INTRA-LABORATORY CORRESPONDENCE
OAK RIDGE NATIONAL LABORATORY

August 13, 1968

To: W. R. Grimes

From: M. A. Bredig

Re: The Chemistry of Volatile and/or Liquid Complex Halides with Potential Applications in Separation Processes.

The observations at the Argonne National Laboratory on the existence of volatile rare earth and uranium chloride complexes with aluminum chloride have stimulated my thinking into channels of what seems to be a rather virgin branch of inorganic chemistry. Some of these thoughts may, or may not, prove to have potential for applications to the removal of rare earths from molten salt reactor mixtures. It is my understanding that considerable interest in this matter has been aroused at the Laboratory, and I am submitting herewith a contribution to the discussions, well aware of its rather speculative nature.

It may be worthwhile to study the fundamental chemistry of potentially volatile complex halides quite thoroughly. Some of many conceivable reactions that come to mind immediately (and as a result of further thinking, additional information, and extended experimentation may have to be discarded later!) are mentioned herewith.

1. Aluminum chloride itself may react according to

\[ RF_3(\text{melt}) + Al_2Cl_6(\text{gas}) \rightarrow RA1Cl_6(\text{gas}) + AlF_3(\text{melt}) \]  

or, with LiF present to help drive the reaction by complexing in the melt,

\[ RF_3(\text{melt}) + Al_2Cl_6(\text{gas}) + 3\text{LiF}(\text{melt}) \rightarrow RA1Cl_6(\text{gas}) + \text{Li}_3\text{AlF}_6(\text{melt}). \]  

The mixed chloride may well be more complex than written here, as seems to have already been recognized at Argonne for both of the volatile complexes NdCl_3(AlCl_3)_n and UCl_6(AlCl_3)_n. The situation is very reminiscent of my suggestions, a few years ago, in connection with Art Shor's master's degree thesis (with Wm. T. Smith, Jr.) on the aluminum chloride - zirconium chloride phase diagram (J. Phys. Chem. 70, 1511 (1966)) concerning the formation (in the liquid state, at that time) of complex molecules such as Zr(AlCl_4)_n or even Zr(Al_2Cl_7)_n, as well as of intermediate complexes and including the most simple one, ZrCl_4.AlCl_3, or ZrCl_3(AlCl_4). Correspondingly, there might be RCl_3(AlCl_3)_n, especially R(AlCl_4)_3 or R(Al_2Cl_7)_3 with a rare earth element as the central atom R of the complex. These heteropolymer complexes may conceivably form from fluoride melts according to equations such as

\[ RF_3 + (n+1)/2 Al_2Cl_6 + 3 \text{LiF} \rightarrow RCl_3(AlCl_3)_n + \text{Li}_3\text{AlF}_6 \]  

{(3)
The basic principles of the formation of such compounds likely to be volatile must prominently include the coordinatively unsaturated nature of $\text{Al}^{3+}$ in $\text{AlCl}_3$ with respect to fourfold coordination (saturation). The other component of the complex, the trichloride $\text{RCI}_3$ or tetrachloride $\text{RCI}_4$, then provides the missing fourth chloride corners forming the bridges to the 3 or 4 $\text{AlCl}_4$ tetrahedra joined to the central $\text{R}$ atom.

2. With this basic principle in mind, the substitution of a trivalent metal $\text{R}$ (rare earth, $\text{Bi}$, or metals mostly of lesser interest for reactor chemistry, such as $\text{Fe}$, $\text{Ga}$, or $\text{In}$) either simply for one $\text{Al}$ in $\text{Al}_2\text{Cl}_6$ or for $\text{Zr}$ in the more complex compound, above, suggests a variety of other substitutions and complexations. These include most importantly beryllium chloride, $\text{BeCl}_2$, also coordinatively unsaturated, and tetrahalides of tetravalent elements such as $\text{Zr}$, $\text{Hf}$, $\text{Th}$, and $\text{U}$, besides silicon, titanium, germanium, tin, or lead. It appears that very little, if anything is known about such combinations and substitutions and the physical properties such as volatility one may encounter therewith. Even regarding one of the simplest and perhaps most probable combinations, namely the simultaneous substitution, in $\text{Al}_2\text{Cl}_6$, of one $\text{Al}^{3+}$ by one $\text{Be}^{2+}$, the other by $\text{Si}^{4+}$, i.e., a compound "$\text{BeSiCl}_6$", or one possibly still further complexed such as "$\text{SiCl}_4.2\text{BeCl}_2$", I have thus far been unable to find anything in the literature.

As far as applications are concerned, one most fanciful and extravagantly optimistic speculation might be a volatilization reaction in which one would contact the fluoride melt with a gaseous complex beryllium-thorium chloride (if it exists), most simply $\text{BeThCl}_6$, but probably more complex, $\text{Th(AlCl}_3)_4$, or the like, somewhat analogous to $\text{Zr(AlCl}_4)_4$ but possibly with tri-coordinated $\text{Be}$ instead of the tetracoordinated $\text{Al}$$. Such a complex $\text{Be-Th halide}$ (other than fluoride) might be the choice for circumventing the introduction of another element such as $\text{Al}$ into the melt and avoiding the preferential reaction that other volatile halides such as $\text{Al}_2\text{Cl}_6$ might undergo with the $\text{Be}$ and $\text{Th}$ of the fluoride melt, instead of the desired metathesis with, and volatilization of, the rare earth elements.

Possibly, $\text{BeCl}_2$ vapor alone might work. There is a Russian report about volatile $\text{BeCl}_2$. $\text{AlCl}_3$ complexes (K. N. Semenko et al., Dokl. Akad. Nauk SSSR 154, 648-9 (1963)). Perhaps the $\text{Al}$ in the beryllium complex could be substituted by other trivalent elements such as the rare earths, according to

$$2 \text{RF}_3 + 9 \text{BeCl}_2 + 6 \text{LiF} \rightarrow 2 \text{R(AlCl}_3)_3 + 3 \text{Li}_2\text{BeF}_4$$

(4)

3. It would naturally be of great interest to know as much as possible about the chemistry of these possibly volatile combinations of multivalent halides which we are discussing here. This would include not only other halogens ($\text{Br}$, $\text{I}$) and halides mixed with respect to the halogen as well as to the metallic element, but also the condensed phases, liquid and solid, in equilibrium with the vapor. As coordinatively saturated molecular liquids, they might not be miscible with the fluoride salt melt, so that their use for liquid extraction even is a vague possibility.
4. As in all other processes considered, the greatest difficulty for any application envisaged is, of course, again the very low value of the activity of the rare earth elements specified as tolerable in the fluoride melt.

M. A. Bredig

xc:  E. H. Taylor
     A. M. Weinberg
     M. W. Rosenthal (2)
     R. B. Briggs
     P. R. Kasten
     H. F. McDuffie
     R. E. Thoma
     F. F. Blankenship
     C. F. Weaver
     G. E. Boyd
     H. G. McPherson
     G. P. Smith
     J. H. Frye, Jr.