts per million and T is in °K. From this expression, the heat of solution is found to be 9.4 kcal/mol.

The data for the solubility of oxygen in lithium exhibit considerable scatter. The reason for this is unclear. Handling, equilibrating, and analytical procedures were carefully employed, hence it is unlikely that any of these factors contributed significantly to the variability observed in the results. The scatter may have been due to the passage of small but variable amounts of oxide particulate through the 20-micron filter used in collecting samples of the oxygen-saturated lithium.

The solubility of nitrogen in lithium was studied less extensively than that of oxygen. Each entry in Table 8 represents the average of only four determinations. Assessment of the reliability of the nitrogen data is made difficult by the fact that (a) the results of the individual measurements were not reported and only average values of the solubilities were given and (b) no measure of experimental uncertainty was given. Examination of Table 8, however, reveals that the data exhibit a marked decrease in the temperature coefficient of solubility above 350°C. Not only is this decrease inconsistent with existing phase-diagram information on the lithium-nitrogen system,⁶⁰ but the heat of solution (~400 cal) calculated from the data in the range 350-

Fig. 11. Solubility of Oxygen in Lithium (Ref. 59a)

Table 8. Solubility of Nitrogen in Lithium (Ref. 59a)

Temperature, $^\circ\text{C}$	Nitrogen Content, percent by weight
250	0.04
300	0.16
350	1.19
400	1.21
450	1.31

450°C is unrealistic. Therefore it is concluded that one or more of the reported solubility values in this range are suspect.

Despite the uncertainty about the reliability of some of the nitrogen measurements and the wide scatter exhibited by the oxygen results, the data have proven useful because they provide an explanation for the fact that oxygen in lithium can be reduced to levels of <100 ppm by cold trapping, but that nitrogen cannot.^{59a} The solubility of nitrogen at temperatures just above the melting point of lithium is too high for cold trapping to be effective.

Remeasurement of the solubilities of oxygen and nitrogen in lithium should be done in order to refine the data in the case of oxygen and to verify the data in the case of nitrogen. The success of cold trapping in lowering oxygen levels and its failure in reducing nitrogen levels provide support, in a general way, for Hoffman's results.^{59a} However, with the methods currently available, remeasurement should result in data of much greater precision and accuracy.

Solubility of Carbon in Lithium. The lithium-carbon system was studied in the composition range 0-50 atom percent carbon by Fedorov and Mein Tsung Su⁶¹ using thermal and X-ray diffraction analysis. The partial phase diagram derived from their findings is reported by Elliott.⁶⁰ This diagram exhibits (a) one compound, Li_2C_2 , which exists in four polymorphic modifications and (b) a eutectic between Li and Li_2C_2 at 1650°C and at a concentration of <1 atom percent carbon. Secrist⁶² studied the system in the composition range 45-100 atom percent carbon and demonstrated that Li_2C_2 was the only stable compound in equilibrium with lithium and graphite in the system. Moreover, in samples that were annealed at various temperatures between 350 and 700°C and then quenched, he observed only one crystalline form of Li_2C_2 . This finding was not consistent with the X-ray results of Fedorov and Mein Tsung Su.⁶¹ Secrist,⁶² however, points out several deficiencies in the X-ray work of these investigators⁶¹ and on this basis questions the reliability of their observation of polymorphism in Li_2C_2 .

C. Nonmetallic Species in Lithium

Hydrogen Species. The most prominent hydrogenous species in lithium is hydride. Its solubility and stability in lithium have already been discussed above.

Carbon, Nitrogen, and Oxygen Species. The chemical state of carbon, nitrogen, and oxygen in lithium has been studied by Kelly, Hobart, and Bjork.⁶³ These investigators added graphite, lamp black, carbonate, cyanide, phthalate, sucrose, and nitrate in known quantities to capsules containing purified lithium. After heating to 600°C for 1 to 65 hours, the samples were cooled, the lithium was hydrolyzed, and the evolved gases were analyzed. For the carbon compounds, the gas monitored was acetylene. Figure 12 shows that, within experimental uncertainty, 100% of the carbon added in each experiment was recovered as acetylene. For the nitrogen-addition experiments, the gas monitored was ammonia. About 98% of the nitrogen added in each case was recovered as NH_3 . On the basis of these findings, it was concluded that in lithium, at 600°C and above, carbon and nitrogen exist as the simple carbide and nitride, respectively.

Below 600°C, available evidence suggests that the chemistry of carbon

Fig. 12. Recovery of Carbon as Acetylene (Ref. 63)

may be more complex. For example, Kelly *et al.*⁶³ observed that carbonate, an impurity arising principally, but not exclusively, from the lithium-manufacture process, exists in lithium and that it decomposes with the formation of carbide and oxide as the temperature is raised toward 600°C. The decomposition most likely proceeds as follows:

Hence, there exists a set of conditions (time and temperature) under which carbide, carbonate, and oxide may coexist in lithium. Results of semiquantitative experiments with carbonate-lithium mixtures indicated total decomposition of carbonate at 700 and 800°C within 1 hour and >90% and ~10% decomposition at 600 and 400°C, respectively, within 65 hours.

The concept has been advanced that oxygen may also interact with transition (and refractory) metals in lithium to form complexes having the stoichiometry $\text{Li}_2\text{O} \cdot n\text{M}_y\text{O}_z$ where M is the appropriate metal.⁶⁴ Such complexes, however, have not been observed directly. If they do exist in solution in lithium, their stability will depend not only on temperature but also on oxygen activity.

A prominent oxygen-bearing impurity is lithium hydroxide. This impurity may be expected to form through the reaction of lithium with moisture. Its formation via the reaction

is unlikely since this reaction is not thermodynamically favored at temperatures and hydrogen pressures of interest to fusion-reactor technology.

Phosphorous Species. Arbiter and Lazerus,⁶⁵ in a study of the potential of distillation for the purification of lithium, observed that phosphine was liberated when distilled lithium was dissolved in water. Since the dis-

Fig. 13. Hydrogen-Activity Meter (Ref. 67)

tillation was conducted in a stainless steel apparatus, we speculate that the observed phosphorus impurity was leached from the walls of the still and was not carried over by the lithium. Moreover, the fact that phosphine formed on hydrolysis suggests that the impurity exists as a phosphide (possibly Li_3P).

D. Analysis

In this section, we discuss methods that have been developed for the detection and determination of hydrogen, tritium, oxygen, carbon, and nitrogen impurities in lithium and other alkali metals. The discussion is extended to other alkali metals to give perspective and to point out those methods that have been applied successfully in systems other than lithium and may have potential use with lithium.

Hydrogen Methods. The hydrogen content of lithium has not been a factor of major importance in studies that have been conducted in the past. Hence, recorded experience with any single method is lacking. Of the methods that have been used for hydrogen in alkali metals, the one that has been used routinely is the isotopic dilution technique.⁶⁶ This method should be applicable to the determination of hydrogen in lithium.

Another method which has gained prominence recently for the measurement of hydrogen in sodium and which should be applicable to lithium is the hydrogen activity meter.⁶⁷ This device, shown schematically in Fig. 13, consists of a 10-mil-thick nickel membrane immersed in sodium, an ion pump, and a vacuum gauge. Hydrogen diffuses through the membrane into an evacuated chamber. In the dynamic mode of operation, the ion pump is operated continuously and the ion-pump current is measured and used as an indication of the hydrogen flux through the membrane. The relationship

between pump current and the hydrogen flux is linear over a large range. With suitable allowance for the permeation properties of hydrogen in the membrane, the hydrogen flux is relatable to the hydrogen activity of the medium.

In another mode of operation, the ion pump is valved out and the hydrogen is allowed to diffuse into the manifold until equilibrium is reached. The equilibrium pressure is measured with an ionization gauge or a capacitance manometer. This mode of operation is preferred for the range from 10^{-4} to 1 Torr; for low pressures ($<10^{-4}$ Torr), the dynamic mode is preferred.

In application to lithium, "pure, low carbon" iron would be used in place of nickel as the membrane material and operation would be in the dynamic mode. The Sieverts' law relationship for the hydrogen-lithium system predicts that, at a hydrogen concentration of ~ 10 ppm, the equilibrium pressure will be in the 10^{-6} Torr range. In this range most pressure gauges lose sensitivity. Hence, measurement of the flux through the membrane, i.e., the dynamic mode of operation, will be required. The ion-pump current should be useful down to the requisite range. (Pressures as low as 10^{-7} to 10^{-8} Torr are measurable this way.) Work in our laboratory suggests that with introduction of a mass spectrometer into the dynamic system a sensitivity increase of a factor of 100 is achievable.⁶⁸ Hence it appears that the sensitivity attainable with existing techniques is more than adequate. Some development work, of course, will be necessary for application to lithium, but this approach appears feasible.

Tritium Methods. Benjamin *et al.*⁶⁹ developed a method for the determination of tritium in 1-gram irradiated lithium samples. It involves (a) extraction of tritium as tritiated hydrogen and (b) determination of the tritium content of the gas, using a heavily shielded counter. The extraction is done by converting the lithium completely to hydride and then decomposing the compound by heating under reduced pressure.

While this is a high-sensitivity method (the method is useful for quantities of tritium having activities greater than 5 disintegrations/minute) and could be adapted for routine use, it is more complicated than a liquid scintillation method currently used routinely for the determination of tritium in sodium.⁷⁰ The scintillation method involves (a) dissolving the sample in water to produce a tritiated hydrogen gas and a tritiated aqueous solution, (b) oxidizing the tritium in the gas over hot CuO and trapping it as tritiated water, (c) distilling the tritium in solution (after careful neutralization) and collecting it as tritiated water, (d) combining the two condensates, and (e) analyzing for tritium by liquid scintillation counting. In sodium, a detection limit of $<1 \times 10^3$ pCi/g has been attained. A comparable sensitivity should be possible (in principle) with lithium.

The tritium monitor which is currently under development for use in sodium systems⁷¹ should also have applicability in lithium systems. This monitor consists simply of a 10-mil-thick iron membrane over which a sweep gas is passed. The sweep gas, containing the tritium or tritiated hydrogen that diffuses through the membrane, is mixed with a counting gas, and the mixture is fed into a proportional counter. The application of this monitoring concept to lithium systems seems feasible, but some development would be required.

Oxygen Methods. Many techniques have been used for the determination of oxygen in lithium. Among these are

- amalgamation
- alkyl halide
- Karl Fischer
- liquid ammonia extraction
- fluorination by KBrF_4
- vacuum fusion
- thermal and fast neutron activation
- gamma activation
- vacuum distillation

Of these methods, no single one has gained wide acceptance. Each possesses characteristics which limit its applicability. Below, the general principles and basic limitations of each method will be considered.

The amalgamation method⁷² involves solution of the metal in mercury followed by separation and titration of the oxide. Experience with this method for the determination of oxygen in lithium has proven unfavorable. In general, the method is limited by its nonspecificity for oxygen.

The alkyl halide method by White *et al.*⁷³ involves reaction of the metal sample with an alkyl halide in a Wurtz-type synthesis to produce an alkane and the metal halide. The unreacted oxide is then extracted and titrated. Attempts to apply this method to the analysis of lithium have failed owing to ill-defined side reactions.

The Karl Fischer method, suggested by Sax and Steinmetz,⁷⁴ involves solution of the metal in mercury, followed by conversion of the insoluble oxide to water, and determination of the water thus formed with Karl Fischer reagent. This technique, while specific for oxygen, is troubled by high blanks and ill-defined side reactions.

The liquid-ammonia extraction method proposed by Jaworowski *et al.*⁷⁵ involves solution of the metal in liquid ammonia followed by filtration and titration of the insoluble oxide. Like the amalgamation method above, this approach is limited by its nonspecificity. It is also hampered by the complexity introduced in handling liquid ammonia.

The fluorination method, introduced by Goldberg *et al.*,^{76,77} involves high-temperature reaction of metal samples with KBrF_4 to form fluorides and to displace molecular oxygen, as well as nitrogen. Oxygen and nitrogen are measured by conventional gasometric techniques. Evidence suggests that this method is routinely applicable to the determination of oxygen and nitrogen in lithium. The range of oxygen and nitrogen that can be measured conveniently is from 0.02 to 10 mg. The method is specific for oxygen and nitrogen and is limited only by the fact that it requires the use of complex apparatus, hazardous chemicals, and large samples in the low ppm ranges.

The vacuum fusion method⁷⁸ involves a preliminary vacuum distillation of the sample from a graphite-containing crucible, followed by an increase in temperature to cause reduction of the oxides and the release of carbon monoxide which is then determined. A detection limit of ~10 ppm oxygen is

claimed. The method is specific for oxygen and is hampered only by the complexity introduced (a) in obtaining a sample for distillation without contamination and (b) in conducting a distillation.

The thermal neutron activation method, developed by Bate and Leddicotte,^{79,80} is based on the formation of 110-minute ^{18}F by the reactions $^6\text{Li}(n,\alpha)\text{T}$ and $^{16}\text{O}(\text{T},n)^{18}\text{F}$. This approach is limited by complexities of standardization, the requirement for the presence of ^6Li , and the need for rapid radiochemical separations.

The fast-neutron-activation method of Steele and Lukens⁸¹ is based on the $^{16}\text{O}(n,p)^{16}\text{N}$ reaction followed by measurement of the induced nitrogen-16 (7.6-sec half-life) activity (6-7 MeV gammas) with a NaI or Ge-Li detector and multichannel analyzer. This method, however, is specific for oxygen and is reported to have a sensitivity limit of ~ 10 ppm. The major limitation of the method is the container used for encapsulation, because the oxygen in the container is also activated. Most materials contain too much oxygen for trace-oxygen analysis.

The gamma-activation approach, developed by Faraday and Bingham,⁸² is based on the formation of the 2.1-minute positron emitter ^{15}O by the reaction $^{16}\text{O}(\gamma,n)^{15}\text{O}$. The method is estimated⁸² to have a detection limit of 10 ppm oxygen and is limited by the background oxygen in container materials and by sample-size factors. The total sample must receive uniform irradiation; hence the sample size cannot exceed beam size, and moreover, the sample must be thin so that gamma particles will penetrate it.

The vacuum distillation approach, first applied to lithium systems by Konovalov *et al.*⁸³ in Russia, and Gahn⁸⁴ in the U.S., involves distillation of the metal at 800°C, followed by solution of the nonvolatile impurities (assumed to be lithium oxide) in water, and determination of oxygen by titration. The alkalinity or lithium content of the impurities is then converted to an oxygen concentration. Gahn⁸⁴ reports that the method is useful for the measurement of oxygen in lithium at the 30-ppm level and lower. The technique is limited, however, by the fact that it is nonspecific for oxygen; hence the presence of nitrides, carbides, and other impurities in the residue will lead to error unless appropriate corrections are made. To make these corrections, the residue must be analyzed for each of the Li-bearing impurities suspected. This may not be possible in all cases.

Of the methods described above, the literature suggests that neutron activation is the one most frequently used in the U.S. This is undoubtedly due to the high sensitivity and low detection limit offered by this approach.

From the above discussion, the need for a simple and convenient method for the determination of oxygen in lithium in the 1-10 ppm range is obvious. In recent years, measurement of the oxygen content of liquid sodium systems by electrochemical cells using thorium-yttria ceramic electrolytes has come into prominence. Stavropoulos and Cafasso,⁸⁵ using the cell $\text{Sn-SnO}_2/\text{ThO}_2\text{-15 wt \% Y}_2\text{O}_3/\text{dilute solution of O in Na}$, determined oxygen in sodium at levels as low as 0.5 ppm. Application of cells of this type to lithium systems will be limited only by the corrosion resistance of the ceramic. In lithium compatibility tests conducted by Hays and O'Connor⁸⁶ with $\text{ThO}_2\text{-Y}_2\text{O}_3$

mixtures at 1093°C, only light attack was observed after 3000 hr. This finding, in itself, suggests that the ceramic may have good potential for short-term use (i.e., it may be useful in a dip-in-and-remove mode). Moreover recent work⁸⁷ has shown that the resistance of $\text{ThO}_2\text{-Y}_2\text{O}_3$ mixtures to attack by liquid sodium can be improved by reducing the impurity content of the ceramic. High-purity thoria-yttria electrolytes with improved corrosion resistance are now commercially available.⁸⁸ These improved electrolyte ceramics may also exhibit increased resistance to attack by lithium. The possibility that a cell such as the one described above may be useful for the determination of oxygen in lithium is not ruled out by any existing information. Hence, this possibility should be investigated.

Carbon Methods. Two methods, the combustion⁸⁹ and the acetylene-evolution⁹⁰ methods, have been utilized for the determination of carbon in lithium. In the combustion method, the carbon contained in lithium samples is totally converted to carbon dioxide by igniting the samples in a stream of oxygen at 900°C in the presence of boric oxide. The carbon dioxide formed is then measured gas-chromatographically. The detection limit of this method has been reported to be 25 ppm.

In the acetylene-evolution method, lithium samples are hydrolyzed and the acetylene so generated is determined by gas chromatography. This is generally followed by acidification of the solution and determination of the carbonate level (if any) in the sample by measurement of the carbon dioxide released. Concentrations as low as 0.5 ppm carbon are detectable by this method.

The combustion method determines the total carbon content of the system and does not require knowledge about the forms of carbon in the sample. The acetylene-generation method, however, does require knowledge that all the carbon in the sample is in the form of carbide or carbonate. Experience has shown (see the preceding section) that, in lithium systems heated above 600°C, the preferred state of carbon is carbide. In such systems, the acetylene-generation method is useful and reliable. For systems that have not been heated above 600°C and in which the form of carbon is unknown, the total combustion method is the preferred one.

Gamma activation has also been shown to have potential for the determination of carbon in lithium.⁸² This technique involves production of ^{11}C by the reaction $^{12}\text{C}(\gamma, n)^{11}\text{C}$ followed by measurement of the induced 20.5-minute activity by positron counting. The detection limit is said to be ~ 10 ppm.⁸² Application of the method is limited by the sample size and thickness requirements described in the preceding section on oxygen methods.

A method that is finding applicability in sodium systems for the determination of carbon at activities as low as 10^{-3} is the carbon diffusion meter.⁹¹ This meter, which may also be useful for determining carbon activity in lithium systems, consists of a 10-mil-wall iron probe through which a decarburizing gas ($\text{Ar-5\% H}_2\text{-0.5\% H}_2\text{O}$) is passed. Carbon diffuses through the probe and reacts with the decarburizing gas to form carbon monoxide. The carbon monoxide is subsequently converted to methane and determined by means of a flame ionization detector. Since pure iron has been reported to exhibit good resistance to corrosion by lithium, the use of iron as a probe material should be investigated. Iron may prove unsatisfactory because the carbon activity at the Fe-Li interface could be high enough to support penetration by lithium. While carbon activities at this

interface can be calculated for an assumed flux through the probe, the threshold carbon activity for lithium penetration of iron is unknown. Therefore, on the basis of existing knowledge, it cannot be predicted whether or not this phenomenon will occur. Hence, the concept that this method may be useful for lithium systems should be tested experimentally.

Nitrogen Methods. Three methods that have been used for the determination of nitrogen in lithium are the micro-Kjeldahl,⁹³ the high-temperature KBrF_4 fluorination,⁷⁷ and the gamma activation⁸² methods. Of the three, the micro-Kjeldahl technique has been used most frequently.

The Kjeldahl method involves the following steps: (a) dissolution of a lithium sample in water and conversion of nitrogen in the sample to ammonia, (b) steam distillation of the solution to separate the ammonia, (c) reaction of the ammonia in the distillate with Nessler's reagent, and (d) photometric measurement of the yellow color that is developed. This procedure is suitable for the determination of nitrogen in lithium at levels as low as 0.5 ppm.

The principle of the fluorination method^{76,77} has been described above and hence will not be repeated here.

The gamma activation method⁸² involves (a) bombardment of a lithium sample with 10.5-Mev gamma particles to induce the $^{14}\text{N}(\gamma, n)^{13}\text{N}$ reaction and (b) determination of the nitrogen content by measurement of the resultant positron activity due to ^{13}N . In the initial application of this technique to lithium, ^{62}Cu and ^{53}Fe activities arising from activation of copper and iron impurities in lithium in trace quantities were found to interfere. While techniques for circumventing this complication are available, their application usually results in a significant loss of sensitivity. The fact that chemical methods (a) provide a sensitivity that is adequate for current needs and (b) are simpler than the activation method probably accounts for the limited attention given to the activation method.

The diffusion membrane method proposed above for carbon may also be useful for the determination of nitrogen in lithium. Iron appears to be a suitable membrane material. While this method has not yet been developed even for use in sodium systems, a concept that is under evaluation involves converting the nitrogen that diffuses through the membrane to ammonia and then determining the NH_3 content of the sweep gas. If this approach proves successful for use in sodium systems, its potential for lithium should be evaluated.

E. Solubilities of Selected Metals and Alloys in Lithium

Of special interest to CTR as structural materials are the refractory metals and their alloys. This interest has arisen principally from the fact that some of these metals possess favorable neutronic properties and low solubility and high corrosion resistance in lithium. The transition metals and their alloys have also received attention as potential CTR structural materials. In general, the corrosion resistance of transition metals and alloys has not been found sufficient for use in fusion reactors with lithium blankets. In view of the fact that solubility and corrosion data for the transition-metal systems are available elsewhere,^{11,92} and are of limited interest as CTR materials, a review of these data will not be repeated here.

Fig. 14. Solubility of Titanium in Lithium
(Refs. 92, 94, 95, and 96)

The subject of solubility and corrosion of metals and alloys has been approached from two sides: (a) measurement of the amount of sample metal dissolved in lithium at saturation, and (b) the effect of lithium on the weight, size, and integrity of metal samples. In this section, a detailed review of solubility information available for the refractory metals will be presented. Corrosion will be covered in the next section.

Titanium. Leavenworth *et al.*^{94,95} measured the solubility of titanium in lithium in the range from 680 to 910°C as a function of nitrogen concentration. The data, shown in Fig. 14, were markedly influenced by the nitrogen content of the lithium. The single value reported by Bychkov *et al.*⁹⁶ is in agreement with the data of Leavenworth *et al.* at the 210-ppm nitrogen concentration in lithium. Details of the experimental procedure used by Bychkov *et al.* are too meager, however, to assess the reliability of this value.

Fig. 15. Solubility of Zirconium in Lithium
(Refs. 92, 96, and 97)

Of the data available, those of Leavenworth *et al.*^{94,95} at the 55-ppm nitrogen level in lithium appear to best represent the solubility of titanium in lithium. Since contamination was inadvertently introduced into their system during sampling, the possibility that impurities other than nitrogen may have influenced the results cannot be precluded. Clearly, it would be of interest to establish whether even lower solubilities would be found if measurements were made in a more highly purified system.

Zirconium. The solubility of zirconium in lithium has been determined by Bychkov *et al.*⁹⁶ and Koenig.⁹⁷ Their results are shown in Fig. 15. Solubilities much larger than those of Bychkov *et al.* (by as much as two orders of magnitude) were observed by Koenig. Koenig's values, however, were obtained from corrosion tests, and experimental details on his procedure and on the purity of the materials that he used are lacking; hence, critical evaluation of these data is difficult. While experimental details of the work of Bychkov *et al.*⁹⁶ are also sparse, the solubilities were obtained by

Fig. 16. Solubility of Niobium in Lithium
(Refs. 92, 95, 96, and 98)

a conventional equilibration method. The data of Bychkov *et al.*⁹⁶ are therefore believed to be the more reliable of the two sets.

Niobium. The solubility of niobium in lithium was measured by Leavenworth *et al.*,⁹⁵ Cleary *et al.*,⁹⁸ and Bychkov *et al.*⁹⁶ Their data are presented in Fig. 16. The early results of Leavenworth *et al.*⁹⁵ clearly show an increase in niobium solubility with an increase in the nitrogen content of the lithium. Since preliminary analyses showed that the nitrogen content of the lithium used in their experiments was less than 10 ppm and since no nitrogen was intentionally added during the tests, it must be concluded that the increase in the nitrogen content to the values shown in Fig. 16 arose from air contamination. Anthrop⁹² correctly notes that the

Fig. 17. Solubility of Molybdenum in Lithium
(Refs. 64, 92, 95, 96, and 98)

possibility of other impurities (e.g., oxygen, and/or carbon) influencing the solubility cannot be precluded since analyses for these other impurities were not made.

In subsequent work, Cleary *et al.*⁹⁸ avoided the problem of contamination by determining the solubility of niobium in lithium in sealed capsules. Measurements were made with (a) "pure" lithium (~38 ppm N), (b) lithium to which 500-10,000 ppm oxygen (as Li_2O) had been added, and (c) lithium to which 500-5,000 ppm nitrogen (as Li_3N) had been added. The data obtained under all three conditions are shown in Fig. 16. Within the scatter, no distinction between the three cases can be made. In this connection, it is important to note that post-test analyses of lithium in capsules to which Li_3N had been added indicated no significant increase in nitrogen level irrespective of the amount of nitrogen added before the start of the experiment. The nitrogen most likely diffused into the Nb cups used in these ex-

periments. Oxygen analyses were not performed because a reliable method for the determination of oxygen in lithium was not available; hence, no information is available on post-test oxygen concentrations.

Bychkov *et al.*⁹⁶ report only a single value of the solubility of Nb in lithium. Moreover, the experimental detail they provide is so meager that it is difficult to assess the reliability of their result.

Of the available data, those of Cleary *et al.*⁹⁸ appear to be the most reliable. The large scatter in their results may be due to sampling difficulties as discussed in the section below. Within this scatter, a temperature dependence of the solubility is barely discernible. For example, at 760 and 1425°C, the average solubility is found to be 19 and 65 ppm, respectively. With the availability of purer materials, and with the improvements that have been made since the work of Cleary *et al.*,⁹⁸ it may be possible in future studies to obtain data of better precision and thereby more firmly establish the solubility of niobium in lithium, the effect of impurities on the solubility, and the temperature coefficient of solubility.

Molybdenum. Four determinations of the solubility of molybdenum in lithium^{64,95,96,98} have been made. The data are shown in Fig. 17. Leavenworth *et al.*⁹⁵ observed the solubility to vary from 6 to 15 ppm between 660 and 900°C with 100 ppm nitrogen in the lithium. In later work, Cleary and co-workers,⁹⁸ using a refined analytical technique, found the solubility of molybdenum to be <1 ppm (the limit of the analytical method). Moreover, additions of lithium nitride and/or oxide to their system did not increase the solubility above this level. While this latter observation tends to suggest that the apparent solubility of molybdenum is not affected by the nitrogen and oxygen content of the lithium, it should be noted that (a) post-measurement analyses for nitrogen indicated no change in the nitrogen level above that originally present at the start of the experiment and (b) analyses for oxygen were not done. Hence, this conclusion is tenuous. Anthrop⁹² points out that the niobium capsules used by Cleary *et al.*⁹⁸ to hold the molybdenum cups may have gettered some of the nitrogen. This would account for their inability to find the added nitrogen upon completion of the measurements.

Recent measurements by Eichelberger *et al.*⁶⁴ support the contention of Cleary *et al.*⁹⁸ that the solubility of molybdenum is much lower than the values reported by Leavenworth *et al.*⁹⁵ Using highly purified molybdenum and high-purity lithium (44 ppm C, 33 ppm O, 13 ppm N), Eichelberger *et al.*⁶⁴ found the solubility to be 9 ± 5 ppm between 1200 and 1600°C. Within the scatter of the data, no temperature dependence of the solubility could be discerned.

The data of Bychkov *et al.*,⁹⁶ also shown in Fig. 17, are in obvious disagreement with the results of the three investigations just discussed. Moreover, Anthrop⁹² points out that the heat of solution of niobium in lithium calculated from the temperature dependence of their data ($\Delta H = 106$ kcal/mol) is unrealistic. On this basis at least one or perhaps both of the experimental points are suspect.

Of the available studies, that of Eichelberger *et al.*⁶⁴ appears to be the one performed most carefully. It should be pointed out, however, that their method of equilibration and sampling (as in all other studies on this system) did not preclude the possibility that particulates or suspended

colloids may have led to "high" values of the "apparent solubility." The wide scatter and the absence of a temperature coefficient of solubility observed in this work is not in conflict with such a possibility. Hence, the true solubility of molybdenum in lithium may be lower than that observed by Eichelberger *et al.*⁶⁴

The comment that suspended particulates or colloids may have vitiated the molybdenum results is not peculiar to the molybdenum system, but is generally applicable to all systems in which the solubilities of sparingly soluble solutes in lithium have been determined by removing a sample of saturated liquid for analysis. (In fact, the inclusion of Nb-containing particulates in samples taken for analysis may also be the reason for the observed wide scatter in the niobium solubility data of Cleary *et al.*⁹⁸ reviewed in the preceding section.) To eliminate this potential problem, future studies on the solubilities of the refractory metals and alloys in lithium should be conducted by a method that does not involve direct sampling of the system. A method that avoids possible errors due to sampling difficulties and particulates in suspension and that should be useful for solutes with low solubilities has been reported by Evans and Watson.⁹⁹ This method, which involves monitoring of the solution and deposition of a known amount of a γ -emitting isotope (with reasonable half-life) of the solute of interest, should be applicable to many of the refractory systems of interest to CTR technology.

Miscellaneous Studies. Solubilities have been measured for molybdenum, niobium, tantalum, titanium, vanadium, and zirconium by Jesseman *et al.*¹⁰⁰ and for hafnium, tungsten, and rhenium by Eichelberger *et al.*⁶⁴ The information on each solute is limited but the available data are summarized in Table 9.

Table 9. Solubilities of Selected Refractory Metals in Lithium

Solute	Solubility, ppm	Temperature, °C
Ti	345 ^a	730
Ti	3700 ^a	1020
Zr	65 ^a	700
Zr	965 ^a	252
Nb	<30 ^a	500
Nb	80 ^a	735
Nb	900 ^a	1015
Mo	<15 ^a	550
Mo	<25 ^a	860
V	150 ^a	725
V	65 ^a	1010
W	1050 ^a	715
W	~ 3 ^b	1200-1600
Ta	725 ^a	19
Ta	1000 ^a	1850
Re	0.6-2 ^b	1200-1600
Hf	~ 6 ^b	1000-1400

^aRef. 100 (oxygen impurity level of Li: 2400 ppm).

^bRef. 64 (impurity levels of Li: 44 ppm C, 13 ppm N, 33 ppm O).

The data of Jesseman *et al.*¹⁰⁰ are questionable for several reasons. First, iron crucibles were used in all their experiments. Iron exhibits a significant solubility in lithium containing large amounts of oxygen. The oxygen level in the experiments of Jesseman and his colleagues was ~2400 ppm; hence their solubility measurements were not made in a binary system but in a multicomponent system. Secondly, the experiments were done in a cursory way and no attempt was made to maintain or control the purity of the materials. Thirdly, their data for the solubilities of Ti, Nb, and Mo in lithium are in serious disagreement with the results of other workers.^{64,94,95,98} Moreover, in the case of vanadium (see Table 9), a negative temperature coefficient of solubility was found. While a negative temperature coefficient cannot be precluded *a priori*, no other cases of negative temperature coefficients of solubility in lithium have been reported. The results of Jesseman *et al.*¹⁰⁰ are presented in Table 9 for the sake of completeness and to highlight the fact that the available information is meager.

In marked contrast to the work of Jesseman *et al.*,¹⁰⁰ Eichelberger and his colleagues⁶⁴ maintained stringent purity control and exercised extreme care and diligence in performing the measurements so that their results are highly regarded.

Solubility of Selected Alloys in Lithium. Eichelberger *et al.*⁶⁴ conducted a series of solubility studies with pure metals and alloys to test the hypothesis that the oxygen content of solute metals may play a major role in determining observed solubilities. The observation that (a) the solubility of Nb from a Nb-1Zr alloy was lower than that from a zone-refined single crystal of the unalloyed metal and (b) the corrosion of this alloy was lower than that of the pure metal in lithium suggested this possible link.

The solubility measurements were carried out with high-purity lithium in the range 1200-1600°C. The solubilities of Ta from T-111 alloy (Ta-8W-2Hf), of Ta and Hf from ASTAR-811C alloy (Ta-8W-1Hf-1Re-0.025C), and of Hf from unalloyed zone-refined metal were measured. The results are shown in Table 10.

The solubility of Ta from both alloys was observed to fall in the 0-3 ppm range. Also, within experimental uncertainty, no temperature dependence was observed. Measurements with pure Ta were not done. No data are avail-

Table 10. Solubility of Refractory Alloys in Lithium^a
(Ref. 64)

Solute	Solubility, ppm	Temp., °C
Ta from T-111 ^b	0-3	1200-1600
Ta from ASTAR-811C ^c	0-3	1200-1600
Hf from ASTAR-811C ^c	6-10	1200-1600
Hf (zone refined)	~6	1600-1400

^aMajor impurities: 44 ppm C, 13 ppm N, 33 ppm O)

^bT-111: Ta-8W-2Hf

^cASTAR-811C: Ta-8W-1Hf-1Re-0.025C

able for comparison except those of Jesseman *et al.*,¹⁰⁰ these investigators report a Ta solubility of 1850 ppm in lithium containing 2400 ppm oxygen. Eichelberger *et al.*⁶⁴ concluded that the addition of a gettering agent (hafnium) to tantalum dramatically reduces the solubility of the metal in lithium. As noted above, the work of Jesseman *et al.*¹⁰⁰ is subject to question for a number of reasons. A reliable value of the solubility of pure Ta in pure Li does not exist. The conclusion of Eichelberger *et al.*⁶⁴ therefore appears somewhat tenuous.

An interesting observation was made by Eichelberger *et al.*⁶⁴ with regard to the apparent solubility of hafnium. The apparent solubility of hafnium measured in experiments with the ASTAR-811C alloy and with the pure metal was found not to be significantly different. To account for this finding the investigators speculated that (a) some of the hafnium in the alloy is present as the oxide since its function is to getter oxygen and (b) lithium interacts with a portion of this oxide forming a complex oxide [e.g., $(\text{LiO})_x \cdot n\text{MO}_y$], thereby permitting solution of the hafnium. That is, the solution of hafnium proceeds via the formation of a complex lithium-hafnium oxide. They suggest further that the oxygen content of the lithium may be the most important factor. The observed equivalence of hafnium solubility for the alloy and the "pure" metal is understandable then in terms of the equivalence of the oxygen content of the lithium in the two experiments.

It is concluded that the effect of the oxygen concentration of solute metal on the apparent solubility of refractory metals in lithium has not been convincingly demonstrated in this work. Moreover, the argument that complex lithium-hafnium oxides may form in solution in lithium is not supported by thermodynamic considerations. Finally, it has been suggested that the movement of oxygen from some selected refractory metals to lithium is accompanied by penetration of lithium and the formation of corrosion-product complex oxides in the metal.^{102,109} If this occurred in the Li-Hf experiments, the method used by Eichelberger *et al.*⁶⁴ could not distinguish between soluble complex oxides and undissolved corrosion-product complex oxides which may have formed and entered the liquid inadvertently. Hence, even the speculation offered by these workers is subject to some question.

As seen from the tables and figures above, the solubility data for refractory metals in lithium are characterized by sparseness, by large scatter, and by frequent lack of agreement among laboratories. Despite this unfavorable situation, it is still possible to make some generalizations about the factors that influence the measurement of solubilities of refractory metals in lithium: (1) The impurity level of the lithium (especially, but perhaps not exclusively, its nitrogen content) appears to be important and should be controlled for meaningful measurements; (2) the impurity level of the solute metal (especially its oxygen content) may be a significant factor in determining the apparent solubility; and (3) sampling and analytical methods used in the past have not always been adequate to the task. Variabilities in the impurity levels of solvent, solute, and sampling methods and difficulties with analyses for metals in the ppm and sub-ppm range in lithium probably account for the discordance which characterizes much of the early data. In recent years, however, methods for the purification of lithium have improved, refractory metals of higher purity have become available, and advances in sampling and analytical techniques for the measurement of structural metals in liquid metals have been made.⁹⁹ Hopefully, the problems that have hampered measurements will be eliminated in future studies.

F. Corrosion of Selected Materials in Lithium

The investigations of the corrosion of metals by liquid lithium generally have been performed under more poorly defined conditions than the investigations of solubilities. This disappointing condition requires that the great majority of the corrosion results be used only as crude guidelines to the behavior of metals and alloys in liquid lithium. Disagreement among investigators concerning the exact rates of corrosion is the rule rather than the exception.

Cowles and Pasternak¹¹ have reviewed the literature up to 1968 on the corrosion of various materials by lithium. It can be seen from their review that the corrosion rates of non-refractory metals and alloys are generally too high at temperatures approaching 1000°C to be of significant interest for controlled thermonuclear fusion reactors. The corrosion experienced by many metals and alloys in liquid lithium is more severe than would be indicated by the preceding section. The effect of impurities such as oxygen, both in the metal and in the lithium, can have a profound effect on the corrosion and penetration rates.

Because of the significant effect of the concentration of certain impurities on the corrosion and penetration rates of various metals, and because the impurity levels were not known or controlled in many of the corrosion studies, a major portion of the earlier work is of questionable value. Selected corrosion studies on refractory metals and their alloys and on some ceramic materials are discussed below.

The metals that are most resistant to attack by lithium at temperatures in the vicinity of 1000°C are those of groups IVB, VB, VIB, and VIIB of the periodic chart. Those that have received the most attention are Ti, Zr, Hf, V, Nb, Ta, Mo, W, and Re, and their alloys. Because of the similarities in the values of the free energy of formation of the oxides, nitrides, and carbides within groups, the corrosion results will be discussed according to groupings in the periodic table.

The metals of Group IVB, Ti, Zr, and Hf, form oxides, nitrides, and carbides that are more stable than the corresponding lithium compounds, and are more stable than the corresponding compounds of the members of Groups VB, VIB, and VIIB. This characteristic has caused Ti, Zr, and Hf to be of great interest as "getter" materials for the removal of O, N, and C from liquid lithium, and as "getter" alloying agents in refractory metal alloys. This application will be discussed later in connection with the corrosion resistance of the main members of the alloys.

The corrosion resistance of Ti, Zr, and Hf to lithium at 800-1000°C in capsule tests and convection-loop tests is very good, as indicated in Table 11. The presence of up to 4000 ppm O in zirconium did not affect its corrosion rate in lithium at 816°C.¹⁰¹ Because Ti, Zr, and Hf are difficult to fabricate, whereas metals such as Nb and Ta are easier to fabricate, the major emphasis of corrosion work has been on the latter metals and their alloys.

The Group VB metals, V, Nb, and Ta, form oxides that are less stable than Li₂O, but their nitrides and carbides are more stable than the corresponding lithium compounds. Because of this, lithium can readily attack and penetrate V, Nb, or Ta when the oxygen content of the refractory metal is above a threshold level. The threshold level is 400 ppm O by weight for Nb at 600°C,

Table 11. Corrosion Resistance of Some Refractory Metals and Alloys to Lithium

Sample	Conditions	Results ^a	Reference
Ti	710-820°C, 1080 hr, convection	nil to light attack	103
Ti	1000°C, 400 hr, capsule	slight attack	104
Zr	816-871°C, 1070 hr, convection	nil attack	103
Zr	1000°C, 400 hr, capsule	nil attack	104
V	817°C, 1194 hr, convection	nil attack	103
Nb	816-1093°C, 8233 hr, convection	nil attack	106
Nb-1Zr	1370°C, 1000 hr, capsule	little attack ^b	105
Nb-1Zr	1150, 6000 hr, capsule	slight attack	107
Nb-1Zr	760-1315°C, 720,000 hr, convection	nil to slight attack	106
Nb-10W-1Zr-0.1C	1205°C, 9437 hr, capsule	no corrosion	107
Ta	816-982°C, 2261 hr, convection	nil attack	106
Cr	816°C, 100 hr, capsule	1 mil dissolution	59b
Mo	1370°C, 1000 hr, capsule	little attack ^b	105
Mo-0.5Ti	816°C, 694 hr, convection	nil attack	106
Mo-0.5Ti-0.1Zr-0.01C (TMZM)	1650°C, 1000 hr, capsule	no attack	105
Mo-50Re			
W	1370°C, 1000 hr, capsule	no attack	105
Re			
W-0.9Nb			
W-15Mo			
W-10Re			
W-25Re			

^aAs reported by the investigators.^bSome evidence of carbide and carbonitride formation.

and 150 ppm O by weight for Ta at 600°C.¹⁰² Apparently, the oxygen migrates to grain boundaries, where it reacts with lithium, forming ternary Li-O-M compounds* that can wedge the grains apart, allowing further lithium penetration and reaction. The penetration of O-containing Nb and Ta is fastest at

*The identity of the corrosion product has not been determined; however, in the case of Nb, it is known not to be Li₂O or LiNbO₃.

600°C, and the rate increases with increasing oxygen content of the refractory metal. After the lithium has removed enough oxygen from the refractory metal to reduce the concentration below the threshold value, lithium penetration stops. If the original oxygen concentration is high enough, the sample metal may be completely penetrated before the oxygen concentration falls below the threshold value. Oxygen in the lithium increases the dissolution rate of Nb and Ta, but has little or no effect on the lithium penetration rate.

The problem of lithium penetration due to oxygen contamination has been greatly ameliorated by the use of oxygen "getter" alloying agents such as Ti, Zr, and Hf, to form alloys such as Nb-1Zr, Nb-28Ta-10.5W-0.9Zr (FS-85), and Ta-8W-2Hf (T-111). The corrosion resistance of a number of these alloys is given in Table 11. In order to maximize the benefit obtained by the use of oxygen getters, it is necessary to employ a heat treatment that encourages the reaction between O and Zr or Hf before the refractory alloy is exposed to lithium. It has been found that an annealing treatment at 1200-1300°C for 1 hour is appropriate for Nb-1Zr, Nb-28Ta-10.5W-0.9Zr, and Ta-8W-2Hf.¹⁰⁸ This treatment results in the combination of sufficient oxygen with the getter to reduce the O concentration below the threshold level, resulting in an alloy with good corrosion resistance to lithium.

More recently, Sessions and DeVan¹⁰⁹ investigated the effect of heat treatment and test temperature on the compatibility of several advanced refractory alloys with lithium. Their results, some of which are summarized in Table 12, showed that (a) attack by lithium at 500°C was less severe than anticipated, based on current corrosion models, (b) at higher oxygen levels (>2000 ppm), corrosion at 500°C was both transcrystalline and intergranular, whereas attack at 1000°C was predominantly intergranular, (c) in general, heat treatment at 1300°C enhanced resistance of the materials tested to corrosion by lithium, and (d) hydrogen pickup during decontamination can be a significant problem with advanced niobium- and tantalum-based alloys when rapid, hydrogen-producing reactions occur.

The nitrogen content of niobium (up to at least 0.1%) does not have a great effect on the corrosion rate by lithium¹⁰¹; however, as indicated above, the nitrogen content of the lithium does have an influence on the solubility of refractory metals in lithium. Similarly, the carbon content of niobium (up to at least 0.1%) does not influence the corrosion rate by lithium at 816°C, as might be expected from the fact that niobium carbide is more stable than lithium carbide.

The same lithium penetration problems encountered with Nb are found for Ta, and the same solution has been employed with success. Alloys such as Ta-8W-2Hf show excellent corrosion resistance, even when the alloy is contaminated with oxygen. Of course, appropriate heat treatments are necessary to react the oxygen with the getter. As shown in Table 11, tantalum-rich alloys show good corrosion resistance at temperatures near 1000°C for at least 2000 hours.

The corrosion resistance of the Group VIB metals, Cr, Mo, and W, in lithium has not been as thoroughly investigated as that of Nb, Ta, and their alloys, but the same general problems and solutions obtain. As shown in Table 11, titanium and zirconium are often used as oxygen getters. Alloys rich in Mo and W show good corrosion resistance to lithium, even under flow conditions, at temperatures well above 1000°C, for at least 1000 hours.

Table 12. Summary of Effect of Oxygen Added at 1000°C on Corrosion of Refractory Alloys in Lithium at 1000°C (Ref. 109)

Alloy	<u>Oxygen Concentration, ppm</u>		Lithium Concentration After Test, ppm	Depth of Corrosion Attack ^a , mils
	Before Test	After Test		
D-43	990	380	b	4
(Nb-10W-1Zr-0.1C)	2000	780	b	12
B-66	1800	250	39	10
(Nb-5Mo-5V-1Zr)	2700	340	11	15-20
FS-85	1200	290	48	5-10
(Nb-28Ta-10W-1Zr)	1900	620	180	15
Cb-752	1400	300	36	3-5
(Nb-10W-2.5Zr)	2500	730	<10	3-5
Cb-753	2000	450	b	5-10
(Nb-5V-1.25Zr)				
T-111	1500	160	68	30
(Ta-8W-2Hf)	2500	300	27	30

^aPredominantly intergranular corrosion attack.

^bNot analyzed.

Of the Group VIIB metals, only rhenium has been considered in connection with resistance to lithium attack. Rhenium is very expensive and probably is not practical as a material of construction, except under unusual circumstances. It does show good corrosion resistance at 1370°C for at least 1000 hours. In addition, rhenium has been used as an alloying agent with molybdenum and with tungsten. These alloys also show excellent resistance to lithium attack (see Table 11).

In some CTR designs it has been proposed that the lithium coolant be electrically isolated from the metallic channel walls by an electronically insulating layer in order to minimize the pumping power requirements.⁴² The number of known materials which might serve in this capacity and might exhibit a significant lifetime in the high-temperature flowing lithium is very small. This is partly because the corrosion resistance of insulating ceramics in lithium has not been studied thoroughly, and partly because lithium is extremely aggressive toward ceramics (mostly oxides).

Results of screening studies of ceramic materials by Elliot et al.¹¹⁰ and Hays et al.⁸⁶ are shown in Table 13. These results are not very different from what might have been expected on the basis of the free energies of reaction with lithium. None of the simple metal oxides are very much more stable than lithia, and all of the commonly used binding agents are less stable than lithia. The result is that all of the single oxide samples containing unstable binding agents were attacked in the tests shown in Table 13. Ceramic samples prepared from a mixture of stable oxides (such as ThO₂-5%

Table 13. Static Corrosion Resistance of Some Ceramics to Lithium

Sample	Temp., °C	Time, hr	Results	Reference
BeO	1093	500	Significant attack, Li penetration	110
MgO	1093	100	Disintegrated	100
CaO	1093	500	Significant attack	100
Y ₂ O ₃	1093	1000	Slight attack	110
Sm ₂ O ₃	1093	1000	Significant attack	110
ThO ₂	1093	1000	Slight attack	110
ThO ₂ -5% Y ₂ O ₃	1093	1000	Very minor attack	110
ThO ₂ -10% Y ₂ O ₃	1093	1000	Very minor attack	110
AlN	1093	1000	Severe cracking	110
BN	1093	100	Disintegrated	110
TiC	1093	2000	Some cracking	110
ZrC	1093	2000	Some cracking	110
TaC	1093	100	Severe attack by high-velocity Li	86
CaZrO ₃	1093	500	Deep cracking and flaking	110
BaZrO ₃	1093	500	Deep cracking and flaking	110
MgAl ₂ O ₄	1093	100	Disintegrated	110

Y₂O₃ and ThO₂-10% Y₂O₃) showed good corrosion resistance at 1093°C for 1000 hours.

Since lithium carbide and lithium nitride are not very stable, it is appropriate to investigate the corrosion resistance of various carbides and nitrides. Very few results are available; however, AlN, BN, TiC, ZrC, and TaC have all been investigated at 1093°C. Of this group of materials, TiC and ZrC show the most promise (Table 13) for resistance to lithium attack.

Double metal oxides are generally more stable than the single oxides from which they are prepared. This provides the opportunity to prepare a double oxide from oxides that are not quite as stable as Li₂O, the product being more stable than Li₂O. Some double oxides were tested in lithium at 1093°C, as shown in Table 13. Cracking and flaking were suffered by CaZrO₃ after 500 hours of exposure, whereas MgAl₂O₄ disintegrated in 100 hours.

A number of insulating ceramics were tested by Cairns *et al.*¹¹¹ in lithium at 375°C. Although this temperature is lower than the temperatures of interest for CTR use, the relative corrosion rates of the ceramics may provide some useful guidelines. The results of Cairns *et al.*¹¹¹ are presented in Fig. 18. It is to be noted that the purity and manner of preparation of BeO had a strong influence on its resistance to lithium. Similar effects can be expected for other ceramics and have already been noted for BN. The most promising ceramics for resistance to lithium at 375°C are hot-pressed, high-purity BeO, Y₃Al₅O₁₂, ThO₂, MgO·Al₂O₃, AlN, and Y₂O₃.

As can be seen from the paucity of verified results on the corrosion of metals, alloys, and electronically insulating ceramics by lithium under well-known purity conditions, there remains a great deal of work to be done before the most suitable materials of construction for CTR application can be identi-

Fig. 18. Corrosion of Insulating Materials by Lithium at 375°C (Ref. 111)

fied. The starting point has been indicated by past work--refractory metal alloys, perhaps with getters such as Ti, Zr, or Hf, and stable oxide, nitride, or double-oxide ceramics. Carbides probably will not provide the desired electronically insulating properties.

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