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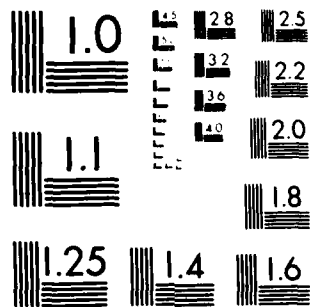
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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) Thermal properties are reported for a variety of materials that have been investigated for their potential application as components of molten sodium tetrachloroaluminate electrolytes, notably fluoroarsenates, fluoroborates and closochloroborates. Effects of catron structure on the stability and spectroscopic properties of tetrachlorocobaltate are also reported.			

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MOLTEN SALT ELECTROCHEMICAL SYSTEMS

Roger K. Bunting

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FINAL
Introduction

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The diminishing availability of conventional energy materials, a consequence of both natural and political phenomena, presents a serious problem to virtually all phases of civilian life and military operations. Energy demands continue to increase. Power sources of improved efficiency and capacity must be developed if these expanding needs are to be met.

The utilization of batteries, both as primary power sources and as load-leveling mechanisms for other power sources, has received considerable attention in recent years. One electrochemical system which has the capacity for high energy density has been shown to be batteries based upon molten salt electrolytes. These systems have been utilized for many years, but only in specialized applications such as thermally activated batteries for ordnance systems, and only as primary batteries operable at relatively high temperatures.¹ At the present time there are no secondary battery systems which utilize molten salt electrolytes.

The utility of aqueous electrolyte systems is severely limited by voltage restrictions imposed by the electrochemical breakdown of water and by the relatively low conductivity of these solutions. Non-aqueous solutions may provide a wider electrochemical potential range, but limitations on ion mobilities still restrict the conductivities of these electrolytes.

Molten salts have extremely high conductivities and, if constituted of electrochemically stable ions, allow a wide range of choice for anode and cathode materials.² Accordingly, this research was undertaken in an effort to

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expand the knowledge of the physical and chemical properties of materials which may prove suitable for application as components of molten salt electrochemical systems.

Previous studies³⁻⁵ have provided a vast body of physical and electrochemical data on sodium tetrachloroaluminate. This report presents the results of some investigations of new materials in conjunction with NaAlCl_4 , as well as some studies on materials unrelated to the tetrachloroaluminate systems.

Experimental Procedure

Apparatus

Moisture or air sensitive materials were handled in a Vacuum Atmospheres dry box under argon. This apparatus was equipped with a molecular sieve drying train through which the argon was continuously circulated, and the moisture level was monitored by a Vacuum Atmospheres Moisture Analyzer AM-2. The system was capable of maintaining a moisture level well below 0.1 ppm. Alternatively, moisture sensitive materials were handled on a standard high vacuum line operating at pressures nominally below 10^{-4} torr.

Thermal stabilities of materials were examined by the monitoring of pressure changes as samples were heated while open to the vacuum system, or by testing on a Perkin-Elmer TGA-2 Thermogravimetric Analyzer with the samples protected from atmospheric moisture by a dry nitrogen flush.

Fusion and other phase changes were determined on a Perkin-Elmer Differential Scanning Calorimeter DSC-1B or DSC-2C with samples sealed in aluminum sample pans, or cooling curves were generated by means of an Omega platinum resistance thermometer Model 199 from which the analog output was fed directly

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into a chart recorder.

Preparation of Salt Melts

Appropriate mole ratios of materials were weighed and combined in a thick-walled Carius tube; the tube was evacuated on the high vacuum line and sealed, then heated in a tube furnace to above the fusion temperature of the mixture. The furnace was placed behind appropriate sheilding and was arranged so that either end could be raised or lowered, in order to effect a back and forth flow of the materials in the molten state. This technique insured a homogeneity of the contents. After cooling the tubes were broken open in the dry box and the contents ground to a fine powder prior to investigation of the phase changes.

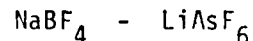
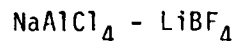
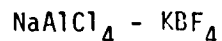
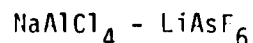
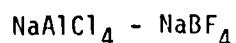
Alternatively, it was found equally effective to weigh appropriate mole ratios of materials into the metal capsule of a "Wiggle Bug" grinding apparatus as designed for the preparation of infrared spectral samples. The contents were shaken in the capsule with a steel ball for a minimum of ten minutes, then a portion of the mixture was sealed into a DSC sample pan and heated to above the fusion temperature. Cooling and reheating on the DSC affirmed the formation of homogeneous mixtures, as well as the reversibility of the phase changes. Exhaustive testing of this procedure demonstrated total reproducibility. Owing to its relative simplicity, most samples investigated in the course of this research were prepared by this latter procedure.

Results and Discussion

Tetrachloroaluminate and Tetrafluoroborate Systems

The following combinations of salts were subjected to a test of their

thermal stabilities by heating under high vacuum as described:



The initial experiments indicated some thermal decomposition (evidenced by gas pressure) in each combination, at temperatures well below the reported decomposition temperatures of the individual components. It was subsequently discovered, however, that when rigorously purified and dried, the tetrachloroaluminate-tetrafluoroborate combinations were sufficiently stable to warrant further investigation.

Potassium tetrafluoroborate was twice recrystallized from distilled water and dried in vacuo at 70°C for 100 hours. Mixtures of KBF_4 and NaAlCl_4 were then prepared as described by adding successive increments of KBF_4 to NaAlCl_4 , up through the composition 55 mole-% KBF_4 . Differential scanning calorimetry was performed on each composition, and these data are shown in Table 1. The data were erratic and non-reproducible at compositions of 60 mole-% and above. A graphical plot of the data is shown in Figure 1.

The irreproducibility of the thermal data for this system in the composition range above 55 mole-% KBF_4 caused considerable concern, and led ultimately to a reinvestigation of the thermal data in the 0 - 55 mole-% range. Though these latter data appear to provide a portion of a well-ordered, typical phase diagram (Figure 1), the differential scanning calorimetry method did not allow a visual observation of the phase change phenomena. Each of the compositions

<u>Sample No.</u>	<u>Mole Fraction KBF_4</u>	<u>Temperature of First Peak</u>	<u>Temperature of Second Peak</u>
1	0.000	---	158
2	0.097	130	145.5
3	0.180	131	134
4	0.220	130	---
5	0.300	130	179
6	0.367	130	217
7	0.495	130	238
8	0.500	---	236
9	0.550	229	278

Table 1. Thermal Data for the $\text{KBF}_4\text{-NaAlCl}_4$ System. Temperatures are in $^{\circ}\text{C}$ and were determined on a Perkin-Elmer DSC-1B

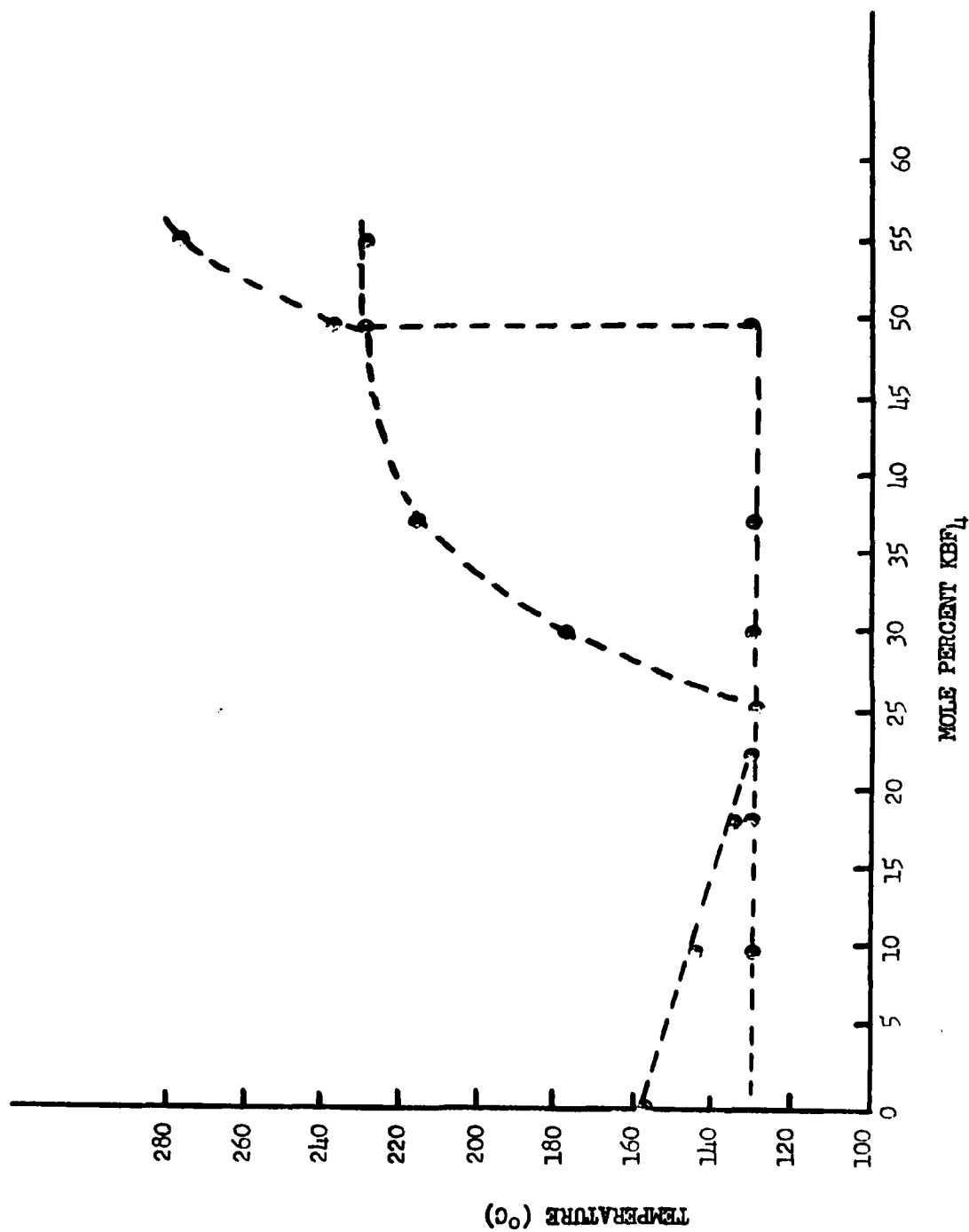


Figure 1. Temperature/Composition Diagram for the NaAlCl₄/KBF₄ System

of Table 1 was therefore reexamined by heating in a glass melting point capillary and observing the mixture as its temperature passed through the region indicated by the DSC as that of the phase change. These experiments revealed that none of the samples actually underwent fusion. An enthalpy change had occurred at the indicated temperatures, as reaffirmed by additional DSC determinations as well as by the method of cooling curves, but in no cases was the enthalpy change associated with melting of the mixture. The exact nature of these enthalpy changes is not known at present, but they may be related to the solid state structural changes of the fluoroborates described below.

Alkali Metal Tetrafluoroborates

The unexpected thermal behavior of the $\text{NaAlCl}_4\text{-KBF}_4$ mixtures prompted a more thorough investigation of the thermal properties of KBF_4 alone. This investigation revealed that there is a solid state phase change in KBF_4 (orthorhombic to cubic, observed microscopically) at a temperature of 286°C .

The remaining alkali metal tetrafluoroborates were examined for similar behavior. Commercial samples of the lithium, sodium and potassium salts were used, while the rubidium and cesium salts were prepared by precipitation from aqueous solutions of fluoroboric acid and the alkali metal bromide. All samples were heated to 60°C in vacuum for 24 hours prior to use.

Except for LiBF_4 , which undergoes decomposition before the phase change, each of the salts gave an endothermic peak (reversible) on the DSC corresponding to the orthorhombic to cubic transition. The enthalpies of these transitions have not been previously reported, and are presented in Table 2.

	<u>Phase change Temperature</u>	<u>ΔH(Cal/g)</u>	<u>ΔH(Kcal/mole)</u>	<u>$\Delta H/T$ (Cal/mole-degree)</u>
NaBF ₄	517°K	14.4	1.58	3.06
KBF ₄	559°K	25.6	3.22	5.76
RbBF ₄	528°K	18.3	3.15	5.96
CsBF ₄	446°K	9.8	2.15	4.82

Table 2. Thermal Data for the Solid State Phase Changes in Alkali Metal Tetrafluoroborates.

The relatively high temperatures at which these phase changes occur suggests that this phenomenon is unlikely to be related to the thermal changes observed in the NaAlCl₄/KBF₄ system. The latter may be the result of exchange of the chloride and fluoride ligands, but inasmuch as these systems appear unsuited for salt melts, they were not further investigated. They will, however, be the subject of investigation at a later date.

Closochloroborate Salts

The closochloroborate salts LiB₁₀Cl₁₀ and LiB₁₂Cl₁₂ have long been known to possess remarkable thermal stability,⁶ and they have more recently been shown to have desirable electrochemical properties when dissolved in thionyl chloride solution.⁷ Commercial samples of each of these salts (Callery Chemical Co.) were dried at 110°C in vacuo for 24 hours. The salts were then mixed with NaAlCl₄ as previously described and subjected to thermal analysis on the

DSC. In each case an endothermic enthalpy change occurred precisely at the melting point of pure NaAlCl_4 . This supports the fact that there is virtually no solubility of the closochloroborates in NaAlCl_4 , and hence these combinations are unsuited for application as a molten salt electrolyte. Visual observation of the mixtures when heated through the melting point of NaAlCl_4 confirmed the lack of solubility of the borates.

Transition Tetrachlorometallates

The transition metal analogs of tetrachloroaluminate, specifically CoCl_4^{2-} , NiCl_4^{2-} and CuCl_4^{2-} , are well established species and have been extensively investigated in aqueous solution. Their solid state properties and their behavior in molten salts have received less attention. The electrochemical properties of these species (e.g., reduction potential) must relate to their structures, and the structures, in turn, relate to the nature of the cation species with which they are associated. Accordingly, an investigation of these materials was undertaken to better understand the structural consequences of the cations, preliminary to any electrochemical application of these species.

Attempts were made to prepare the tetrachlorocobaltate, -nickelate and -cuprate salts of the 2-, 3- and 4-substituted acetylpyridinium cations, since these cations provide a systematic variation in steric effects. The entire series of 2-, 3- and 4-acetylpyridinium salts could be isolated in the anhydrous state only in the case of cobalt, and only this series will be discussed.

The acetylpyridinium chlorides were prepared by bubbling gaseous HCl through acetone-ether solutions of the acetylpyridine. These salts were then added in a 2:1 mole ratio to an ethanol solution of anhydrous CoCl_2 . Refluxing

of these mixtures resulted in the formation of the 2-, 3- and 4-acetylpyridinium tetrachlorocobaltates. The thermal properties of these compounds are recorded in Table 3. Since these compounds have not previously been prepared, their partial elemental analyses are also included in the table. The similarities in the decomposition enthalpies of the three salts shown in Table 3 suggests that the same mode of decomposition occurs in each case.

The infrared spectra of the three tetrachlorocobaltate salts were obtained as reflectance spectra and are presented in Table 4. Each salt shows intense absorption near 300 cm^{-1} , which is assigned to a Co-Cl vibration of an essentially tetrahedral Co(II) species.⁸ However, the shoulders at slightly lower energy on these bands indicate some distortion from perfect T_d symmetry.

Compound	Decomposition Temp. ($^{\circ}\text{C}$)	ΔH Decomp (Kcal/mol)	Analyses		
			C	H	N
$(2\text{-AcPyH})_2\text{CoCl}_4$	142	8.9	Calcd: 37.78	3.62	
			Found: 37.59	3.75	
$(3\text{-AcPyH})_2\text{CoCl}_4$	91	7.2	Calcd: 37.78	3.62	
			Found: 37.80	3.69	
$(4\text{-AcPyH})_2\text{CoCl}_4$	137	7.6	Calcd: 37.78	3.62	6.2
			Found: 37.78	3.67	6.6

Table 3. Thermal and Analytical Data for Tetrachlorocobaltate Salts.

	Band Assignment			
	ν_{PyH^+}	$\nu_{\text{C=O}}$	$\nu_{\text{C=N}}$	$\nu_{\text{Co-Cl}}$
$(2\text{-AcPyH})_2\text{CoCl}_4$	2318s	1707vs	1601s	302vs 295sh 282sh
$(3\text{-AcPyH})_2\text{CoCl}_4$	2325s	1688vs	1598s	301vs 285sh 275sh
$(4\text{-AcPyH})_2\text{CoCl}_4$	2300s	1695vs	1592s	298vs 275m

Table 4. Assignment of Infrared Spectral Bands for Acetylpyridinium Tetrachlorocobaltates. Frequencies are in cm^{-1} .

The electronic spectral parameters for the CoCl_4^{2-} species in these three compounds are given in Table 5, along with the electronic transitions that occur in the cationic species. Table 6 gives the d-d transition assignments and the approximate ligand field parameters for these species. Close agreement is noted between the ligand field parameters for these three salts, and these values are in good agreement with the value of $Dq = 350 \text{ cm}^{-1}$ reported for the quinolinium salt.⁹ The low value calculated for the 4-acetylpyridinium salt suggests a distortion due to the greater steric requirements of this cation rather than a hydrogen bonding effect. But the fact that the ligand field parameters show little variation for these and the quinolinium salts

	$\nu_2(^4A_2 \rightarrow ^4T_1(F))$	$\nu_3(^4A_2 \rightarrow ^4T_1(P))$	Cation Transitions
$(2\text{-AcPyH})_2\text{CoCl}_4$	5.79	15.43sh 14.56 14.04	27.78sh 21.51 18.25
$(3\text{-AcPyH})_2\text{CoCl}_4$	6.12	15.85sh 14.97 14.49sh	29.40sh 22.27 18.87
$(4\text{-AcPyH})_2\text{CoCl}_4$	5.82	15.02sh 14.08 13.61sh	26.32sh 20.83 17.54

Table 5. Electronic Spectra of Acetylpyridinium Tetrachlorocobaltates. Frequencies are in kK.

	$\nu_2(^4A_2 \rightarrow ^4T_1(F))$	$\nu_3(^4A_2 \rightarrow ^4T_1(P))$	$\nu_1(\text{Calcd})$	Dq	B
$(2\text{-AcPyH})_2\text{CoCl}_4$	5790	14,460	3340	334	697
$(3\text{-AcPyH})_2\text{CoCl}_4$	6120	14,840	3530	353	690
$(4\text{-AcPyH})_2\text{CoCl}_4$	5820	14,200	3010	301	661

Table 6. d-d Transition Assignments and Approximate Ligand Field Parameters (in cm^{-1}).

suggests that the electrochemical stability of the tetrachlorocobaltate salts will be little affected by the choice of cation. The significant consequences of the cation may be more a matter of its effect on melting point and thermal stability of such salts. These properties will be the subject of a future investigation.

Publication

A portion of this research effort has been submitted for publication:

"Spectroscopic Investigation of the Tetrachlorocobaltate(II), -nickelate(II) and -cuprate(II) Salts of 2-, 3- and 4-Acetylpyridinium Cations," D. X. West, T. J. Parsons and R. K. Bunting, Inorg. Chim. Acta.

Personnel

The author was assisted in this work by a colleague, D. X. West, and by two undergraduate research assistants, T. J. Parsons and R. B. Ashman.

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