INTRODUCTION

A nuclear reactor fueled by a molten salt was first suggested in 1947 as a means of powering aircraft. Development proceeded during the next ten years, culminating in the construction and brief operation of the Aircraft Reactor Experiment in 1954. The fuel of this reactor was a molten mixture of NaF, ZrF$_4$, and UF$_4$. It was moderated with BeO and contained in Inconel.

In 1956 development was begun of a molten salt-fueled reactor suitable for electric power generation and the breeding of $^{233}$U from $^{232}$Th with thermal neutrons. This led to the Molten Salt Reactor Experiment, construction of which was authorized in 1960. Critical operation began in 1965 and continued with considerable success for four years. This reactor was fueled with a melt containing $^7$LiF, BeF$_2$, ZrF$_4$, and UF$_4$. It was moderated with graphite and was contained in Hastelloy N. Since the shutdown of the MSRE in 1969, development of a molten salt breeder reactor has continued until early this year, when this program was terminated at the Oak Ridge National Laboratory.

A molten salt breeder reactor is, perhaps more than any other, a chemist's reactor (Slide 1). The fuel is dissolved and circulated in a relatively unique coolant. The $^{233}$Pa which is bred must be removed soon after it is formed to avoid loss of a significant fraction by neutron capture. The fission products must be removed continuously by suitable chemical means to maintain the neutron economy. The present status of the MSBR concept has recently been summarized in ORNL-4312. In this report, Grimes et al. review the extensive information now available about the chemistry of MSBR fuel.

Research sponsored by the U. S. Atomic Energy Commission under contract with Union Carbide Corporation.
Much of this knowledge is based on the direct measurement of heterogeneous equilibria involving saturating gaseous and/or solid phases. In two previous reviews I have tabulated these equilibria and others derived from them, along with related thermochemical data to provide a brief, quantitative description of this chemistry. These tables of equilibrium constants, formation free energies and electrode potentials have proven quite useful to many of us who have been involved in the molten salt reactor program. This is perhaps not surprising when we consider that at MSR temperatures of ~600°C, reaction rates ought to be high and equilibrium conditions thereby closely approximated.

In this talk it is my purpose to present certain generalizations about the chemistry and thermodynamics of MSBR fuel solutions and then by the use of the equilibrium measurements and the thermochemical data to consider how the state of oxidation (the redox potential) and the oxide content of the fuel determine the chemical behavior of the structural metals, the actinide and the fission product elements.

2. FUEL SOLVENT

The only elements and isotopes aside from the actinides with low enough thermal neutron capture cross sections to serve as major constituents of an MSBR fuel are:

Be, Bi, $^{11}$B, C, D, F, $^{7}$Li, $^{15}$N, 0

How fortunate it is for us that from this short list nature has supplied us with a binary system LiF + BeF$_2$ (Slide 2) from which we can obtain a fuel solvent. In the binary phase diagram we find mixtures which melt below 500°C from 30 to about 58 mole % BeF$_2$, and which can dissolve the required amounts of ThF$_4$ and UF$_4$. 
or PuF$_3$. The most favorable physical properties are found near the composition
LiF–BeF$_2$ (67–33), that of the compound Li$_2$BeF$_4$ which barely melts congruently.
This composition has been chosen as the reference composition for most of the
chemical equilibria which have been studied.

3. THE STABILITY OF FLUORIDES

Note that fluoride and oxide are the only anions which can be present
in appreciable amounts in an MSBR fuel. The relative stability of the fluoride
compounds of the various elements is indicated approximately by the heat of
formation per mole of fluoride. This is plotted in slide 3 for the metallic
elements. We see that the pre-transition elements of Groups I to IV of the
Periodic Table in their normal group valence generally have heats of formation
more negative than -100 kcal/mole of fluoride. This is also true of the tetra-
valent actinides. The transition elements, which include the structural metals
fall between -80 and -100 kcal/mole of fluoride. Again we perceive a fortunate
situation, namely, that the elements lithium and beryllium, as well as thorium,
protactinium, uranium and plutonium, all form fluorides which are considerably
more stable than those of the structural metals chromium, iron, nickel and
molybdenum. This means that the fuel constituents will not react with —
corrode — such metals to an appreciable extent.

4. RELATIVE STABILITY OF FLUORIDES AND OXIDES

The relative stability of fluorides and oxides is indicated by the
reaction shown in Slide 4. The heat of this reaction should vary in about the
same way as the free energy of the reaction

$$\frac{1}{2} \text{MF}_2(d) + \frac{1}{2} \text{O}_2^-(d) \rightleftharpoons \text{F}^-(d) + \frac{1}{2} \text{MO}_{2/2}(c)$$

except for small entropy and $\Delta C_p$ effects which should be about the same at a given
elevated temperature for different cations $M^{2+}$. In this reaction we choose to
write the metal oxide as a solid since these compounds tend to be higher melting than the corresponding fluorides. We see that the heat of reaction plotted in the slide shows a reasonable correlation with $\frac{Z^2}{r^+}$, the ion charge squared over the ion radius, for pretransition metal cations, becoming more negative as $\frac{Z^2}{r^+}$ increases. This corresponds to a decreasing solubility of the oxide in the molten fluoride. It is not surprising therefore that BeO is fairly insoluble in LiF-BeF$_2$ melts and that ThO$_2$, PaO$_2$, UO$_2$ and PuO$_2$ are increasingly insoluble. As we shall see, Pa$_2$O$_5$ has a low solubility indeed.

We see also in this slide that the transition and post-transition metals should form insoluble oxides. Since they also form less stable fluorides, however, not many of their oxides will be important to us. We will find that an element with more than one valence state often exhibits a lower valence in a fluoride phase and a higher valence in an oxide phase which is at equilibrium with it. We will find it convenient to display these equilibria in (Pourbaix) diagrams in which the oxide ion concentration is plotted as the abscissa and the oxidation (redox) potential is plotted as the ordinate.

5. ACTIVITY COEFFICIENT EFFECTS

In several investigations the effect of melt composition on the equilibrium under study was determined, thus yielding information about activity coefficients of the melt components. The activity coefficients of BeF$_2$ in LiF-BeF$_2$ melts was measured by Hitch and myself using the cell shown in Slide 5. The cell reaction involves the melt component BeF$_2$. The activity coefficient of LiF was determined by a Gibbs-Duhem integration. Shaffer et al. studied reactions involving the reduction of LiF and CeF$_3$ to the metals in bismuth by thorium metal. Such reactions are of interest in the chemical reprocessing of
MSBR fuels. We see that the variation of the distribution coefficients should reflect the variation of the quotients of activity coefficients. Finally, Barton et al. has measured the solubility of the sparingly soluble CeF₂ as a function of melt composition, giving a direct measure of the variation of the activity coefficient of CeF₂. The compositions which have been studied are shown in Slide 6. The resulting data have been smoothed by means of a model which assumes that these various cations are usually present in solution as neutral or anionic fluoride complexes. The resulting activity coefficient curves are shown in Slide 7. We see that the activity coefficients of the major components seem to depend primarily on the mole fraction of LiF present. The standard states have been chosen so that activity coefficients for the solutes are unity when they are present at low concentration in Li₂BeF₄, while the activities of LiF and BeF₂ are taken to be unity in Li₂BeF₄. This convention locates the central portion of the curves. The uncertainties reached at the extremes of the composition range covered are estimated to be ± 10% for CeF₂, ± 20% for BeF₂ and ±30% for LiF and ThF₄. The activity coefficient of UF₄ should behave about as that of ThF₄. Based on other, experimental data, the activity coefficients of PuF₃, UF₃ and NiF₂ should behave about as that of CeF₂. Note that while the variations of activity coefficients is appreciable, it is no more than a factor of ten from the reference composition value.

6. ENTROPIES

The entropy of a reaction can often be estimated accurately enough from available data and empirical correlations to predict the temperature dependence of an equilibrium constant or a free energy more accurately than such can be measured. With this in mind we have sought correlations for the entropies of dissolved components in LiF-BeF₂ melts. One result is shown on Slide 8, where
we find first that the entropy difference between a crystalline fluoride and oxide of the same cation at 1000°K is roughly proportional to the charge on the cation. The line drawn through the filled circles corresponds to the relationship

$$S_{MF_z(c)} = S_{MO_z/2(c)} + 7.48Z/Z^\ast$$

The worst deviation is about four entropy units. Also shown is a plot of the entropy difference between a fluoride dissolved in Li$_2$BeF$_4$ and the corresponding crystalline oxide. Except for Ni$^{2+}$ and Ce$^{3+}$ ions, which are low, the correlation with the cation charge is even better. The line has been drawn with the same slope as before and gives the relationship

$$S_{MF_z(d)} = S_{MO_z/2(c)} + 7.5x + 9$$

Thus it appears that the entropy of solution of a metal fluoride is about 9 e.u. regardless of the cation charge. The above relationship has been used to estimate entropies of dissolved fluorides from the entropies of the corresponding oxides.

7. REACTION OF HF AND OXIDE

HF has been an important reagent in our studies of molten fluorides. One of its most important uses has been concerned with the chemistry and the removal of oxide in molten fluorides. In Slide 9 I have listed some of the important equilibria which have been measured. The first is the principal reaction by which oxide is removed from the melt. As we see the equilibrium is quite favorable. The second reaction applies if BeO saturation is reached, which we see occurs at quite low oxide concentrations. The third reaction, showing the formation of hydroxide ion interferes with the removal of oxide. It can also be
responsible for the holdup of much larger amounts of HF in the melt — as OH\(^-\) plus F\(^-\) — than would result from the small solubility\(^10\) of HF alone. The removal of oxide by hydrofluorination has served as the basis of the analysis for oxide in the MSRE fuel, giving results to \(\pm 15\) ppm at \(\approx 60\) ppm oxide.

8. REACTIONS OF HF WITH SULFIDE AND IODIDE

Hydrofluorination also removes sulfide and iodide from Li\(_2\)BeF\(_4\) melts (Slide 10). Only the lower limit of the equilibrium constant for the first reaction could be estimated\(^11\) because H\(_2\)S could not be removed from the system without some loss by reaction with the container used. The removal of iodide by HF\(^12\) is especially interesting since this suggests a means of continuously removing this important fission product — and precursor of \(^{135}\)Xe — from an MSBR fuel.

9. STRUCTURAL AND NOBLE METALS

We have already noted that most of the transition and post-transition metals are expected to be unreactive toward molten fluorides. The reactivity of the important structural metals was determined early in the MSR program by Blood\(^13\) using the equilibria shown in Slide 11. These elements and molybdenum are the constituents of Hastelloy N, the container alloy of the MSRE. The most reactive of these metals is chromium and, as we shall see, it reacts to a small extent with one of the MSBR fuel constituents, UF\(_4\). The relative nobility of iron and nickel is indicated by the increasing equilibrium constants for the reactions shown.

The oxides of these metals are sparingly soluble. Slide 12 summarizes some equilibria which have been derived from the measured reactions in Slide 11 and the known formation free energies of the oxides. We see that with both BeO and NiO present, the concentration of nickel in solution is quite low. The
concentration of Cr$^{2+}$ and Mo$^{3+}$ in solution depends on the redox potential of the system since the metal is at a higher valence in the oxide. A more informative comparison of these equilibria will be made presently.

For the moment we note that the order of increasing nobility of the various metals depends on whether or not oxide is present. Thus we see in Slide 13 that molybdenum is more noble in the absence of oxide, as is chromium and nickel. In this series note also how active tantalum is because of the stability of TaF$_5$. Nickel is a relatively noble metal. Niobium is an especially interesting case. We have recently found that Nb$^{5+}$ ion forms a stable oxyion NbO$_2^+$ in molten fluorides.

10. THE ACTINIDES

The potentials of various couples of thorium, protactinium, uranium, and plutonium in molten fluorides are indicated in Slide 14. Under the reducing conditions of an MSBR fuel, we have Th$^{4+}$, Pa$^{4+}$, U$^{4+}$ with some U$^{3+}$, and Pu$^{3+}$. The ratio U$^{4+}$/U$^{3+}$ will probably fall in the range 10-100 for an MSBR fuel and will serve us as a convenient measure of the redox potential.

The dioxides of Th$^{4+}$, Pa$^{4+}$, U$^{4+}$ and Pu$^{4+}$ show a decreasing solubility in that order. Since all have the fluorite structure and nearly the same lattice parameter they can form solid solutions. The exchange equilibria of each with ThO$_2$ is indicated in Slide 15. These are related to the simple solubility equilibria involving the pure oxides. The exchange constant equals the ratio of the separate solubility product constants. The quantity actually measured was the exchange quotient $Q_{Th}^N$, the quotient of mole fractions. The activity coefficients in the oxide solid solution could be estimated from the dependence of $Q_{Th}^U$ on the composition of the oxide phase. The exchange quotients which have been observed correlate well with the lattice parameters of the separate oxides.
This is shown on Slide 16. The solubility of PuO₂ is very low. As we shall see, however, it cannot appear as a separate phase except under quite oxidizing conditions.

The important oxide of protactinium is Pa₂O₅ (or an addition compound of it) which has been found to be so insoluble that it should be possible to precipitate it from a reactor fuel under mildly oxidizing conditions to achieve a good separation even at the low Pa concentrations (≤ 100 ppm) which will occur. The situation is summarized in Slide 17. Here the Pa⁵⁺ concentration remaining in solution is plotted vs the activity of UO₂. The latter must reach ≤ 0.95 before a rich solid solution of UO₂ is precipitated. At this point the Pa⁵⁺ concentration has decreased to ≤10 ppm. While there is some uncertainty in this number, it is a remarkably good separation.

11. THE LANTHANIDES

Among the fission products, the rare earths are important because they have a high aggregate yield and include some nuclides with high neutron capture cross sections. Moreover, they form very stable fluorides. This is indicated by the electrode potentials listed in Slide 18, where we see that lanthanum (and the other rare earths) fall between the Li⁺/Li° and the Th⁴⁺/Th° couples. It has proven possible to remove the rare earths by reductive extraction into bismuth, though thorium is also reduced and must be later separates. Unfortunately the rare earth oxides are not insoluble enough to offer a method of separation.

12. FUEL CHEMISTRY

Up to now we have generally been considering the chemical behavior of various elements one at a time in molten fluorides. Let us now consider an MSBR fuel exposed to a Hastelloy N container and graphite. The composition will
be LiF-BeF$_2$-ThF$_4$ (72-16-12) with a few tenths mole % UF$_4$ and/or PuF$_3$ and, as 
operation continues, some PaF$_4$.

In Slide 19 we consider the behavior of the alloy constituents Cr, 
Fe, and Ni in a Pourbaix diagram where the oxide concentration is plotted vs. 
the redox potential, here expressed as the $U^{4+}/U^{3+}$ ratio. We see that only small 
amounts of chromium can be oxidized from the alloy when the $U^{4+}/U^{3+}$ ratio is 
in the expected range of 10-100. A much lower ratio is precluded by the danger 
that $U^{3+}$ might react with graphite to form uranium carbide. We also see that 
the oxides of chromium, iron, and nickel can appear as separate solid phases 
only under increasingly more oxidizing conditions.

In Slide 20 the behavior of the actinides is indicated. At the normal 
redox potential, if oxide is introduced into the fuel, a solid solution contain-
ing over 90% UO$_2$, plus some PaO$_2$ and ThO$_2$, is produced. This obviously must be 
avoided by limiting the oxide content of the circulating fuel. Under mildly 
oxidizing conditions we see that PaO$_2$ can be precipitated, and under still 
more oxidizing conditions we can precipitate a solid solution rich in PuO$_2$.

In Slide 21 I show a similar diagram representing the behavior of 
niobium. The fission product $^{95}$Nb is an important one since experience with the 
MSRE suggests that it appears in solution as a soluble species at a redox 
potential which is near the optimum $U^{4+}/U^{3+}$ ratio and so might serve as a useful 
radiochemical redox indicator. This diagram, which is based on recent results of 
Ting and Weaver et al. makes this plausible, but cautions us that the potential 
where this occurs will depend on the oxide concentration as well because of the 
formation of NbO$_2$$. It will depend also, of course, on the state of the metal. 
This is true of all the metal-phase boundaries I have shown in slides 19, 20, 
and 21. The metal phases which will be in equilibrium with an MSBR fuel are 
not yet known, but it seems likely that they will be of small particle size and
of a composition quite different from the container alloy.

13. THE CHEMICAL EFFECT OF FISSION

The expected behavior of the important fission products in an MSBR is indicated in Slide 22. The noble gases Xe and Kr are known to be quite insoluble in molten fluorides. The groups VII, I, II, III, and IV fission products should be dissolved in the fuel salt in their normal valences. The remainder — of which Nb, Mo, Te, and Ru are the most important contributors should be reduced to the metallic state under the reducing conditions which would be normally maintained in a reactor. Also indicated in the slide are values of the product of the fission yield and the valence of each fission product. This serves to show that with reducing conditions maintained and with rapid removal of Xe and Kr, the sum of the charges on all the fission products is less than +4 per mole of uranium burned, being nearly +3. Hence as burnup of the uranium fuel (mostly UF\(_4\)) proceeds, UF\(_3\) or other reducing agent must be added to maintain reducing conditions. Otherwise the deficiency of cation equivalents will be made up by the oxidation of UF\(_3\) present and then by corrosion of the container, i.e., the fission process is oxidizing.

14. TELLURIUM

Intergranular cracking of Hastelloy N surfaces was noted in the MSRE. While the investigation of this effect was not completed at the time the program was terminated, the examination of MSRE surveillance specimens and other tests strongly suggested that it was caused by fission-product tellurium. If the depth of penetration, which was only a few mils, was diffusion limited, this intergranular cracking is not too serious since the depth of penetration should then increase as the \(1/4\) power of the time. If the depth of penetration was limited by the supply of tellurium, the means which might be employed to reduce this
effect will depend on the chemistry of tellurium in the fuel salt. It remains to be determined whether it is present in the elemental form or as telluride ion. As the element it is volatile at the temperatures involved and could be removed by the more vigorous sparging to be employed in an MSBR. As Te\(^{2-}\) ion it might be precipitated by addition of an appropriate cation. It seems quite possible that intergranular cracking does not occur when a few percent of titanium is added to Hastelloy N. Such additions were planned in any case to decrease the radiation embrittlement of the alloy.

15. CONCLUSIONS

I think you will agree that the chemistry of a molten salt breeder reactor is rich and interesting. This is to be expected since, after all, we have the actinides and the fission products present in an exotic solvent at a cheerful red heat.

This chemistry has been favored by nature in several important ways:

(i) The solvent salts LiF and BeF\(_2\), practically the only ones which can serve in such a reactor, are stable towards the structural metals, they form mixtures which are sufficiently low melting, and they can dissolve the desired amounts of fissile and fertile fluorides. (ii) The fertile and fissile fluorides ThF\(_4\), UF\(_4\) and PuF\(_3\) are stable enough not to react with the container metals, with the minor exception of chromium. (iii) The protactinium which is bred and which must be removed quickly from an MSBR can be separated selectively as an oxide if the presently proposed method of reductive extraction into bismuth is not used. (iv) Many of the fission products are removed from the circulating fuel either as gases or as insoluble metal particles which seem to collect at the salt-gas interface.
Balanced against these chemical advantages we have the disadvantages that: (1) the rare earths are difficult to remove because of their stability as fluorides, though a process has been developed for this. (2) Tellurium attacks the container metal and a means of chemical control or alloy modification may be necessary. (3) A problem not yet mentioned is the production of tritium which is appreciable in this reactor. It diffuses primarily through the walls of the heat exchanger into the intermediate coolant circuit where means for trapping or removing it are needed. In my view these problems will be solved by chemical-thermodynamic methods as readily, or more readily than others already solved in the development of molten salt reactors, if and when this promising concept is again actively pursued.
References


For 1000 MW(e), the fuel salt flow rate through the core is 55,000 gpm, but less than 1 gpm passes through the processing plant. Electricity is produced from supercritical steam with an overall efficiency of 44%.
Fig. 5.1 Phase diagram of the system LiF-BeF$_2$. 
\[ y(1) = \int_{x_0}^{x} u(t) \, dt \]
SOES OF INFORMATION ABOUT ACTIVITY COEFFICIENTS IN LIP-BEFT2-TBF2 MELTS

CAR:  BeF2LIP, BeF3LIP, H2, F2

\[ \text{BeF}_2 + 2\text{HF} \rightarrow \text{BeF}_3(\text{g}) + \text{H}_2 \]  
(Hirch and Rave)

Reaction: \( \frac{1}{4} \text{Th}^4(\text{B}) + \text{Me}_2(\text{g}) = \frac{1}{4} \text{ThF}_4(\text{g}) + \text{Me}^+(\text{B}) \)

\[ D_{\text{Me}} = X_{\text{Me}} \text{F}_{\text{MeF}_2} \]

\[ K_1 = \frac{D_{\text{Me}} D_0^{1/2}}{D_{\text{Me}} D_0^{1/2}} \]  
(Shaffer, Monjeon, Grimes)

Reaction: \( \text{CaF}_2(g) = \text{CaF}_2(\text{s}) \)

\[ K_3 = X_{\text{CaF}_2} \text{F}_{\text{CaF}_2} \]  
(Barton et al.)
REFERENCE COMPOSITION

\( D_{\text{Th}}, D_{\text{Li}} \)
\( D_{\text{Ce}}, D_{\text{Th}}, D_{\text{Li}} \)
\( X_{\text{CeF}_3} \)
\[ S_{\text{MECO}}(w) = S_{\text{MO2CO}}(w) + 7.5z + 9 \]
Reactions of HF and Oxide in ZLIF-BeF₂ (600°C):

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{HF(g)} + \text{O}^{2-} \rightarrow \text{HF}_2 ) (Methane)</td>
<td>( P_{\text{HF}_2} = 4 \times 10^{-4} )</td>
</tr>
<tr>
<td>( \text{HF(g)} + \text{BeO(c)} \rightarrow \text{BeF}_2(g) + \text{H}_2\text{O(g)} ) (Methane)</td>
<td>( P_{\text{BeF}_2} = 170 )</td>
</tr>
<tr>
<td>( \text{HF(g)} + \text{O}^{2-} = \text{OH}^+ + \text{F}^- ) (Methane)</td>
<td>( X_{\text{OH}^+} = 160 )</td>
</tr>
<tr>
<td>( \text{HF(g)} \rightarrow \text{HF(g)} ) (Field, Skaffin)</td>
<td>( X_{\text{HF}} = 0.002 )</td>
</tr>
<tr>
<td>( \text{BeO(c)} \rightarrow \text{Be}^{++} + \text{O}^{2-} ) (Hitch, Bonds)</td>
<td>( X_{\text{O}^{2-}} = 0.004 )</td>
</tr>
</tbody>
</table>
\[
\frac{\frac{dH}{dt} + L}{s^2} \geq 10^4
\]

\[
2H + H_2 = 2H + H_2(0)
\]

Resolution studies indicate that at 600°C.
Reduction of Structural Metal Fluorides in LiH-BaF$_2$ (600°C)

\[
\frac{p^2_{HF}}{P_{H_2} X_{MF_2}}
\]

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$H_2(g) + CrF_2 \rightarrow 2HF(g) + Cr(c)$</td>
<td>$5.5 \times 10^{-6}$</td>
</tr>
<tr>
<td>$H_2(g) + FeF_2 \rightarrow 2HF(g) + Fe(c)$</td>
<td>0.13</td>
</tr>
<tr>
<td>$H_2(g) + NiF_2 \rightarrow 2HF(g) + Ni(c)$</td>
<td>16,000</td>
</tr>
<tr>
<td>(Blood)</td>
<td></td>
</tr>
</tbody>
</table>
### Reaction of Strontium Metal Oxide in ZCPEBSe (500°C)

<table>
<thead>
<tr>
<th>Reaction</th>
<th>$X_{\text{fr}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{NiO} + \text{Be}^{2+} = \text{Ni}^{2+} + \text{BeO}$</td>
<td>$X_{\text{Ni}^{2+}} = 0.0004$</td>
</tr>
<tr>
<td>$\text{FeO} + \text{Be}^{2+} = \text{Fe}^{3+} + \text{Be}$</td>
<td>$X_{\text{Fe}^{3+}} = 0.016$</td>
</tr>
<tr>
<td>$\frac{1}{2} \text{CrO}_2 + \frac{1}{2} \text{Be} = \text{Cr}^{3+} + \text{BeO}$</td>
<td>$X_{\text{Cr}^{3+}} = 0.0007$</td>
</tr>
<tr>
<td>$\frac{3}{4} \text{MnO} + \frac{1}{4} \text{Be} = \text{Mn}^{2+} + \frac{3}{2} \text{BeO}$</td>
<td>$X_{\text{Mn}^{2+}} = 4 \times 10^{-8}$</td>
</tr>
<tr>
<td>Oxide Form</td>
<td>Reduction Potential (V)</td>
</tr>
<tr>
<td>------------</td>
<td>------------------------</td>
</tr>
<tr>
<td>Na$_2$O/Na$^+$</td>
<td>-0.75 V</td>
</tr>
<tr>
<td>Cr$^{2+}$/Cr$^0$</td>
<td>-0.45 V</td>
</tr>
<tr>
<td>Fe$^{2+}$/Fe$^0$</td>
<td>-0.47 V</td>
</tr>
<tr>
<td>Ni$^{2+}$/Ni$^0$</td>
<td>-0.37 V</td>
</tr>
<tr>
<td>Cl$_2$/Cl$^-$</td>
<td>0.79 V</td>
</tr>
<tr>
<td>Cr$_2$O$_3$(s)/Cr$^0$</td>
<td>-0.73 V</td>
</tr>
<tr>
<td>Nb$_2$O$_5$/Nb$^0$</td>
<td>-0.56 V</td>
</tr>
<tr>
<td>NbO$_2$(s)/Nb$^0$</td>
<td>-0.26 V</td>
</tr>
<tr>
<td>Fe$_3$O$_4$(s)/Fe$^0$</td>
<td>-0.24 V</td>
</tr>
<tr>
<td>CO(g)/C$^0$</td>
<td>-0.14 V</td>
</tr>
<tr>
<td>NiO(s)/Ni$^0$</td>
<td>0.01 V</td>
</tr>
</tbody>
</table>
\[ \frac{k_2}{k_1} = \frac{K_1 \cdot (\frac{y_{ax} \cdot X_{ax}}{x_{ax}}) \left( \frac{y_{ax} \cdot y_{ax}}{x_{ax} \cdot x_{ax}} \right)}{k_2} = \frac{K_1 \cdot (y_{ax} \cdot X_{ax})}{k_2} \]
SLIDE 16

\[ \text{Figure 1: } \]

- The oxide figures 1 session taken

\[ \text{Eq. (5) in quotient maintained} \]

\[ \text{tinum continuously estimating} \]

\[ \text{it was} \]

\[ \text{ich is prob} \]

(10)

(11)
| Electrode Potential in 2LiF-BaF$_2$ (600°C): |
|-----------------|-----------------|-----------------|
| Li$^+$/Li(g)    | -2.66v          | Cr$^{2+}$/Cr(0)  | -0.45v |
| La$^{3+}$/La(0-) | -2.29v          | Fe$^{2+}$/Fe(0)  | -0.08v |
| Th$^{4+}$/Th(0-) | -1.87v          | HF(g)/H$_2$F$^-$ | 0      |
| Be$^{2+}$/Be(0-) | -1.85v          | Ni$^{2+}$/Ni(0)  | 0.38v  |
| U$^{4+}$/U$^{2+}$ | -1.15v          | F$_2$(g)/F$^-$   | 2.87v  |
\[ \text{Mole Fraction Oxide} \]

Graph showing data points and lines for:
- \( X_{\text{Ni}^{2+}} = 10^{-3} \)
- \( X_{\text{Fe}^{2+}} = 10^{-3} \)
- \( X_{\text{Ca}^{2+}} = 10^{-3} \)

Axes:
- \( 10^2 \) to \( 10^6 \) on the x-axis
- \( 10^{-8} \) to \( 10^{-6} \) on the y-axis
Table V. Chemical Consequences of Fission in an MSBR

<table>
<thead>
<tr>
<th>Fission Product</th>
<th>Assumed Eq. Ox. State (Z)</th>
<th>Yield* (Y)</th>
<th>YZ</th>
</tr>
</thead>
<tbody>
<tr>
<td>Br + I</td>
<td>- 1</td>
<td>0.015</td>
<td>- 0.015</td>
</tr>
<tr>
<td>Kr + Xe</td>
<td>0</td>
<td>0.608**</td>
<td>0</td>
</tr>
<tr>
<td>Rb + Cs</td>
<td>+ 1</td>
<td>0.004</td>
<td>0.004</td>
</tr>
<tr>
<td>Sr + Ba</td>
<td>+ 2</td>
<td>0.072</td>
<td>0.144</td>
</tr>
<tr>
<td>Lanthanides + Y</td>
<td>+ 3</td>
<td>0.538</td>
<td>1.644</td>
</tr>
<tr>
<td>Zr</td>
<td>+ 4</td>
<td>0.318</td>
<td>1.272</td>
</tr>
<tr>
<td>Kβ</td>
<td>0</td>
<td>0.014</td>
<td>0</td>
</tr>
<tr>
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<td>0</td>
</tr>
<tr>
<td>Tc</td>
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<td>0.059</td>
<td>0</td>
</tr>
<tr>
<td>Ru</td>
<td>0</td>
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</tr>
<tr>
<td></td>
<td></td>
<td>1.953</td>
<td>3.049</td>
</tr>
</tbody>
</table>

*From Ref. 39.

**With rapid stripping from the system.