



The Chemistry of Molten Li_2BeF_4

Edwin M. Larsen, Layton J. Wittenberg

June 1986

UWFDM-705

, Presented at the 7th Topical Meeting on the Technology of Fusion Energy, Reno, Nevada, 15–19 June 1986.

FUSION TECHNOLOGY INSTITUTE

UNIVERSITY OF WISCONSIN

MADISON WISCONSIN

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government, nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

The Chemistry of Molten Li_2BeF_4

Edwin M. Larsen, Layton J. Wittenberg

Fusion Technology Institute
University of Wisconsin
1500 Engineering Drive
Madison, WI 53706

<http://fti.neep.wisc.edu>

June 1986

UWFDM-705

, Presented at the 7th Topical Meeting on the Technology of Fusion Energy, Reno, Nevada, 15–19 June 1986.

THE CHEMISTRY OF MOLTEN Li_2BeF_4

Edwin M. Larsen

Layton J. Wittenberg

Fusion Technology Institute
1500 Johnson Drive
University of Wisconsin-Madison
Madison, Wisconsin 53706

June 1986

UWFDM-705

Presented at the 7th Topical Meeting on the Technology of Fusion Energy, Reno, NV, 15-19 June 1986.

THE CHEMISTRY OF MOLTEN Li_2BeF_4

EDWIN M. LARSEN and LAYTON J. WITTENBERG, University of Wisconsin
Fusion Technology Institute, Nuclear Engineering Department
1500 Johnson Drive, Madison, WI 53706-1687
(608) 262-2940 and (608) 263-1709

ABSTRACT

The $\text{LiF}\cdot\text{BeF}_2$ system is a potential tritium breeder for a fusion power reactor. The chemical consequences of the $\text{TF}(\text{HF})$ generation are examined, particularly reactions proposed for moderating the corrosive properties of $\text{TF}(\text{HF})$.

THE Li_2BeF_4 SOLVENT SYSTEM

The use of molten Li_2BeF_4 as a tritium breeding blanket was considered by Grimes and Cantor in 1972.¹ Renewed interest^{2,3} in $\text{LiF}\cdot\text{BeF}_2$ compositions as tritium breeding blankets for MINIMARS (a conceptual design study of a commercial tandem mirror fusion reactor), suggests that a review of the chemical and physical properties of this system is appropriate at this time. A large fraction of the data presented here is derived from the publications^{1,4,5} of the molten salt breeder (fission) reactor program which prospered at Oak Ridge National Laboratories during the late 1960's and early 1970's.

The predictions of chemical reactivity are based on the thermochemical data at 1000 K (Tables 1 and 2). To use these data we must have balanced chemical equations, states of reactants and products and defined standard states. In discussing the thermochemistry of this solvent system the conventions used by Baes⁴ are adopted. "The standard state for most solutes is the hypothetical one mol fraction ideal solution in $0.67 \text{ LiF} - 0.33 \text{ BeF}_2 \dots$ (and) for the major components ... the solvent composition is taken as the standard state, i.e., $a_{\text{LiF}}, a_{\text{BeF}_2}, a_{\text{Be}^{2+}}, a_{\text{Li}^+},$ and a_{F^-} all are unity in $0.67 \text{ LiF} - 0.33 \text{ BeF}_2$." The free energy change for the reaction, ΔG_r^0 , is equal to

Table 1. Free Energies of Formation - 1000 K

	$-\Delta G_f^0$ (kJ mol ⁻¹)	Ref.
$\text{BeF}_2(\ell)$	874.0	(8)
$\text{BeF}_2(\text{d})^*$	894.5	(1)
$\text{LiF}(\text{s})$	520.1	(7)
$\text{LiF}(\ell)$	517.35	(7)
$\text{LiF}(\text{d})^*$	523.8	(1)
$\text{Li}_2\text{BeF}_4(\ell)$	1950.1	(8)
$\text{HF}(\text{g})$	277	(7)
$\text{H}^+\text{F}^-(\text{d})^*$	203.1	(4)
$\text{LiH}(\ell)$	11.96	(7)
$\text{LiH}(\text{d})^{*+}$	12.97	

* (d) = dissolved in Li_2BeF_4
(s), (ℓ), (g) = solid, liquid,
gas respectively

+ (estimated)

$(\sum \Delta G_f^0 (\text{products}) - \sum \Delta G_f^0 (\text{reactants}))$, and the equilibrium constant for the reaction is related to ΔG_r^0 by the expression

$$\ln K = \frac{-\Delta G_r^0}{RT}$$

The phase diagram for the $\text{LiF}\cdot\text{BeF}_2$ system is shown in Figure 1.⁶ There is a low melting (636.6 ± 0.5 K) eutectic at the composition

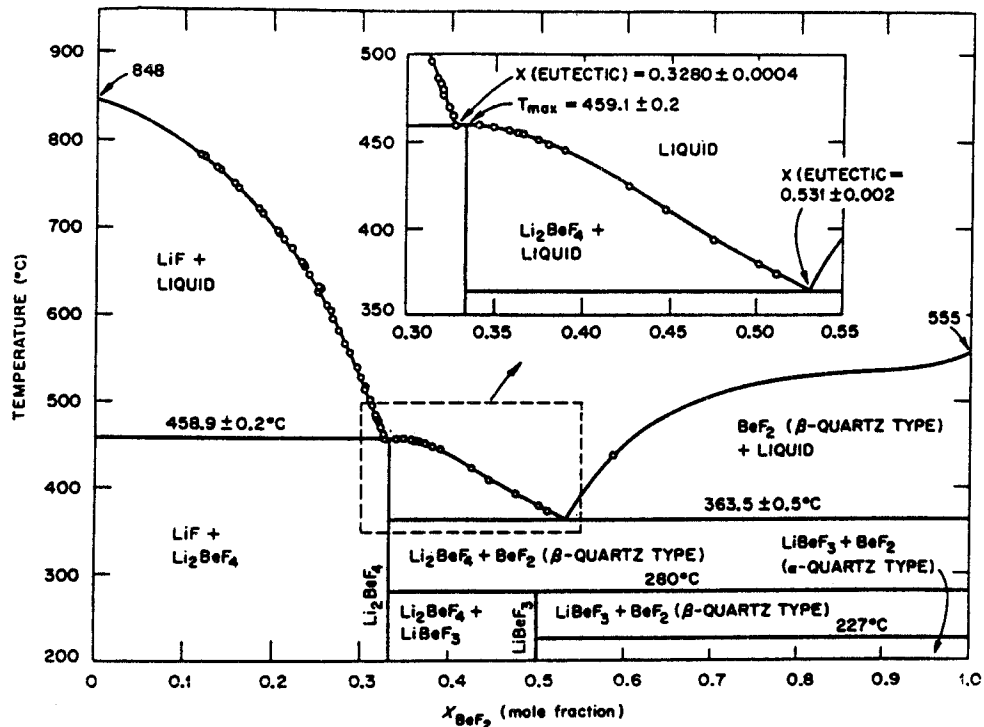
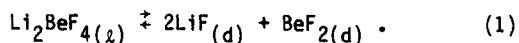


Fig. 1. Phase diagram of the LiF-BeF₂ system. Reproduced with permission from K.A. Romberger, J. Braunstein, R.E. Thomas, *J. Phys. Chem.*, **76**, 8, 1154 (1972) copyright (1972) by the American Chemical Society.

0.531 ± 0.002 mol fraction BeF₂, 0.469 mol fraction LiF, and an invariant point at 732 K in the region 2LiF·BeF₂; whether the latter corresponds to a eutectic, incongruent or congruent melting compound has been debated. A reexamination⁶ of this question established the presence of a eutectic at 732.1 ± 0.2 K and 0.3280 ± 0.0004 BeF₂ mol fraction, and a congruent melting compound at 732.2 ± 0.2 K and 0.333 mol fraction BeF₂. The shallow maximum in the phase diagram at this point is consistent with substantial decomposition of this compound to the component metal fluorides as described by Eq. (1) and a free energy change for the reaction of + 7.90 kJ mol⁻¹ at 1000 K (calculated from the data in Table 1 where the subscripts are defined):



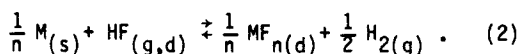
The value for the equilibrium constant, $K_1 = [\text{LiF}(d)]^2[\text{BeF}_2(d)]/[\text{Li}_2\text{BeF}_4(l)]$, is 0.385 and the composition of the system, expressed in mol fractions, is calculated to be LiF = 0.53, BeF₂ = 0.27 and Li₂BeF₄ = 0.20.

THE CHEMISTRY OF TRITIUM IN Li₂BeF₄

Tritium is "born" in Li₂BeF₄ principally by the nuclear reaction ${}^6_3\text{Li}({}^1_0\text{n})$ and is formally present as TF. At equilibrium (1000 K) the saturation pressure of TF above Li₂BeF₄ is about 3.5 Pa which corresponds to a TF concentration of 3.5 × 10⁻⁷ moles TF per liter of Li₂BeF₄. Owing to the chemical reactivity of TF it is necessary to consider the corrosion of structural metals potentially of use in the breeder blanket. To make such a prediction the thermodynamic data^{1,4,7,8,9} in Tables 1 and 2 are used; data for HF are used in the absence of data for TF. The important reaction is expressed in Eq. (2)

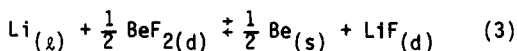
Table 2. Free Energies of Formation of Fluorides of Structural Metals (1000 K)

	$-\Delta G_f^0$ (kJ mol ⁻¹ /g-atom F ⁻)	Ref.
NiF ₂ (d)	231	(4)
CoF ₂ (s)	264	(7)
FeF ₂ (d)	278	(4)
NbF ₅ (g)	303	(4)
CrF ₂ (d)	315	(4)
TaF ₅ (g)	344	(4)
VF ₃ (s)	357.4	(9)
TiF ₄ (g)	357.7	(9)
TiF ₃ (s)	399.3	(9)



The metals whose fluorides have ΔG_f^0 values more negative (or slightly less) than that for HF(g) (-277) or HF(d) (-203) will react and thus corrode the container. All the metals in Table 2 will react. Tungsten and molybdenum are two other metals to consider, but no prediction can be made owing to the lack of data for the reduced states of the fluorides. Cantor and Grimes¹ suggested the use of coatings or HF-resistant alloys such as Hastelloy to minimize the corrosion problem. It must be kept in mind that the entire tritium recovery system has to be constructed with HF resistant materials if the major tritium species is TF.

Alternatives to the use of HF-resistant materials include internal redox systems¹ such as Ce³⁺/Ce⁴⁺ or sacrificial metals which preferentially react with HF in an oxidation-reduction reaction to produce hydrogen. The internal redox couples complicate the solvent system. The alkali metals, which can be used as sacrificial metals, are capable of reducing the beryllium in the solvent to elemental beryllium (Eq. (3)). This is a favorable reaction with



$$\Delta G_r^0 = -76.6 \text{ kJ/mol}$$

with a large positive equilibrium constant, K_3 ,

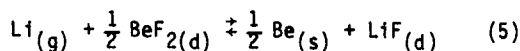
$$K_3 = [LiF(d)]/[BeF_2(d)]^{1/2} \cdot a_{Li(l)} \\ \cong 1.1 \times 10^4 .$$

The beryllium will continue to precipitate until lithium, the limiting reagent, reaches its dissolved equilibrium concentration at which point a liquid lithium phase should appear. However, under conditions where the BeF₂(d) and LiF(d) concentrations do not differ significantly from the pure solvent, the activity of liquid lithium, as calculated from K_3 , would be only $\sim 10^{-4}$. This is an unacceptable result since liquid lithium cannot form at an activity of less than unity.

At equilibrium, however, in the presence of beryllium metal, there must be some dissolved elemental lithium present. Is this concentration of lithium significant? Is it important in providing a reducing environment in the breeder? Although no liquid lithium phase will form, a partial pressure of lithium, which is some fraction of the saturation pressure, will be present in equilibrium with dissolved lithium. The system will now be described by Eq. (5) which is the sum of Eqs. (3) and (4):



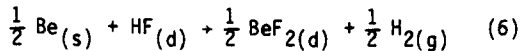
$$\Delta G_r^0 = -58.4 \text{ kJ mol}^{-1}$$



$$\Delta G_r^0 = -135 \text{ kJ mol}^{-1} .$$

Since $K_5 = \frac{1}{P_{Li(g)}}$ and $K_5 = 1.2 \times 10^7$, the vapor pressure of lithium above this system is 8.5×10^{-3} Pa (8.4×10^{-8} atm). The concentration of dissolved lithium can be calculated from Henry's law, $C(Li) = P(Li) \times K_H$, assuming ideality and a value for the constant K_H . This value is not known but upper and lower bounds can be established if we assume that the solubility of Li is no greater than that of HF and no less than that of neon. The K_H 's¹⁰ are 8×10^{-3} mol/l/atm and 7×10^{-5} mol/l/atm for HF and Ne, respectively. Considering the chemical properties of

the two solutes used here, it is logical to conclude that the equilibrium concentration of dissolved lithium in Li_2BeF_4 calculated from Henry's law will be $\sim 10^{-10}$ mol/l. It seems clear that the lithium generated in situ by the addition of beryllium will be of no significance as a HF scavenger, since beryllium metal will act as a scavenger for HF (Eq. (6))



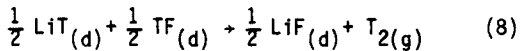
$$\Delta G_r^0 = -244 \text{ kJ/mol}^{-1} .$$

It has been suggested³ that elemental lithium, either generated in situ by the addition of Be (Eq. (3)) or added directly would reduce the bred tritium to lithium tritide as described by Eq. (7). Such a reaction solves the corrosion and permeation problems simultaneously



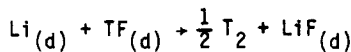
$$\Delta G_r^0 = -167 \text{ kJ mol}^{-1}$$

by immobilizing the tritium as LiT. With a favorable free energy change for reaction (Eq. (7)) this seems like a reasonable idea. However, consideration must be given to the fact that LiT is a reducing agent and will react with TF according to the reaction described by Eq. (8)



$$\Delta G_r^0 = -154 \text{ kJ mol}^{-1} .$$

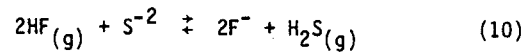
The sum of Eqs. (7) and (8) yields the overall reaction Eq. (9)



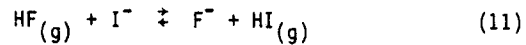
$$\Delta G_r^0 = -321 \text{ kJ mol}^{-1} \quad (9)$$

which is equivalent to the generic Eq. (2). With a large value of ΔG_r^0 we can conclude that lithium tritide will not form in this reaction system.

Other HF scavenging reagents⁵ include metal sulfides and iodides. The sulfides and iodides yield H_2S , and HI respectively, neither H_2S nor



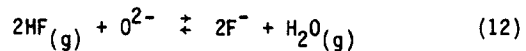
$$\frac{(P_{\text{H}_2\text{S}})}{(P_{\text{HF}})^2 (X_{\text{S}^{2-}})} > 10^4$$



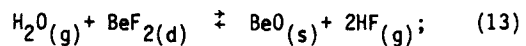
$$\frac{(P_{\text{HI}})}{(P_{\text{HF}})(X_{\text{I}^-})} = 590 .$$

HI are particularly attractive products on which to base a tritium recovery scheme.

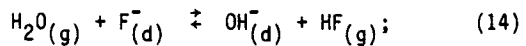
Oxides will react according to Eq. (12) with hydrogen fluoride to produce fluoride ion



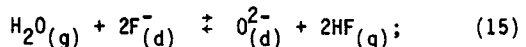
and water and can be considered as HF scavengers. The magnitude of the equilibrium constants are such that, at equilibrium, significant quantities of both reactants and products are present; thus, the presence of any water in the starting material will assure the presence of HF in the reaction system far in excess of that generated as TF in the breeder. The following reactions of $\text{Li}_2\text{BeF}_4(l)$ have been studied^{11,12} and the equilibrium quotients $P_{\text{H}_2\text{O}}/P_{\text{HF}}$ have been determined in Li_2BeF_4 at 700°C for BeO saturated melts,



$$\frac{(P_{\text{HF}})^2}{(P_{\text{H}_2\text{O}})} = 4 \text{ kPa}$$



$$\frac{P_{\text{HF}}}{(P_{\text{H}_2\text{O}})} [\text{OH}^-] = 2 \times 10^{-1} \text{ mol kg}^{-1}$$



$$\frac{(P_{\text{HF}})^2 [\text{O}^{2-}]}{(P_{\text{H}_2\text{O}})} = 4 \times 10^{-2} \text{ kPa mol kg}^{-1} .$$

Although Li_2BeF_4 does not react explosively with water to produce hydrogen as does molten elemental lithium, one can conclude that Li_2BeF_4 in contact with steam at 1000 K will react to produce HF. At $P_{\text{H}_2\text{O}} = 100$ kPa, the HF partial pressure would be 20 kPa and BeO(s) would be present.

CONCLUSIONS

1. The major tritium species in the Li_2BeF_4 blanket will be T_2 due to the corrosion of structural metals by TF (Eq. (2)). If equilibrium is achieved only the very small equilibrium concentration of TF would be present.
2. The data show that the use of elemental lithium to scavenge TF will result in the precipitation of beryllium metal (Eq. (3)). At equilibrium the dissolved elemental lithium concentration will be about 10^{-10} mol/l. No liquid lithium phase will exist, nor will lithium tritide be formed (Eq. (7, 8, and 9)).
3. Sulfides, iodides scavenge TF but in turn produce T_2S , TI (Eq. (10,11)).
4. Water will react with Li_2BeF_4 to produce a significant partial pressure of HF.

ACKNOWLEDGEMENT

The authors wish to thank Dr. Charles F. Baes, Jr., Chemistry Division, Oak Ridge National Laboratory, for his cooperation and constructive suggestions. This work was supported by the U.S. Department of Energy.

REFERENCES

1. W.R. GRIMES, S. CANTOR, "Molten Salts as Blanket Fluids in Controlled Fusion Reactors," Chemistry of Fusion Technology, p. 161, D. Gruen, Ed., Plenum Publishing Corp., New York (1972).
2. R.W. MOIR, J.D. LEE, R.C. MANINGER, W.S. NEEF, A.E. SHERWOOD, D.H. BERWALD, J.H. DEVAN, J. JUNG, "Helium-Cooled FLiBe-Breeder, Beryllium-Multiplier Blanket," UCRL-91828, Lawrence Livermore National Laboratory.
3. J.D. LEE, Tech. Ed. "MINIMARS Conceptual Design," UCID-20559, Vol. I., p. 18-52., Lawrence Livermore Laboratory (1985).
4. C.F. BAES, JR., "The Chemistry and Thermodynamics of Molten Salt Reactor Fluoride Solutions," Proc. Symp. Reprocessing Nuclear Fuels, Nuclear Metallurgy, Aug. 25 to 27 (1969), Iowa State Univ., Ames Iowa, Vol. 15, p. 617, CONF-69801, P. Chiotti, Ed.
5. C.F. BAES, JR., "The Chemistry and Thermodynamics of Molten Salt Reactor Fuels," J. Nucl. Materials, 51, 149 (1974).
6. K.A. ROMBERGER, J. BRAUNSTEIN, R.E. THOMA, "New Electrochemical Measurements of the Liquidus in the LiF-BeF₂ System," J. Phys. Chem., 76, 8, 1154 (1972).
7. JANAF Thermochemical Tables 2nd Ed. NSRDS-NBS 37, U.S. Dept. of Commerce National Bureau of Standards, 1971.
8. JANAF Thermochemical Tables, J. of Phys. and Chem. Reference Data, 3, 311-480 (1974).
9. L.B. PANKRATZ, Thermodynamic Properties of Halides, U.S. Dept. of Interior, Bureau of Mines, 1984.
10. P.E. FIELD, "Gas Solubility in Molten Salts," in Adv. in Molten Salt Chem., 3, 75, Plenum Press, New York, NY (1975).
11. P.E. THOMA, H. INSLEY, H.A. FRIEDMAN, G.M. HEBERT, "Equilibrium Phase Diagram of the Lithium Fluoride-Beryllium Fluoride-Zirconium Fluoride System," J. Nucl. Materials, 27, 166 (1968).
12. A.L. MATHEWS, C.F. BAES, JR., "Oxide Chemistry and Thermodynamics of Molten LiF-BeF₂ Solutions," Inorg. Chem., 7, (1968).
13. J.S. WATSON, W.R. GRIMES, D.E. BRASHEARS, "Cost of Reprocessing Fuel from a Molten Salt Fusion/Fission Hybrid Reactor Blanket," Fusion Technol., 8, 1, Part 2B, 2113 (1985).