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THE CHEMISTRY AND THERMODYNAMICS OF MOLTEN
SALT REACTOR FLUORIDE SOLUTIONS⁽¹⁾

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ABSTRACT

A solvent of lithium and beryllium fluorides (about 2 moles of LiF per mole of BeF₂) is used in the fuel salt, the coolant salt, and the flush salt of the Molten Salt Reactor Experiment. As a result of the chemical development work done for this reactor concept, considerable chemical and thermodynamic information has been acquired concerning this solvent and its solutions with actinide, lanthanide, and structural metal fluorides. It is the purpose of this paper to review this information, much of which is not yet generally available.

The data were obtained mainly by measurements of heterogeneous equilibria; i.e., by equilibration of melts with gaseous mixtures containing hydrogen, hydrogen fluoride, or water and by determinations of solid-liquid phase equilibria.

The results of these measurements gave direct information about such important chemical problems as: (1) The corrodibility of structural metals and the reducibility of the structural metal

(1) Research sponsored by the U.S. Atomic Energy Commission under contract with the Union Carbide Corporation.

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ions, Ni^{2+} , Fe^{2+} , Cr^{2+} ; (2) reactions with water vapor to form oxide and hydroxide ions, and the removal of these ions; (3) the precipitation and solubility of the oxides of beryllium, uranium, zirconium, thorium and the rare earths; (4) the stability of uranium(IV) toward reduction to the trivalent state and possible subsequent disproportionation; and (5) the solubilities and solid solution formation of rare earth fluorides. Equally important has been the wider usefulness of this information when the methods of thermodynamics are brought to bear. Thus the data obtained could be used to: (1) correlate, revise, and extend existing thermochemical data on fluorides and oxides; (2) determine activity coefficients of the components LiF , BeF_2 , UF_4 , and NiF_2 in these molten salt solutions; (3) calculate electrode potentials involving a variety of solute ions; and (4) estimate solubilities and reactivities of compounds not directly investigated.

Thus the chemical development program for the Molten Salt Reactor concept provides a number of interesting examples of the interrelationship between thermodynamics and problems in reactor chemistry and engineering.

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THE CHEMISTRY AND THERMODYNAMICS OF MOLTEN
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1. Introduction

The Molten Salt Reactor Experiment (MSRE), which went critical at ORNL in June, 1965, is fueled by a molten $\text{LiF-BeF}_2\text{-ZrF}_4\text{-UF}_4$ mixture and moderated by graphite. While it will not demonstrate breeding, this reactor experiment is intended to show that a molten-salt fueled reactor is a possible, indeed an attractive, means by which to achieve thermal breeding. A recent collection of papers has described this reactor and the extensive development work which led to its construction and operation [1].

In considering possible materials which could serve as constituents in such a thermal breeder reactor, Grimes [2] reached the conclusion that the choice of major salt components is largely limited to mixtures of Li^7F and BeF_2 by the need for neutron economy, low volatility, and chemical stability. While in the LiF-BeF_2 system (Fig. 1) mixtures with melting points below 500°C occur in the range 0.33 - 0.73 mole fraction BeF_2 [3], compositions near 0.33 BeF_2 appear the most suitable. (Here, and elsewhere, numbers preceding a salt component denote mole fraction).

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The composition of the MSRE fuel salt is 0.65 LiF, 0.291 BeF₂, 0.05 ZrF₄, 0.009 UF₄. That of the coolant and flush salt is LiF - 0.34 BeF₂.

As part of the development of the MSRE, a considerable amount of chemical and thermodynamic information has been gathered about LiF-BeF₂ melts near this composition. Most such information has been gained by the use of heterogeneous equilibria involving reactions of gases or solids, or both, with the liquid phase. In general, these studies gave fairly direct information about important chemical questions related to the MSRE.

It is the present purpose to review this information, much of which is not yet generally available, and to indicate its application to the chemistry of the MSRE. It will then be summarized by thermodynamic methods as a means of extending its usefulness. This seems fitting and proper at this stage in the development of the molten salt reactor concept. Future such reactors evidently will employ salt mixtures similar to those of the MSRE considered here; hence, a knowledge of the thermodynamics of these solutions should prove generally useful.

2. Reactions in LiF - 0.33 BeF₂

Table I lists the reactions studied, the form of the equilibrium constants, and values of a and b in the following expression which gives the numerical value of the equilibrium constants in LiF - 0.33 BeF₂

$$\log K = a + b(10^3/T) \quad (1)$$

This expression, implying a constant heat ($\Delta H = -2.3Rb$) and entropy ($\Delta S = 2.3Ra$) of reaction, adequately approximates the measured values in the temperature range studied (usually 500 - 700°C). The concentration scale is the mole fraction; e.g.,

$$x_{MF_2} = n_{MF_2} / (n_{MF_2} + n_{LiF} + n_{BeF_2}) \quad (2)$$

Gas pressures are expressed in atmospheres, and at the low pressures and high temperatures involved, gases are assumed ideal.

The standard states for reactants and products generally can be seen from the form of K. Here and elsewhere for most solutes the standard state is the hypothetical one mole fraction

Table I
Reactions in LiF-0.33BeF₂
[log K = a + b (10³/T)]

Reduction Reactions Involving Hydrogen ^a		K ^b	a	b	Est. ± Error in log K	Source ^c
1	H ₂ (g) + NiF ₂ (d) ⇌ Ni(s) + 2HF(g)	(P _{HF}) ² /(P _{H₂})(x _{NiF₂})	8.37	-3.60	0.04	Ref. 4
2	H ₂ (g) + FeF ₂ (d) ⇌ Fe(s) + 2HF(g)	(P _{HF}) ² /(P _{H₂})(x _{FeF₂})	5.20	-5.31	0.02	Ref. 4
3	H ₂ (g) + CrF ₂ (d) ⇌ Cr(s) + 2HF(g)	(P _{HF}) ² /(P _{H₂})(x _{CrF₂})	5.12	-9.06	0.06	Ref. 4
4	$\frac{1}{2}$ H ₂ (g) + UF ₄ (d) ⇌ UF ₃ (d) + HF(g)	(P _{HF})(x _{UF₃})/(P _{H₂} ^{$\frac{1}{2}$})(x _{UF₄})	4.07	-9.33	0.02	Ref. 5
5	H ₂ (g) + BeF ₂ (d) ⇌ Be(s) + 2HF(g)	(P _{HF}) ² /(P _{H₂})	7.21	-21.56	0.1	Refs. 6,7
<u>Metathesis Reactions Involving Gases</u>						
6	H ₂ O(g) + BeF ₂ (d) ⇌ BeO(s) + 2HF(g)	(P _{HF}) ² /(P _{H₂O})	4.23	-5.67	0.02	Ref. 9
7	2H ₂ O(g) + ZrF ₄ (d) ⇌ ZrO ₂ (s) + 4HF(g)	(P _{HF}) ⁴ /(P _{H₂O}) ² (x _{ZrF₄})	11.21	-10.66	0.04	Ref. 10
8	H ₂ O(g) + 2F ⁻ (d) ⇌ O ²⁻ (d) + 2HF(g)	(P _{HF}) ² (x _{O²⁻})/(P _{H₂O})	4.20	-8.64	0.08	Ref. 9
9	H ₂ O(g) + F ⁻ (d) ⇌ OH ⁻ (d) + HF(g)	(P _{HF})(x _{OH⁻})/(P _{H₂O})	-1.03	-2.08	0.04	Ref. 9
10	H ₂ S(g) + 2F ⁻ (d) ⇌ S ²⁻ (d) + 2HF(g)	(P _{HF}) ² (x _{S²⁻})/(P _{H₂S})	log K(873°K) < -4		----	Ref. 12
11	HI(g) + F ⁻ (d) ⇌ I ⁻ (d) + HF(g)	(P _{HF})(x _{I⁻})/(P _{HI})	log K(763°K) ≤ -3		----	Ref. 13
<u>Metathesis Reactions Involving Solid Oxides</u>						
12	ZrO ₂ (s) + 2BeF ₂ (d) ⇌ ZrF ₄ (d) + 2BeO(s)	x _{ZrF₄}	-2.75	-0.69	0.05	6,7; Ref. 15
13	UO ₂ (s) + 2BeF ₂ (d) ⇌ UF ₄ (d) + 2BeO(s)	x _{UF₄}	-2.07	-1.74	0.07	12,14; Ref. 15
14	ZrO ₂ (s) + UF ₄ (d) ⇌ ZrF ₄ (d) + UO ₂ (s)	(x _{ZrF₄})/(x _{UF₄})	-0.67	1.05	0.05	Ref. 15
15	ThO ₂ (s) + UF ₄ (d) ⇌ ThF ₄ (d) + UO ₂ (s)	(x _{ThF₄})/(x _{UF₄})	log K(1023°K) ≈ 1.2		----	Ref. 18

Table I (continued)

Solubility Reactions	K^b	a	b	Est. $\pm$ Error in log K	Source ^c
16 $\text{BeO(s)} \rightleftharpoons \text{Be}^{2+}(\text{d}) + \text{O}^{2-}(\text{d})$	$x_{\text{O}^{2-}}$	-0.04	-2.96	0.08	6,8
17 $\text{ZrO}_2(\text{s}) \rightleftharpoons \text{Zr}^{4+}(\text{d}) + 2\text{O}^{2-}(\text{d})$	$(x_{\text{Zr}^{4+}})(x_{\text{O}^{2-}})^2$	-2.82	-6.62	0.09	7,8
18 $\text{UO}_2(\text{s}) \rightleftharpoons \text{U}^{4+}(\text{d}) + 2\text{O}^{2-}(\text{d})$	$(x_{\text{U}^{4+}})(x_{\text{O}^{2-}})^2$	-2.15	-7.66	0.1	14,17
19 $\text{ThO}_2(\text{s}) \rightleftharpoons \text{Th}^{4+}(\text{d}) + 2\text{O}^{2-}(\text{d})$	$(x_{\text{Th}^{4+}})(x_{\text{O}^{2-}})^2$	$\log K(1023^\circ\text{K}) \approx -8.6$		---	15,18
20 $\text{NiO(s)} \rightleftharpoons \text{Ni}^{2+}(\text{d}) + \text{O}^{2-}(\text{d})$	$(x_{\text{Ni}^{2+}})(x_{\text{O}^{2-}})$	-2.58	-4.39	---	Eqs. 25, 26, Ref. 32
21 $\text{FeO(s)} \rightleftharpoons \text{Fe}^{2+}(\text{d}) + \text{O}^{2-}(\text{d})$	$(x_{\text{Fe}^{2+}})(x_{\text{O}^{2-}})$	-0.52	-4.12	---	Eqs. 25, 26, Ref. 32
22 $\text{NiF}_2(\text{s}) \rightleftharpoons \text{NiF}_2(\text{d})$	x_{NiF_2}	0.30	-2.07	0.01	Ref. 4
23 $\text{FeF}_2(\text{s}) \rightleftharpoons \text{FeF}_2(\text{d})$	x_{FeF_2}	2.45	-3.05	0.01	Ref. 4
24 $\text{LaF}_3(\text{s}) \rightleftharpoons \text{LaF}_3(\text{d})$	x_{LaF_3}	1.58	-3.38	0.02	Ref. 20
25 $\text{CeF}_3(\text{s}) \rightleftharpoons \text{CeF}_3(\text{d})$	x_{CeF_3}	1.64	-3.38	0.02	Ref. 20
26 $\text{SmF}_3(\text{s}) \rightleftharpoons \text{SmF}_3(\text{d})$	x_{SmF_3}	1.97	-3.38	0.02	Ref. 20
27 $\text{PuF}_3(\text{s}) \rightleftharpoons \text{PuF}_3(\text{d})$	x_{PuF_3}	1.30	-3.15		Ref. 19

^a The notations (s), (d), and (g) indicate respectively the solid, dissolved, and gaseous states.

^b P_i is expressed in atmospheres; x_i is the mole fraction and, for $\text{LiF}-0.33\text{BeF}_2$, is equal to moles of i/kg of salt/30.03.

^c Numbers other than reference numbers and numbers of equations in text refer to reactions in this table.

solution. Exceptions are LiF , BeF_2 , Be^{2+} , Li^+ , and F^- , for which the solvent composition $\text{LiF} - 0.33 \text{ BeF}_2$ is taken as the standard State. The notation (s), (d), and (g) denote, respectively, solid, dissolved, and gaseous states. In the majority of reactions listed, F^- is the only anion involved, and for simplicity the dissolved components are written in the molecular form, though this is not intended to imply the actual species present in solution. When anions other than F^- appear in the reaction, ionic species are written. In some cases this is done to avoid the choice of a neutral component in the liquid phase and in others to indicate that complete dissociation of an anion (e.g., O^{2-}) and a cation (e.g., Zr^{4+}) is assumed.

Estimates of activity coefficients as a function of solvent composition and solute concentration are discussed in Section 3. On the basis of these estimates, the values of K indicated in Table I include, where necessary, a correction of the original measurements to a melt composition of $\text{LiF} - 0.33 \text{ BeF}_2$.

2.1 Hydrogen Reduction Reactions

The reduction of the bivalent fluorides of nickel, iron and chromium by hydrogen in $\text{BeF}_2 - 0.38 \text{ LiF}$ was investigated by Blood [4] in a series of careful transpiration experiments. The equilibrium quotients which were measured for the reaction

were found to be independent of x_{MF_2} at the low concentrations studied. These concentrations were limited by the solubilities of the fluorides. The reduction of UF_4 dissolved in $\text{LiF} - \text{BeF}_2 - \text{UF}_4$ melts by hydrogen as well as the reduction of UF_4 solid to UF_3 solid has recently been investigated by Long [5]. He summarized his results by the following expressions: For the reduction of UF_4 to UF_3 in solution

$$\log(x_{\text{UF}_3} P_{\text{HF}} / x_{\text{UF}_4} P_{\text{H}_2}^{\frac{1}{2}}) = 3.995 - 9.329(10^3/T) + 3.77x_{\text{UF}_4} + 2.09(x_{\text{BeF}_2} - .30) \quad (4)$$

For the reduction of UF_4 solid to UF_3 solid

$$\log(P_{\text{HF}} / P_{\text{H}_2}^{\frac{1}{2}}) = 3.57 - 6.87(10^3/T) \quad (5)$$

While the reduction of BeF_2 in $\text{LiF}-0.33\text{BeF}_2$ by hydrogen is inaccessible to direct measurement, recently Dirian [6] and Romberger [7] have made measurements on the following cell

The cell reaction was taken to be

With P_{HF} and P_{H_2} corrected to 1 atm, the potential was found to be

$$E = -2.436 + 0.715(T/10^3) \text{ v.} \quad (7)$$

From this the equilibrium constant expansion in Table I has been calculated. The two electrodes — $\text{Be}^{2+} \mid \text{Be}$ and $\text{F}^-, \text{H}_2, \text{Pd} \mid \text{HF}$ — were judged to be reversible from polarization measurements.

These results show that nickel is the most noble of the three structural metals studied, Ni^{2+} being readily reduced by hydrogen (Fig. 2). Chromium was the least noble, Cr^{2+} being reduced by hydrogen with difficulty. The sparging of molten fluorides with hydrogen to reduce structural metal impurities is routinely used as a purification step. The concentrations of Ni^{2+} , Fe^{2+} and Cr^{2+} and the ratio $\text{U}^{4+}/\text{U}^{3+}$ in $\text{LiF}-0.33\text{BeF}_2$ expected under two sets of conditions is indicated in Fig. 2. On the left of the figure, wherein the equilibrium constants are plotted, it appears that only Ni^{2+} is extensively reduced by a mixture of H_2 and HF , both at unit activity (1 atm). Nickel is a relatively inert container material for $\text{LiF}-\text{BeF}_2$ melts in the presence of excess hydrogen. On the right of Fig. 2 are much more reducing conditions which approximate those in the MSRE. The concentration of Cr^{2+} is set at 100 ppm in equilibrium with the pure metal. It is seen that Fe^{2+} and Ni^{2+} should be reduced essentially completely to the metals and some U^{4+} should be reduced to U^{3+} . The reaction of U^{4+} in the MSRE fuel with the container metal (INOR-8, a nickel-base alloy containing about 7% Cr, 5% Fe and 16% Mo)

is the only corrosion reaction expected, and the extent of this

reaction should be small [8]. In the absence of UF_4 (i.e., the flush salt) no reaction between the salt and the container metal is expected.

2.2 Metathesis Reactions Involving HF and H_2O

Extensive equilibrium measurements of reactions between water in hydrogen carrier gas with LiF-BeF_2 melts were made by Mathews and Baes [9]. Equilibrium quotients for the reaction

(wherein beryllium oxide was present as a saturating solid phase) were measured from 500 - 700°C over the composition range $x_{\text{BeF}_2} = 0.3 - 0.8$, limited at one extreme by the LiF liquidus (Fig. 1) and at the other by rapidly increasing viscosity. The results were summarized by the expression

$$\log (P_{\text{HF}}^2/P_{\text{H}_2\text{O}} x_{\text{BeF}_2}) = a + b x_{\text{LiF}}^2 + c x_{\text{LiF}}^4 \quad (10)$$

wherein a , b and c all were linear functions of $1/T^\circ\text{K}$

$$a = 3.900 - 4.418(10^3/T),$$

$$b = 7.819 - 5.440(10^3/T),$$

$$c = -12.66 + 5.262(10^3/T)$$

From this expression the activities of BeF_2 and, by a Gibbs-Duhem integration, the activities of LiF were estimated (Fig. 5). In the same investigation, measurements were made upon melts not saturated with BeO . In addition to the reaction

for the formation of oxide ion, it became evident, both from these measurements and from those upon BeO saturated melts, that hydroxide ion also was formed

While the equilibrium quotients for these two reactions were less accurately determined than was the previous one for BeO saturated melts (ca. $\pm 20\%$ and $\pm 10\%$ respectively compared to $\pm 5\%$) because of limitations inherent in the transpiration method used, they were sufficient to show that both oxide and hydroxide increase in

stability with increasing temperature. The stability of hydroxide with respect to oxide, however, decreases with increasing temperature and it is low enough that hydroxide can be readily decomposed in these fluoride melts by sparging with an inert gas (e.g., hydrogen).

Similar measurements have also been made by Baes and Hitch [10] in which the LiF-0.33BeF_2 contained added ZrF_4 . With $x_{\text{ZrF}_4} > \sim 3 \times 10^{-4}$, ZrO_2 is the stable saturating oxide solid, hence the following equilibrium may be written

From these measurements the activity coefficient of ZrF_4 could be estimated (Fig. 5) as well as the solubility of ZrO_2 (Sect. 2.5). It was also found that the equilibria (11 and 12) for the formation of oxide and hydroxide ions were shifted to the right with increasing x_{ZrF_4} ; i.e., in the direction of greater stability of these ions.

These results are generally consistent with previous observations that LiF-BeF_2 melts are readily freed of oxide contamination by treatment with gaseous mixtures of H_2 and HF , another routinely used purification step. The measured equilibrium quotients in LiF-0.33BeF_2 were used to calculate the efficiency of HF utilization in such a treatment as a function of temperature and HF partial pressure with the assumption that equilibrium is maintained between the gas stream, the molten salt, and any BeO solid present. This calculation (Fig. 3) shows that the efficiency in the removal of oxide to a final value of 16 ppm ($x_{\text{O}_2} = 3.3 \times 10^{-5}$) is quite high over a wide range of conditions. The removal of oxides from LiF-0.33BeF_2 melts by H_2 - HF sparging during the preparation of flush salts and coolant salts for the MSRE [11] was performed on 100 kg batches in cylindrical vessels with a single gas delivery line. It appeared that about 2/3 of the calculated efficiency was obtained even in this relatively simple equipment.

In the presence of ZrF_4 and ZrO_2 the increased stability of oxide and hydroxide render more difficult the removal of oxide from such melts than is the case with the solvent salt. Because of this, in the purification of $\text{LiF-BeF}_2\text{-ZrF}_4$ melts it was found expedient to decant the molten salt away from the precipitated ZrO_2 as a simple means of removing most of the oxide before HF-H_2 treatment.

2.3 Metathesis Reactions Involving $\text{HF-H}_2\text{S}$ and HF-HI

An attempt has been made to study the removal of sulfide from LiF-0.33BeF_2 melts by HF-H_2 sparging [12]

but, unfortunately, the effluent $\text{H}_2\text{S/H}_2$ mixture reacted with the relatively cooler surfaces of the nickel exit tubing used. The sulfide was evidently precipitated from the melt, presumably as BeS , though no direct evidence of this was obtained. In tests on the removal of iodide by HF-H_2 sparging [13]

there was also interference caused by reaction of the effluent gases with the metal surfaces in the gas exit lines. Because of these difficulties it is possible, at present, only to assign lower limits to the equilibrium constants of reactions (15) and (16).

These preliminary results do serve to confirm, however, observations that the HF-H_2 treatment used in purifying molten salts seems to remove any sulfide, as well as oxide, which may be present as an impurity. The use of HF sparging also may prove a valuable means of removing the iodine precursor of the important fission product, Xe^{135} , in an operating reactor.

2.4 Metathesis Reactions Involving Solid Oxides

By combination of reactions 9 and 14, it is possible to calculate that both BeO and ZrO_2 will co-exist at equilibrium with LiF-0.33BeF_2 containing oxide ion

when ZrF_4 is present at concentration of approximately 3×10^{-4} mole fraction. With larger amounts of added ZrF_4 , ZrO_2 becomes the less soluble (stable) oxide.

It was decided to include ZrF_4 in the MSRE fuel composition to prevent the precipitation of UO_2 which otherwise would result from inadvertent oxide contamination of the fuel. Measurements of the metathesis reaction

have shown that the mole ratio of ZrF_4 to UF_4 at equilibrium with both UO_2 and ZrO_2 , while varying somewhat with temperature and melt composition, remains well below that chosen for the fuel salt [14,15]. As a consequence, a considerable amount of Zr^{4+} — an amount easily detected by chemical analysis of the fuel salt — would be precipitated by oxide contamination before any UO_2 should precipitate.

In connection with these studies, it was ascertained that, contrary to published UO_2 - ZrO_2 phase diagrams [16], $(\text{U-Zr})\text{O}_2$ solid solutions are not formed in the temperature range 500 - 700°C. Because of the obvious importance of this to the MSRE, experiments have been carried out in which both UO_2 - ZrO_2 mixtures and $(\text{U-Zr})\text{O}_2$ solid solutions prepared by fusion were equilibrated with LiF-BeF_2 melts. At the present writing, no solid solution formation has been detected below 1100°C [17].

The metathesis equilibrium in Table I involving UO_2 and ThO_2 is an estimate from results of Shaffer et al, in LiF-0.4 NaF [18].

2.5 Oxide Solubilities

The oxide concentration in LiF-0.33BeF_2 saturated with BeO may be estimated by combining the equilibrium results for reactions (9) and (11). The solubility increased rapidly with temperature, but no strong dependence on x_{BeF_2} was found. In these measurements [9], the mole fraction of oxide at BeO saturation probably was less than 0.002. Hence, the activities of BeF_2 and LiF which were derived from them are probably not appreciably different from the corresponding activities in oxide-free mixtures.

From the similar measurements in ZrF_4 -containing melts [10] the solubility product of ZrO_2 could be estimated. With increasing x_{ZrF_4} , the concentration of oxide at ZrO_2 saturation at first falls as would be expected from the equilibrium

However, it then levels off and subsequently rises with further increases in x_{ZrF_4} (Fig. 4). This could be caused, at least in part, by the formation of a complex ion, ZrO^{2+}

or it could be caused entirely by the influence of the changing melt composition on the activity coefficients of the species Zr^{4+} and O^{2-} . The plot in Fig. 4 indicates approximately the "oxide tolerance" of MSRE fuel salt-flush salt mixtures; i.e., the amount of dissolved oxide these mixtures can contain without oxide precipitation. It is seen that the oxide tolerance increases rapidly with temperature, especially near the fuel composition ($x_{\text{ZrF}_4} \cong 0.05$), indicating that any excess oxide present might be removed by collecting ZrO_2 on a relatively cool surface in the MSRE system.

The solubility products of NiO and FeO , indicated in Table I, were estimated from the previously cited equilibrium results (Sect. 4.3).

2.6 Fluoride Solubilities

Table I also summarizes the solubility measurements by Blood [4] of FeF_2 and NiF_2 , those by Barton [19] of PuF_3 , and those by Ward, et al [20] of rare earth trifluorides. These last investigators found fluoride solid solution formation and pointed out that this could provide a useable method for removing rare-earth fission products from a reactor fuel stream by exchange reactions.

3. Effect of Melt Composition Upon Activity Coefficients

In several of the investigations cited above the effect of melt composition on equilibrium was studied and from these results

the corresponding variation of a number of activity coefficients can be determined. The curves shown in Fig. 5 represent these variations as a function of the solvent composition (left-hand figure) and as a function of the mole fraction of solute added to $\text{LiF}-0.33\text{BeF}_2$ (right-hand figure). The standard states remain the same; i.e., for the solvent components it is $\text{LiF}-0.33\text{BeF}_2$ and for the solutes it is the hypothetical mole fraction solution in $\text{LiF}-0.33\text{BeF}_2$.

The curves (Fig. 5, on the left) for LiF and for BeF_2 are derived from Eqn. 10, γ_{BeF_2} being obtained directly and γ_{LiF} being obtained by a Gibbs-Duhem integration. The curves for PuF_3 and CeF_3 are based on the solubility measurements of Barton [19] and of Ward, *et al* [20]. The curves for UF_4 are based on Long's results (Eqn. 4) with the assumption that γ_{UF_3} is similar to γ_{CeF_3} and γ_{PuF_3} . The curve for ZrF_4 is from the preliminary measurements of Baes and Hitch (Eqn. 14). The curve for NiF_2 is an estimate based on the observation that γ_{NiF_2} in $\text{NaF}-\text{ZrF}_4$, (as indicated by reaction 3 [4]) varies less with ZrF_4 in this solvent than does γ_{CeF_3} (as indicated by its solubility [20]).

These activity coefficient curves were used, where necessary, to correct equilibrium measurements to the reference composition $\text{LiF}-0.33 \text{ PuF}_2$. It is seen that the variation of activity coefficients with composition is not large and that, in general, the various curves are ordered according to the ratio of charge to ion radius (z/r) for the cation. As more data become available, it will be of considerable interest to test the correlation of γ_{MF_z} with z/r , since it could provide a simple basis for estimates of activity coefficients where data on the effect of melt composition are lacking.

4. Thermodynamic Correlations

4.1 Heats and Free Energies of Formation (ΔH^f and ΔG^f).

From the equilibrium measurements (Table I) and published values of ΔH^f and ΔG^f for $\text{HF}(\text{g})$ and $\text{H}_2\text{O}(\text{g})$ [21], formation heats and free energies may be calculated for $\text{BeO}(\text{s})$, $\text{BeF}_2(\text{s})$, $\text{NiF}_2(\text{s})$,

and $\text{FeF}_2(\text{s})$ in the temperature range of interest here (Table II). In addition, Long has calculated ΔH^f and ΔG^f for UF_3 from his measurements (Eqn. 5), adopting the corresponding values given by Rand and Kubaschewski [22] for $\text{UF}_4(\text{s})$. In general, the agreement of these calculations with previous estimates is satisfactory, except in the case of $\text{NiF}_2(\text{s})$. Grimes has previously indicated [23] that the present values for $\text{NiF}_2(\text{s})$, based on Blood's measurements, differ considerably from - and are probably more nearly correct than - previous estimates for $\text{NiF}_2(\text{s})$ based on measurements of Jellinek and Rudat [24]. Long's values for $\text{UF}_3(\text{s})$ agree with a previous estimate by Brewer [25] but differ considerably from estimates by Glassner [26] and Rand and Kubaschewski [22].

Included in Table II are other heats and free energies of formation from the literature [27,28]. These were used in the calculation of $\Delta \bar{H}^f$ and $\Delta \bar{G}^f$ values for dissolved components (Table III); i.e., the partial molal heats and free energies of formation for the components in the solution standard states defined previously.

The $\Delta \bar{H}^f$ and $\Delta \bar{G}^f$ values in Table III for $\text{LiF}(\text{d})$, $\text{BeF}_2(\text{d})$, $\text{NiF}_2(\text{d})$, $\text{FeF}_2(\text{d})$ and $\text{CrF}_2(\text{d})$ come most directly from the equilibrium measurements, with ΔH^f and ΔG^f for $\text{HF}(\text{g})$, $\text{H}_2\text{O}(\text{g})$, and $\text{LiF}(\text{s})$ only being required from the literature. In the case of the tetravalent fluorides, literature values of ΔH^f and ΔG^f for the corresponding oxides were utilized, but these in general are more accurately known than are those for the fluorides. The values of $\Delta \bar{H}^f$ and $\Delta \bar{G}^f$ for the rare earths are based on the solubility measurements [20] and on Brewer's estimates for the solids [28].

The partial molal free energies of formation (Table III) indicate the relative stabilities of the dissolved fluorides. In terms of ΔG^f per g atom of fluoride LiF is the most stable, followed by the rare earths. BeF_2 and ThF_4 next fall together, then UF_4 and ZrF_4 . Least stable are the structural metal fluorides.

Table II
Formation Heats and Free Energies of Fluorides and Oxides
(700-1000°K)

	Compound ^a	$-\Delta H^f$, kcal	$-\Delta G^f$ (1000°K), kcal	Est. $\pm$ Error, kcal	Source ^b
1	HF(g)	65.19	66.20	0.3	Ref. 21
2	H ₂ O(g)	59.07	46.04	0.1	Ref. 21
3	LiF(s)	146.50	123.39	0.7	Ref. 21
4	BeO(s)	145.47	118.84	0.6	5,6, (2)
5	BeF ₂ (l)	237.00	207.57	0.6	5,6,(1),Eq. 10
6	ZrO ₂ (s)	260.4	216.0	1	Ref. 21
7	UF ₄ (s)	448.5	381.1		Ref. 22
8	UO ₂ (s)	258.0	218.0	1	Ref. 22
9	UF ₃ (s)	351.9	299.8		(7),(1),Eq. 5
10	ThO ₂ (s)	293	250	4	Ref. 27
11	LaF ₃ (s)	421	360	7	Ref. 28
12	CeF ₃ (s)	416	355	7	Ref. 28
13	SmF ₃ (s)	405	344	7	Ref. 28
14	NiF ₂ (s)	156.33	118.69	0.4	1,22,(1)
15	FeF ₂ (s)	168.62	135.64	0.4	2,23,(2)

^a The notations (s), (l), and (g) indicate respectively the solid, liquid, and gaseous states.

^b Numbers not in parentheses refer to ΔG values for reactions in Table I. Numbers in parentheses refer to ΔG values in this table.

Table III
Formation Heats and Free Energies for Solutes in LiF-0.33BeF₂
(773-1000°K)

	Solute ^a	$-\Delta H^f$, kcal	$-\Delta G^f$ (1000°K), kcal	Est. $\pm$ Error, kcal	Source ^b
1	Li ⁺ + F ⁻	142.70	124.79		(3), Eq. 10
2	La ³⁺ + 3F ⁻	405.5	351.8		24, (11)
3	Ce ³⁺ + 3F ⁻	400.5	347.0		25, (12)
4	Sm ³⁺ + 3F ⁻	389.5	337.5		26, (13)
5	Be ²⁺ + 2F ⁻	242.75	211.80		5, (1)
6	Th ⁴⁺ + 4F ⁻	-	424.0		19, (10), [5], [13]
7	Zr ⁴⁺ + 4F ⁻	451.85	386.21		17, (6), [5], [13]
8	U ⁴⁺ + 4F ⁻	444.61	386.48		18, (8), [5], [13]
9	U ³⁺ + 3F ⁻	336.73	296.19		4, (1), [8]
10	Cr ²⁺ + 2F ⁻	171.82	150.41		3, (1)
11	Fe ²⁺ + 2F ⁻	154.69	132.92		2, (1)
12	Ni ²⁺ + 2F ⁻	146.87	110.61		1, (1)
13	Be ²⁺ + O ²⁻	131.91	105.10		16, (4)
14	Be ²⁺ + 2OH ⁻	170.54	159.35		8, 9, (2), [13]
15	Be ²⁺ + 2I ⁻	-	≤ 66 (763°K)		11, (1), [5], ΔG^f (HI)
16	Be ²⁺ + S ²⁻	-	< 79 (873°K)		10, (1), [5], ΔG^f (H ₂ S)

^a The standard state of the ions is the hypothetical mole fraction solution in LiF-0.33BeF₂, with the exception of Li⁺, Be²⁺, and F⁻, for which the standard state is LiF-0.33BeF₂.

^b Numbers not in parentheses, numbers in parentheses, and numbers in brackets refer respectively to items listed in Tables I, II, and in this table.

4.2 Electrode Potentials

The results in Table III are expressed perhaps in a more familiar way in Table IV as electrode potentials for various half cell reactions with

The standard states remain the same. The manner in which these are calculated is most easily shown by pointing out that any combination of half cell reactions which gives a complete reaction of the form

will yield the $\Delta \bar{G}^f$ value given in Table III. (n is the number of equivalents of charge and F is the Faraday).

The positions of the various cations in the electrochemical series in LiF-0.33BeF_2 is seen to be quite similar to that in aqueous solutions. This is illustrated on the left side in Fig. 6, wherein the E° values in LiF-0.33BeF_2 at 1000°K are plotted vs the E° values for the same half-cell reaction in aqueous solutions at 25°C [29]. It is notable from this comparison that the structural metals are relatively more noble in the molten fluoride than they are in water. Also U^{4+} is more stable with respect to U^{3+} in the molten fluoride. When the E° values in the fluoride solvent are compared to values in LiCl-KCl eutectic given by Liu [30] (on the right in Fig. 6) the same differences persist. To this extent it might be said that the molten chloride solvent is more like water than like LiF-0.33BeF_2 . These differences — the relative nobility of the structural metals Fe, Ni, and Cr and the relative stability of U^{4+} with respect to U^{3+} — tend to favor LiF-0.33BeF_2 as a reactor fuel solvent. The correlation in Fig. 6 could prove a useful means of estimating the E° values ($\Delta \bar{G}$ values) of reactions for which data are lacking.

A number of other observations, in part evident from the equilibrium measurements, are more clearly apparent from the E° values in Table IV. The stability of the trivalent rare earth cations is such that direct reduction to the metals as a means of

Table IV
Calculated Electrode Potentials in LiF-0.33BeF₂^a
(773-1000°K)

Half Cell Reactions ^b	E° (1000°K), v.	Temperature Coefficient mv/°C
Li ⁺ + e ⇌ Li(s)	-2.541	0.821
La ³⁺ + 3e ⇌ La(s)	-2.21	0.821
Ce ³⁺ + 3e ⇌ Ce(s)	-2.14	0.817
Sm ³⁺ + 3e ⇌ Sm(s)	-2.01	0.795
Be ²⁺ + 2e ⇌ Be(s)	-1.721	0.715
Th ⁴⁺ + 4e ⇌ Th(s)	-1.73	-
Zr ⁴⁺ + 4e ⇌ Zr(s)	-1.316	0.755
U ⁴⁺ + 4e ⇌ U(s)	-1.319	0.674
U ³⁺ + 3e ⇌ U(s)	-1.410	0.630
U ⁴⁺ + e ⇌ U ³⁺	-1.044	0.807
Cr ²⁺ + 2e ⇌ Cr(s)	-0.390	0.505
Fe ²⁺ + 2e ⇌ Fe(s)	-0.011	0.516
Ni ²⁺ + 2e ⇌ Ni(s)	-0.473	0.830
HF(g) + e ⇌ F ⁻ + $\frac{1}{2}$ H ₂ (g)	0	0
$\frac{1}{2}$ I ₂ (g) + e ⇌ I ⁻	<-0.45	-
$\frac{1}{2}$ S ₂ (g) + 2e ⇌ S ²⁻	<-0.10	-
$\frac{1}{2}$ O ₂ (g) + 2e ⇌ O ²⁻	0.558	0.134
$\frac{1}{2}$ O ₂ (g) + $\frac{1}{2}$ H ₂ (g) ⇌ OH ⁻	1.734	0.472
$\frac{1}{2}$ F ₂ (g) + e ⇌ F ⁻	2.871	0.044

^a Calculated from $\Delta\bar{G}$ values in Table III.

^b Standard states for ions are defined in footnote (a) of Table III.

removing rare-earth fission products would be accompanied by reduction of Be^{2+} as well as U^{4+} . Trivalent uranium should disproportionate.

However, the difference in E° values for the $\text{U}^{4+}/\text{U}^{3+}$ and the Cr^{2+}/Cr couples is so large that the amount of U^{3+} produced by reaction with the container metal should be small (Eqn. 8) and, in fact, the reduction of U^{4+} to U^0 by chromium

should not be significant [8]. The strongest reducing agent which can be used in $\text{LiF}-0.33\text{BeF}_2$ without reducing the solvent components is beryllium metal, which indeed has been used as a reducing agent during purification of such melts [11]. With ZrF_4 present, a weaker reducing agent (e.g., zirconium metal) must be used.

4.3 Estimated Solubilities of Other Oxides

From the equilibrium data, the free energy change associated with the following reaction is known

By combining this with $\Delta\bar{G}^f$ values for the fluorides in Table III, $\Delta\bar{G}^f$ values for the corresponding dissolved oxides are obtained. These values in turn may be compared to published values for ΔG^f of the solid oxides to yield an estimate of the corresponding solubility products

$$\log K_{\text{sp}} = -(\Delta\bar{G}^f - \Delta G^f)/2.3 \text{ RT} \quad (26)$$

Such calculations show that, aside from the oxides already considered (BeO , ZrO_2 , UO_2 , ThO_2) the oxides of Ni^{2+} and Fe^{2+} are the only others of the cations listed in Table III which are predicted to have low solubility (Table I). The less soluble of these two is NiO . The predicted value of x_{NiF_2} in $\text{LiF}-0.33\text{BeF}_2$

saturated with BeO and NiO is $\approx 10^{-4}$ at 1000°K . This is higher than is expected for a typical reactor system, i.e., neither NiO (nor FeO) is expected as a stable solid phase under normally reducing conditions.

Less exact but useful estimates of the solubilities of other oxides can be made from the following reaction

$$\Delta G = 1/z G^f(\text{MO}_{z/2}) - 1/z \Delta G^f(\text{MF}_z) - \Delta \bar{G} (1/2 \text{O}_2^{2-} - \text{F}^-) \quad (28)$$

wherein the last ΔG term corresponds to reaction (25) above. A survey of available ΔG^f data for oxides and fluorides of Group I, II, III, and IV cations, and of the bivalent first transition metal cations indicates that aside from the oxides already considered only Al^{3+} and perhaps Sc^{3+} should be significantly insoluble. This scarcity of insoluble oxides is caused by the relative greater stability of fluorides. It offers little help in the search for refractory materials which might prove useful agents for ion exchange or precipitation reactions which could be made the basis for fuel reprocessing schemes. For example, an attractive possibility would be the removal of rare earth fission products by ion exchange reactions involving rare-earth oxides of suitable low neutron capture cross section, but these oxides are expected to be too soluble in a $\text{LiF}-0.33\text{BeF}_2$ and should cause the precipitation of BeO (or UO_2 , if UF_4 is present).

4.4 Formation of Carbides

Direct reactions between constituents of the MSRE fuel and graphite to form carbides may be represented by the following general reaction for which chromium metal was chosen as the reducing agent.

$$\Delta G = \Delta \bar{G}^f(\text{CrF}_2(\text{d})) - 2/z \Delta \bar{G}^f(\text{MF}_z(\text{d})) + 2/z \Delta G^f(\text{MCy}(\text{s})) \quad (30)$$

Values for the free energy change associated with this reaction at 1000°K are listed in Table V. They indicate that Zr, U, and Th carbides should not be formed.

5. Conclusions

The mutually re-enforcing relationship between chemistry and thermodynamics in a reactor development program is, I think, well illustrated in the case of the molten salt reactor program. The chemical information most urgently needed in order that development of the MSRE might proceed was obtained by direct experiment. But, by conducting these experiments in a sufficiently controlled manner that the chemical equilibria involved could be identified and the associated equilibrium constants measured, each experiment could contribute to a growing knowledge of the thermodynamics of the pertinent molten salt systems. This knowledge, in turn, has been useful in several ways. It has extended the significance of the chemical information upon which it is based, it has indicated where new chemical problems may arise and how to deal with them, and it provides a growing structure which will continue to grow in extent as more data are acquired, and in usefulness as more problems appear which require solutions.

Table V
Carbide Formation

Carbide	ΔG^f (1000°K), ^a kcal	ΔG (Reaction, 1000°K), kcal
ZrC(s)	-38	24
UC ₂ (s)	-42	22
ThC ₂ (s)	-48	39

^a Ref. 27, page 587.

Figure Captions

- Fig. 1. The System LiF-BeF_2 . ORNL-Dwg. 65-2526
- Fig. 2. Oxidation-Reduction Reactions in LiF-0.33BeF_2 .
Left; reaction of Cr, Fe, and Ni with HF (1 atm) and H_2 (1 atm); right; mole fractions of FeF_2 , NiF_2 and the $x_{\text{UF}_3}/x_{\text{UF}_2}$ ratio in equilibrium with 10^{-4} mole fraction CrF_2 and chromium metal.
ORNL-Dwg. 65-4608 Rev.
- Fig. 3. HF-H_2 Sparging. Calculated efficiency of oxide removal from LiF-0.33BeF_2 by sparging with HF-H_2 mixtures. The overall utilization of HF required to lower the residual oxide content to 10^{-3} mole/kg is plotted vs the initial oxide content. The total pressure is 1 atm. ORNL-Dwg. 65-4187
- Fig. 4. Oxide Concentration at Saturation in LiF-0.33BeF_2 as a Function of the Concentration of ZrF_4 Added.
ORNL-Dwg. 65-2542R.
- Fig. 5. Variation of Activity Coefficients in LiF-BeF_2 , 600°C .
Left, as a function of x_{BeF_2} at low solute concentration; right, γ_{ZrF_4} as a function of x_{ZrF_4} and γ_{UF_4} as a function of x_{UF_4} added to LiF-0.33BeF_2 . z/r is the cation charge to radius ratio.
- Fig. 6. Electrode Potentials in LiF-0.33BeF_2 (vs $\text{HF/H}_2, \text{F}^-$ electrode) at 1000°K Compared (left) to Aqueous Electrode Potentials at 25°C and Compared (right) to Electrode Potentials in LiCl-KCl Eutectic (vs Ag^+/Ag) at 450°C .
ORNL-Dwg. 65-4607R.

FIGURE 1.

The System LiF-BeF_2 .

ORNL-Dwg. 65-2526

Fig. 2

Fig 17

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Fig 6 12

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