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THE UNIVERSITY OF ALBERTA

STUDIES OF PERCHLORATE AND CHLOROALUMINATE MELTS

by

Ⓒ UDO ANDERS

A THESIS

SUBMITTED TO THE FACULTY OF GRADUATE STUDIES

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The undersigned hereby certify that they have read, and recommend to the Faculty of Graduate Studies for acceptance, a thesis entitled

"STUDIES OF PERCHLORATE AND CHLOROALUMINATE MELTS"

submitted by UDO ANDERS, in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

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Date. July 28, 1969 ...

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PART I

THE ELECTROCHEMISTRY OF FUSED LITHIUM PERCHLORATE

A B S T R A C T

The limiting reactions which occur during electrolysis of fused lithium perchlorate are shown to be

$$Li^+ + e^- \rightarrow Li°$$

and

$$ClO_4^- \rightarrow \tfrac{1}{2}Cl_2 + 2O_2 + e^-$$
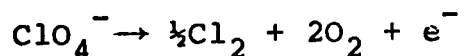
at the cathode and anode respectively. The otherwise explosive reaction between the lithium metal generated and the fused perchlorate was prevented by alloying the lithium with silver. A cathodic peak observed at -1.5 volts with respect to a Ag(I)/Ag(O) electrode is attributed to the reaction

$$ClO_4^- + 2e^- \rightarrow ClO_3^- + O^=$$
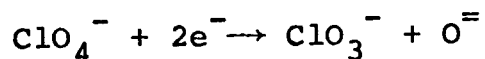
Unlike the analogous peak process observed in fused nitrates, the electron:chlorate ratio is not 2:1 even though the expected 2:1 electron:oxide ratio is obtained. This and other behavior is explained on the basis of an oxide and peroxide-catalyzed decomposition of perchlorate and chlorate.

Attempts were made to anodize metals into the melt; in no case except silver (for which the expected Nernstian behavior was observed) was this possible, oxide formation being generally observed instead.

I N T R O D U C T I O N

The electrochemistry of molten salts has received intense study during the past decade. The increased interest in molten salts as solvents is partly caused by technical development: the application in fuel cells (1,2) is perhaps the most pertinent example at the present time. Mixtures of halides, especially the alkali halides, are generally used as solvents in technical applications due to their easy purification, high stability and wide electrochemical span.

Another important class of anions are the oxyanions. Though not of the same technical importance as the halides they have been of considerable academic interest. The oxyanions most thoroughly investigated were the silicates (3), borates (4), carbonates (5), nitrates (6,7,8), nitrites (9,10,11), sulfates (12) and metaphosphates (13). Their most striking feature as compared to the alkali halides is the appearance of an additional cathodic peak in voltammetry in the current-voltage diagram. Consequently, one will have to discuss the reactions corresponding to the limiting reactions as well as to the cathodic peak when characterizing oxyanions. It will be shown later that the cathodic peak reaction will have a modifying effect on the cathodic limiting reaction.

The anodic limiting reactions of the oxyanions all involve oxygen evolution. The product, besides oxygen, is generally the anhydride corresponding to the aqueous acid of the oxyanion. The following examples can be stated.

The electrolytic oxidation of carbonate was formulated (5) in the following manner:

$$CO_3^{2-} - 2e^- \rightarrow CO_2 + \tfrac{1}{2}O_2$$
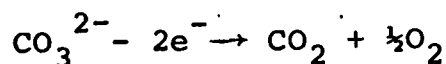
There is, however, a deviation from 100% current efficiency in the above reaction which has been explained on the basis of a simultaneous oxidation of the platinum electrodes:

$$Pt + CO_3^{2-} - 2e^- \rightarrow Pt^{4+} + CO_2 + \tfrac{1}{2}O_2$$
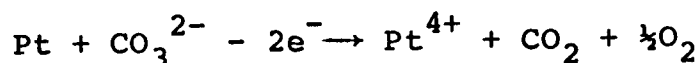
The anodic decomposition for the nitrite was first proposed by Lyalikov and Novik (10) and affirmed later by Swofford and McCormick (9) and also by Calandra and Arvia (11). The anodic process results in the production of NO_2 via

$$NO_2^- - e^- \rightarrow NO_2$$
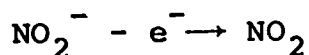
The anodic overall reaction in the case of the nitrates (15) is similarly given by

$$NO_3^- - e^- \rightarrow NO_2 + \tfrac{1}{2}O_2$$
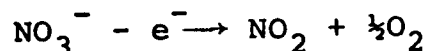
Considerable controversy exists concerning the possible intermediate NO_2^+ (9,15,16,17). Although the existence of the nitronium ion NO_2^+ has been substantiated in

highly acidic aqueous media, it has not been observed directly in molten nitrates. Topol, Osteryoung and Christie (16) could not confirm the presence of NO_2^+ with either voltammetry or chronopotentiometry. Inman and Braunstein (17), on the other hand, reported the detection of it by chronopotentiometric methods. No details, however, were given by the latter authors. No conclusion can apparently be drawn in this matter at this stage.

The anodic limiting reaction in the case of the sulfates (12) was established as

$$SO_4^{2-} - 2e^- \longrightarrow SO_3 + \tfrac{1}{2}O_2$$
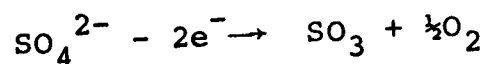
which is very similar to the metaphosphates (13) whose reaction at the anode was given by

$$2PO_3^- - 2e^- \longrightarrow P_2O_5 + \tfrac{1}{2}O_2$$

No quantitative determinations of the electron to products ratio was attempted in most of the cases.

The cathodic limiting reactions are in all cases characterized by the deposition of the cationic melt constituent. These reactions are not stoichiometric in the presence of the oxyanions. This is due to another cathodic process which will be referred to from this point on as the "cathodic peak reaction" because of the sharp peak shown in voltammetry by this reaction.

A few well-established examples for the cathodic peak reactions shall now be mentioned.

The carbonates (5) have been observed to undergo the following reaction at the cathodic peak:

$$CO_3{}^{2-} + 4e^- \longrightarrow C + 3O^{2-}$$
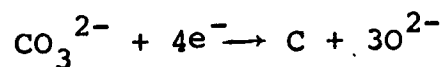
CO and CO_2 have been discussed (5) as intermediates in this reaction.

The first discussion of the cathodic reduction of the fused nitrate anion comes from Hills and Johnson (7). The following reaction schemes were postulated

$$NO_3{}^- + 2e^- \longrightarrow NO_2{}^- + O^{2-}$$

and

$$NO_3{}^- + e^- \longrightarrow NO_2 + O^{2-}$$
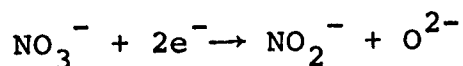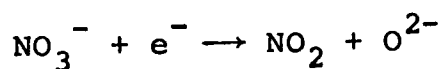
No quantitative analysis of the products was reported. Swofford and Laitinen (6) reinvestigated the nitrate system and arrived at the following equation, in agreement with the equations proposed by Hills and Johnson:

$$NO_3{}^- + 2e^- \longrightarrow NO_2{}^- + O^{2-}$$
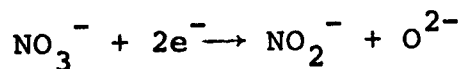
The analytical determinations of the amounts of oxide and nitrite produced by the above reaction were done as follows. The compartment analyzed for oxide was dissolved in water and the hydroxide produced titrated with standard 0.01 M HNO_3 while that to be analyzed for nitrite was dissolved in a standard solution of 0.01 N $KMnO_4$ and back-titrated with a solution of 0.01 N Fe(II). This

was the first procedure used to establish unambiguously the stoichiometry of a typical cathodic peak reaction.

The amounts of oxide and nitrite found (6) corresponded within a few percent to the proposed equation. The electron:nitrite:oxide ratio was close to 2:1:1.

Bartlett and Johnson (8) recently investigated the nitrate system again. They conducted preparative electrolysis at controlled potentials before, at, and after the cathodic peak. While they agreed with Swofford and Laitinen (6) that the main reaction was due to the formation of nitrite and oxide they proposed three additional side reactions:

$$NO_3^- + 3e^- \rightarrow NO + 2O^{2-}$$
$$NO_3^- + 5e^- \rightarrow \tfrac{1}{2}N_2 + 3O^{2-}$$
$$NO_3^- + 8e^- \rightarrow N_2O + 5O^{2-}$$
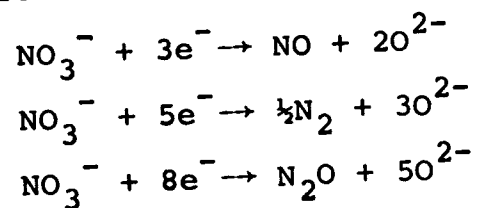
No analytical details, however, were given for the characterization of the gaseous products.

In the case of the nitrites it has so far only been shown that NO was one of the products (8) when an electrolysis was performed at the cathodic peak. Heavy corrosion of the platinum electrodes seems to have been responsible for the lack of further information.

The metaphosphates (13) undergo reaction at the cathodic peak in the following manner:

$$4PO_3^- + 5e^- \rightarrow P + 3PO_4^{3-}$$
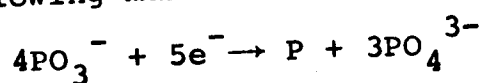
This reaction deviated from the ones before in that no oxide seemed to be formed. However, it is well known (13,18,19) that oxide reacts with PO_3^-:

$$2PO_3^- + O^{2-} \rightarrow P_2O_7^{4-}$$

$$P_2O_7^{4-} + O^{2-} \rightarrow 2PO_4^{3-}$$
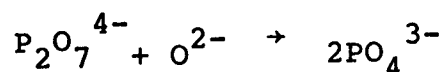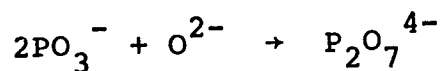
and one can therefore formulate the initial reaction as

$$PO_3^- + 2e^- \rightarrow PO_2^- + O^{2-}$$
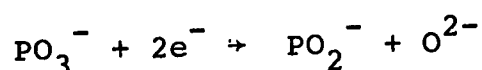
The species PO_2^-, like CO and CO_2 in the case of the carbonates, is an unstable species under the experimental conditions. It is further reduced to phosphorus which is now stable:

$$PO_2^- + 3e^- \rightarrow P + 2O^{2-}$$
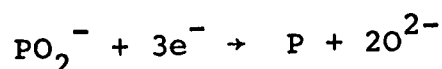
The sulfates are known to yield sulfur, sulfide, and oxide (12,14).

As can be seen it is not possible to give a general mechanism for the cathodic peak reaction. Only the primary production of oxide which may, however, as in the case of metaphosphates, undergo further reaction with the oxyanion is observed in all systems.

Since the limiting reaction occurs at a more cathodic potential than the cathodic peak reaction these two processes will occur simultaneously. This means that not only is the cation, generally an alkali metal, deposited in a pure form as in the case of the halides but at the same time oxide and other breakdown products of the

oxyanion may be co-deposited. If metal ions other than those being melt constituents have to be deposited and if their deposition potential happens to lie between the cathodic peak and the limiting reaction then there will be impurities co-deposited with the metal. A typical illustration of this fact (12) is the co-production of NiS and NiO when deposited from a solution of Ni(II) in molten sulfate:

$$SO_4^{2-} + 5Ni^{2+} + 8e^- \longrightarrow NiS + 4NiO$$
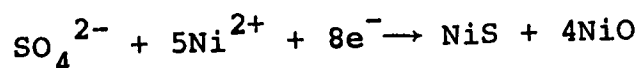
While this process would be unwanted in the case of deposition of pure nickel the same process can be sought after in special cases. The production of a layer of GaP on pure Si (20) is such an example in which GaP was deposited from a solution of Ga(III) in a bath consisting mainly of $NaPO_3$. No attempt was made to formulate the overall reaction.

The oxyanions discussed so far were those of group IVA, VA and VIA elements. Molten oxyanions of group VIIA elements on the other hand have hitherto received very little attention. The only electroanalytical investigations reported concern the double layer capacity of the mercury - electrolyte interface in molten $LiClO_4$-$NaClO_4$ (21), the formation of the chloride complexes of lead and cadmium in molten $LiClO_4$ (22) and the solubility product of silver halides in molten $LiClO_4$ (23). The authors of the last paper used a Ag(I)/Ag(0) reference electrode and showed that the Ag(I)/Ag(0) couple displayed

Nernstian behavior in molten $LiClO_4$ when Ag(I) was added as $AgNO_3$. No direct coulometric generation of Ag(I) from silver was apparently attempted.

The only study of the electrochemistry of the solvent $LiClO_4$ itself was made by Johnson and Denning (24). These authors observed gas evolution on passage of current at a platinum cathode together with the deposition of black material. They also mentioned the explosive tendency of the cathode compartment which they ascribed to elementary lithium being formed behind an oxide layer and coming into contact with molten lithium perchlorate when the oxide layer fell away.

Apart from the molten state $LiClO_4$ has been the object of studies in organic media. Maki and Geske (25) electrolized a 0.1 M solution of $LiClO_4$ in acetonitrile and obtained from the anode compartment an ESR signal which they assigned to a $\cdot ClO_4$ radical. Both Cl^{35} and Cl^{37} have a nuclear spin of 3/2 which, in the case of the $\cdot ClO_4$ radical, gives rise to four equally spaced lines. No Hyperfine structure due to the two different chlorine nuclei was observed because of line broadening. The number of radicals present in a steady state at an electrolysis current of 3 mA was estimated at 5×10^{16} spins. The radical was scavenged finally by the solvent with regeneration of the ClO_4^- anion.

Cauquis and Serve (26) reinvestigated the electrolysis of $LiClO_4$ in the different solvent nitromethane and essentially confirmed the earlier results of Maki and Geske.

E X P E R I M E N T A L

Solvent

The perchlorates of group IA elements and ammonium are white crystalline solids. $LiClO_4$ alone has a well defined melting point. The others decompose upon melting or within a very short temperature range of the melting point.

The heats of formation of the metal perchlorates are very nearly the same as the heats of formation of the corresponding chlorides (27). The reaction

$$MClO_4 \rightarrow MCl + 2O_2$$

thus takes place with little net energy change (27).

Lithium perchlorate stands out among the perchlorates as being the only one that is stable in the molten state. It melts without decomposition at 247°C and does not begin to show an appreciable decomposition rate until the temperature is raised over 400°C (28). All experiments reported in this part were done at 260°C ± 10°C.

$LiClO_4$ is fairly hygroscopic. Its molar heat of hydration (29) is 14.2 kcal/mole and the water of hydration is extremely difficult to remove. Berglund and Sillen (30) found that some water remained in the sample held at 300°C for 12 hours. The $LiClO_4$ used in the present study was anhydrous reagent grade (Amend

Chemical Company). While it was dried under high vacuum for 3 days at 150°C, 100 - 150 ml of water were collected per kilogram melt. The procedure of drying the salt below its melting point was found to be more effective (31) than trying to remove the water from the melt. It was then melted and purged with dry chlorine for 30 minutes to remove any remaining oxidizable impurities (32); during this time the original dark melt became completely clear. This process was followed by nitrogen purging for 12 hours in order to remove the chlorine from the system. During the experiments nitrogen purging was kept up at a slow rate in order to keep the melt free from traces of water. The initial chloride content was in the range of 2×10^{-4} moles/kg melt. It did not increase to more than 1×10^{-2} moles/kg melt during the time of the investigations as shown by argentometric titration.

Apparatus

The cell (Figure 1) consisted of a Pyrex vessel with 24/40 and 14/20 standard taper joints. Pyrex feed-through tubes to which sintered glass disks of D porosity (Ace Glass Co., Vineland, N.J.) were fused served as isolation compartments. Holes in the feed-through wall above the melt level maintained equal pressure between the compartments and cell. The electrodes, each of which was kept in a separate isolation compartment, were silver wires

FIGURE 1

Fused Perchlorate Cell

A, silver wire (reference electrode);

B, pressure equalization vent;

C, metal wire for anodization, or micro-
   electrode;

D, silver wire (working electrode);

E, melt surface;

F, porous glass disk.

$\overline{\underline{S}}$ 14/20

$\overline{\underline{S}}$ 24/40

$\overline{\underline{S}}$ 14/20

A
B
C
D
E
F
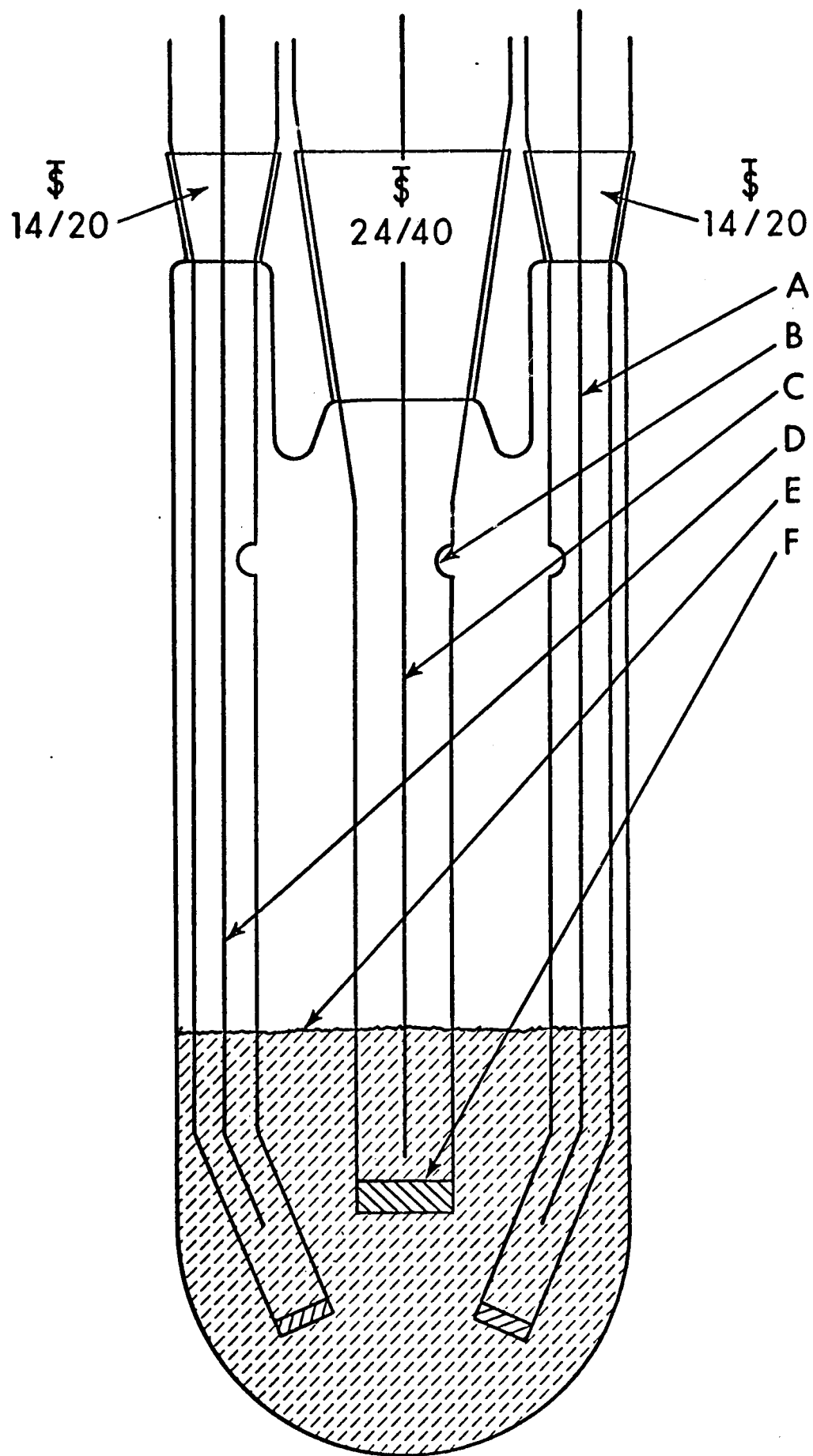
(reference and working electrodes), other metal wires (for anodization studies), and platinum microelectrodes. The heating unit consisted of a heating mantle and a heating tape regulated by variable transformers. For mass spectrometric samples, a Pyrex U-type cell (Figure 2) was constructed in which the anode and cathode compartments were separated by a sintered glass disk. The two electrodes were connected to tungsten leads sealed through the compartment tops. The cathode was a massive silver electrode while platinum served as the anode. Tubes leading through liquid nitrogen traps to a vacuum manifold were connected to both electrode compartments.

The voltammetric scans were performed with an Anotrol Model 4100 Potential Controller (Magna Electronics) using a platinum microelectrode, sealed in glass and ground flush, of 0.9 mm^2 geometrical area. An Anotrol 4510 Scan Unit was used in combination with a EUW-20A (Heath Co.) multispeed recorder. A model IV Coulometric Current Source (E. H. Sargent and Co.) was used for the anodization of metal electrodes.

Chemicals

The Li_2O (Alfa Inorganics, Inc.), Na_2O_2 (calorific grade, Allied Chemical), $LiClO_4 \cdot 3H_2O$ (reagent grade, G. F. Smith Chemical Co.), and KOH (analytical grade, British Drug Houses) were used as received. Samples of $LiNO_3$ (Alfa Inorganics, Inc.), $KClO_3$ (reagent grade,

FIGURE 2

U-type Cell

A, mass spectrometer tube;

B, tungsten wire;

C, seal;

D, connection from tungsten to electrode metal;

E, melt surface;

F, porous glass disk.

TO VACUUM

TO VACUUM

₹ 14/20

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A
B
C
D
E
F

x
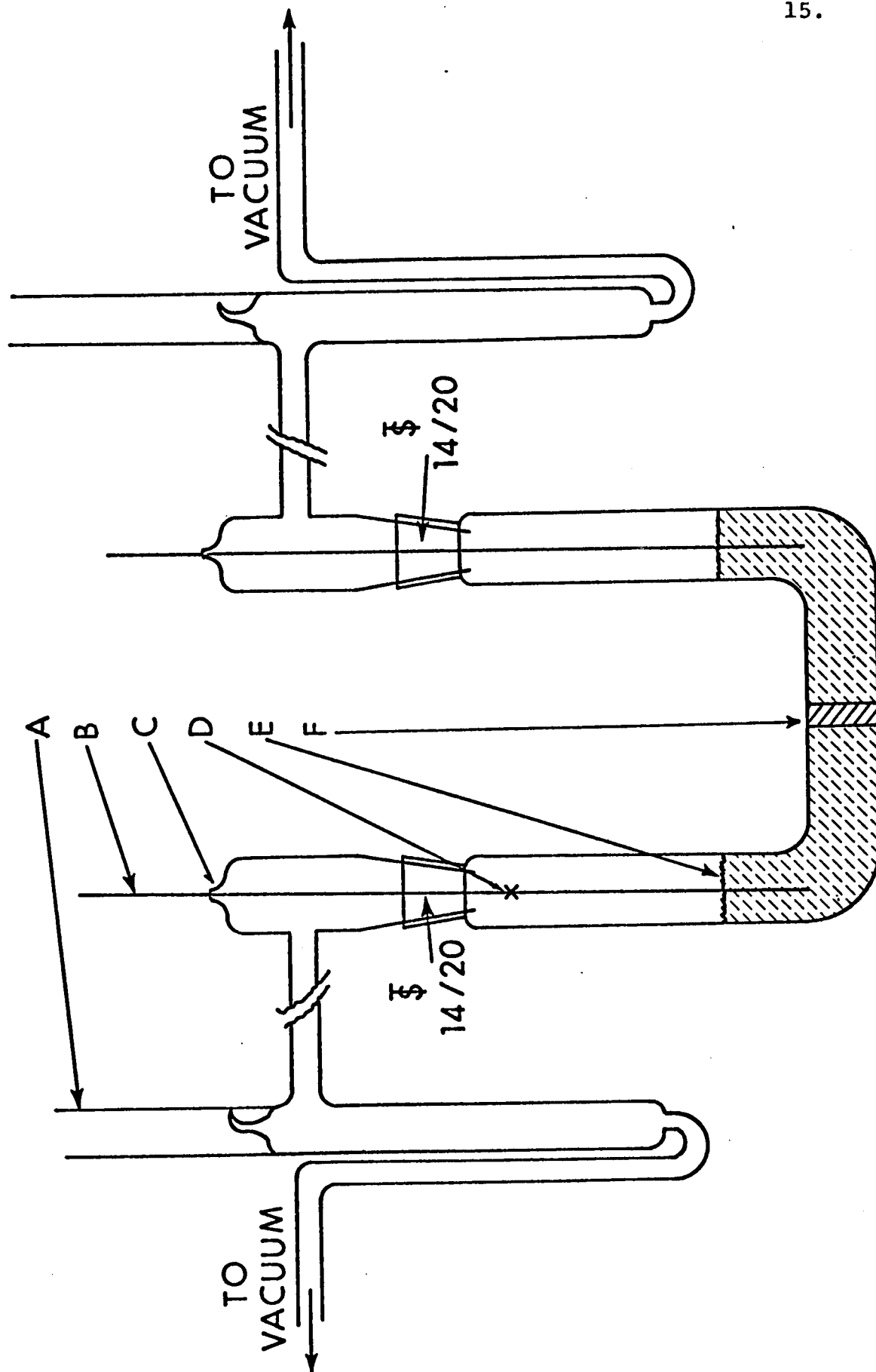
Nichols Chemical Co.), and $KHSO_4$ (reagent grade, Fisher Scientific) were vacuum-dried over magnesium perchlorate before use. Metal wires were cleaned mechanically and dried with acetone before use.

Procedure

A reference electrode based on the Ag(I)/Ag(O) couple (about 0.2 molar or 0.1 molal) was generated coulometrically for each experiment, and all potentials in this paper are given with reference to this electrode. Nernstian behavior corresponding to a one-electron change was observed for silver in this solvent on oxidation and reduction, in agreement with the work of Bombi and co-workers (23). Oxide was determined by acidimetric titration of the hydroxide formed after hydrolysis of the contents of a compartment, and chloride was determined by conventional argentometric titration. The method of Chen (33) was used to determine small amounts of ClO_3^- in the presence of large amounts of ClO_4^-; the same method indicated the absence of ClO_2^- and ClO^- in all samples.

R E S U L T S   A N D   D I S C U S S I O N

Voltammetric scans of the pure $LiClO_4$ melt with a platinum microelectrode gave the curve shown in Figure 3. At the anode the limiting electrode reaction occurs at +1.7 v, the rising portion being spread out over approximately 0.3 v. The cathodic limiting reaction occurs at -2.7 v. There is an additional cathodic peak at -1.5 v.

The cathodic limiting reaction is the deposition of lithium metal. Since pure lithium metal reacts explosively with the lithium perchlorate solvent (24) and since cathodic lithium deposition was inevitable during the investigation, it was necessary to reduce the activity of the lithium formed to as low a value as possible. It was found that alloy formation with silver served well for this purpose provided large enough silver electrodes and low enough current densities were used; current densities were approximately 0.1 amp/cm^2 and the total charge approximately one meq/cm^2. This alloy formation reduced but did not completely halt the reaction between lithium and the melt; gentle gas evolution was continuous and the amount of lithium found in the silver was less than that calculated from coulombs passed. Platinum and tungsten electrodes did not show as large a capacity for lithium metal and explosions occurred with both.

POTENTIAL
vs.
Ag(I)/Ag REFERENCE, VOLTS
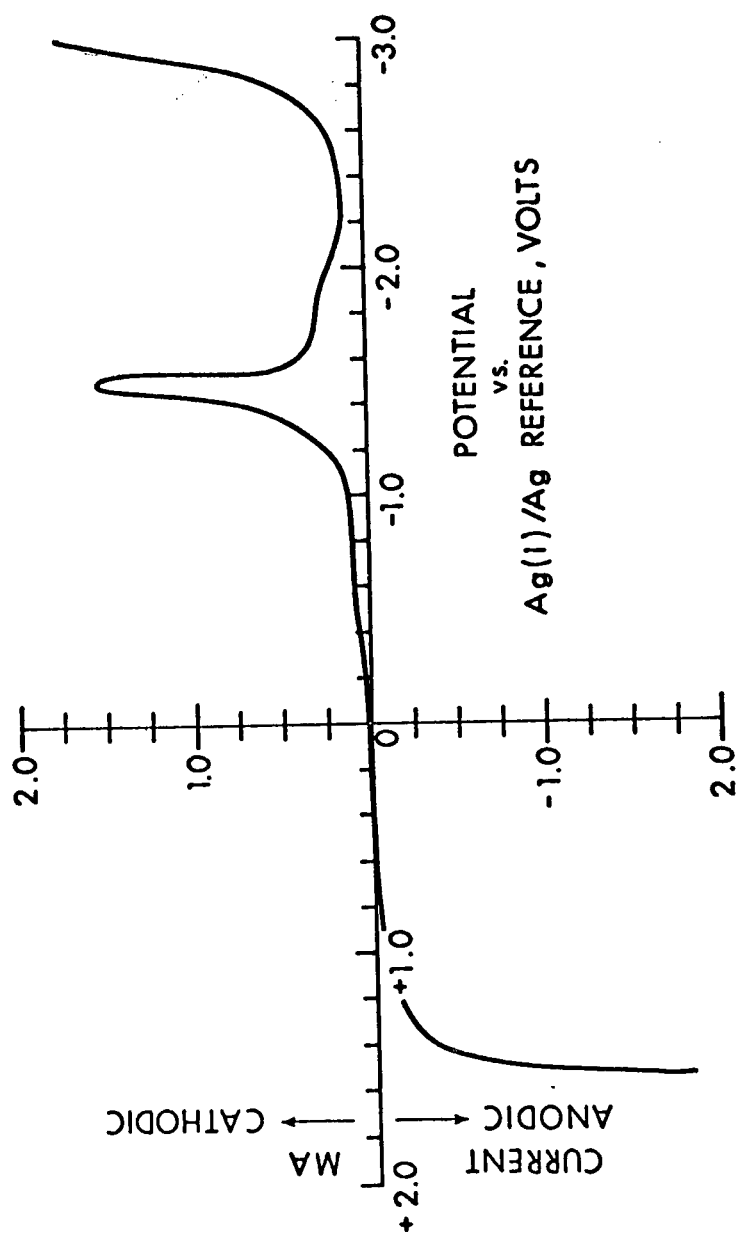
Figure 3. Voltammogram of fused lithium perchlorate. Platinum microelectrode, geometrical area 0.9 mm^2.

The overall process for the anodic limiting reaction appears to be

$$ClO_4^- \longrightarrow 2O_2 + \tfrac{1}{2}Cl_2 + e^-$$
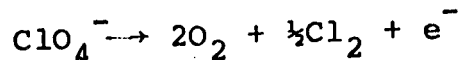
The slow curvature of the voltammogram as the anodic limiting process begins to occur may indicate an irreversible reaction (34) or other complication. The gases produced at the anode during electrolysis of pure $LiClO_4$ in the U-type cell (Figure 2) were pumped off under vacuum and trapped with liquid nitrogen. Mass spectrometric analysis on a MS-9 spectrometer (Associated Electrical Industries) showed no fragments containing Cl-O bonds. Only chlorine was detected.

There is a very small but reproducible wave at $E_{\frac{1}{2}} = -0.5$ v, which by analogy with nitrate systems (35) is probably due to residual traces of water. Except for this, the only voltammetric feature visible between the anodic and cathodic limiting reactions was a cathodic peak at -1.5 v. This appeared similar to the peak observed in fused nitrates. The nitrate peak was interpreted (6,8,9) as due to the process

$$NO_3^- + 2e^- \longrightarrow NO_2^- + O^{2-}$$
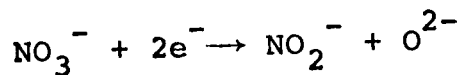
In nitrate melts the ratio $e^-:NO_2^-:O^{2-}$ was found to be 2:1:1. In a perchlorate melt the analogous process would be

$$ClO_4^- + 2e^- \longrightarrow ClO_3^- + O^{2-}$$
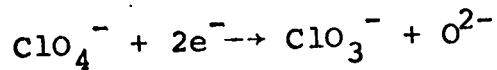
When compartments of fused $LiClO_4$ were electrolyzed at

the peak potential of -1.5 v, the $e^-:O^{2-}$ ratio found was

2.1 (std. dev. 0.2) to 1.0. No reproducible $e^-:ClO_3^-$

ratio was observed, although comparison of the IR spectra

(Perkin-Elmer 337, Nujol mull) of electrolyzed and un-

electrolyzed $LiClO_4$ revealed a new band at 970 cm^{-1} which

(by comparison with a known sample of $KClO_3$) is due to the

ClO_3^- ion (36). Chloride ion was also always present as

shown by reaction with silver nitrate.

Attempts were made to determine the source of the

peak by addition of reagents. Addition of H^+ (as $KHSO_4$)

or OH^- (as KOH) produced no apparent change in the peak.

Addition of ClO_3^- (as $KClO_3$) also produced no change in

the peak, indicating that it could not be due to the

reaction

$$ClO_3^- + 2e^- \rightarrow ClO_2^- + O^{2-}$$
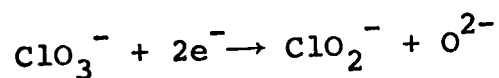
in fact, this reaction does not seem to occur within the

decomposition range of the melt. Addition of H_2O

(as $LiClO_4 \cdot 3H_2O$) showed a small increase in the peak and

violent evolution of water vapor.

The similarity between the cathodic peak observed in

this study and those observed in nitrate melts (6,8)

suggested the possibility of similar thermal equilibria

in nitrate and perchlorate melts,

$$NO_3^- \rightleftarrows NO_2^- + \tfrac{1}{2}O_2$$

and

$$ClO_4^- \rightleftarrows ClO_3^- + \tfrac{1}{2}O_2$$
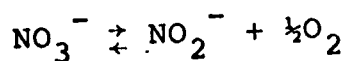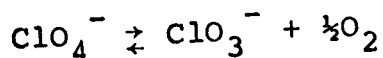
both producing oxygen. The dissolved oxygen formed might then be the material which undergoes electrochemical reduction,

$$\tfrac{1}{2}O_2 + 2e^- \rightarrow O^{2-}$$
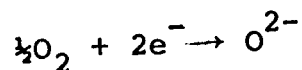
explaining the 2:1 electron:oxide ratio. However, although addition of NO_3^- (as $LiNO_3$) increased the cathodic current in the peak region, careful examination indicated that the NO_3^- and ClO_4^- peaks were different although quite close in potential (Figure 4), so that they in fact correspond to different processes. These peaks are not, then, due to dissolved oxygen. To prove this, the melt was saturated with dry oxygen gas; this had no effect on the height or position of the peak.

The major difficulty in the assignment of the peak to the

$$ClO_4^- + 2e^- \rightarrow ClO_3^- + O^{2-}$$
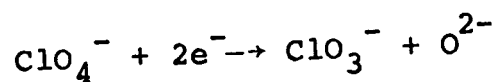
reaction was clearly that no consistent $e^-:ClO_3^-$ ratio was found for the electrolysis of fused $LiClO_4$, unlike the nitrate melts in which the expected 2:1 ratio was obtained. Chlorate was always present but generally in amounts less than expected (Table I). Decomposition of the perchlorate solvent would cause inconsistent $e^-:ClO_3^-$ ratios as observed, chlorate being an intermediate in the decomposition, and also account for the observed chloride. Since the expected ratio of $e^-:O^{2-}$ was obtained, oxide could not be
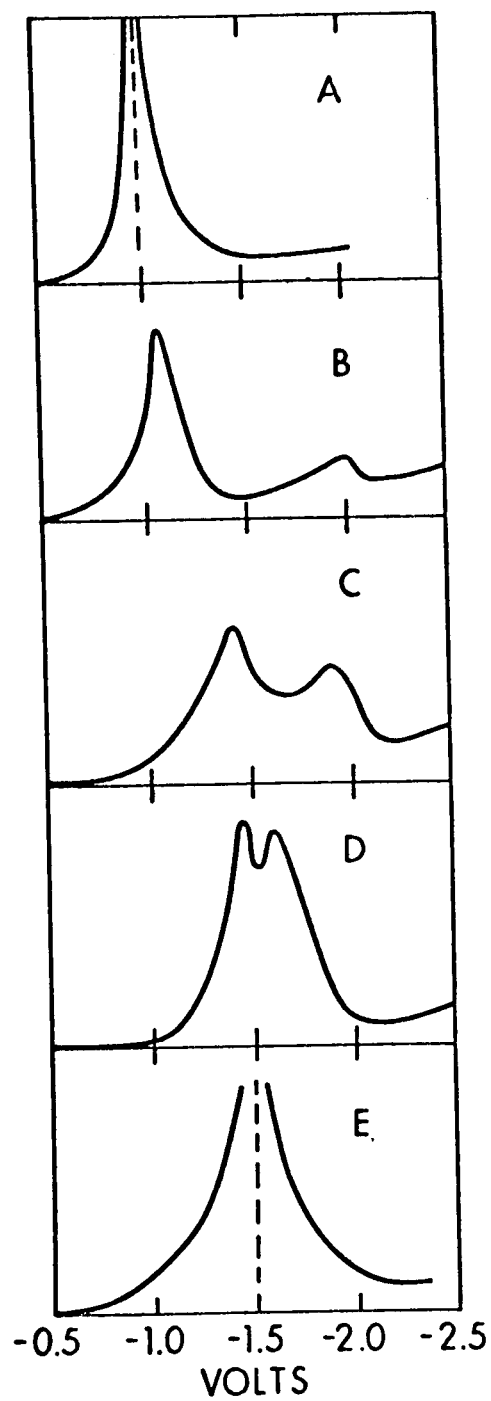
Figure 4. Voltammetric peak detail. A, pure
LiNO₃; B, C, D, LiClO₄ with decreasing
amounts of LiNO₃; E, pure LiClO₄.

TABLE I

STOICHIOMETRY OF CATHODIC PEAK

mequivalents electricity	mmoles OH^-	mmoles ClO_3^-	mmoles Cl^-
0.34		0.024	
0.90		0.023	
0.013		0.012	
3.3	2.9		1.6
3.4			3.0
3.4			4.1
3.1	2.8		1.7
1.8			0.38
1.7	1.8	1.25	0.27
1.4	1.2	0.29	0.22
1.8	2.0	0.70	0.31
1.8	1.8	3.7	0.28
0.26	0.27		0.040

generated or used by this decomposition process; if involved, oxide must act as a catalyst. The gas evolved during electrolysis is therefore the oxygen produced by the oxide-catalyzed decomposition of chlorate and perchlorate to chloride. To test this, O^{2-} was added (as Li_2O); obvious decomposition began at once and continued for at least 12 hours. Since the addition of OH^- (as KOH, which seems highly soluble in fused $LiClO_4$) did not induce the catalytic decomposition, water was added (as $LiClO_4 \cdot 3H_2O$) to samples in which obvious decomposition was occurring. Gas evolution ceased immediately, as would be expected if the decomposition were oxide-catalyzed; the addition of water would remove the oxide:

$$H_2O + O^{2-} \longrightarrow 2OH^-$$
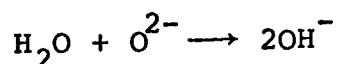
Additional evidence for an oxide-catalyzed decomposition is that the freshly generated oxides of magnesium and aluminum produced as discussed below also catalyzed melt decomposition although to a much lesser degree. It is well known that addition of metal oxides produces decomposition of both chlorate and perchlorate melts to chloride (28,37,38).

The catalytic decomposition which sets in after the O^{2-} is formed could occur by the following mechanism:

$$ClO_4^- + O^{2-} \longrightarrow ClO_3^- + O_2^{2-}$$

$$ClO_3^- + O^{2-} \longrightarrow ClO_2^- + O_2^{2-}$$

$$ClO_2^- \xrightarrow{\text{fast}} Cl^- + O_2(g)$$

$$2O_2^{2-} \longrightarrow 2O^{2-} + O_2(g)$$

$$\text{net:} \quad ClO_4^- \longrightarrow Cl^- + 2O_2(g)$$
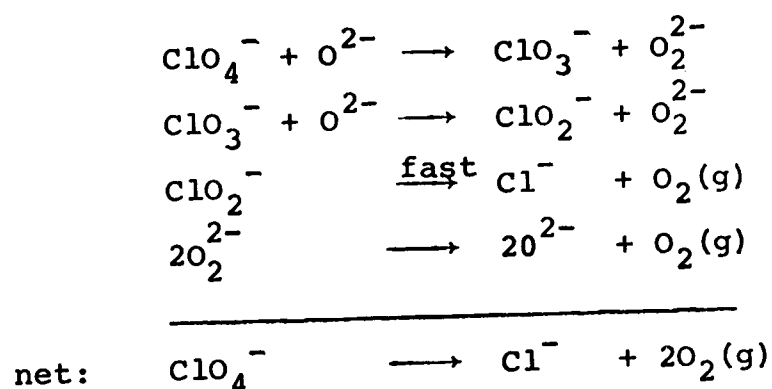
The postulated peroxide intermediate has been found in heated samples of $LiClO_4$-Li_2O by Markowitz and Boryta (28). Addition of peroxide (as Na_2O_2) to the $LiClO_4$ melt induced immediate obvious decomposition as expected. It was also demonstrated that the reaction

$$4ClO_3^- \longrightarrow 3ClO_4^- + Cl^-$$
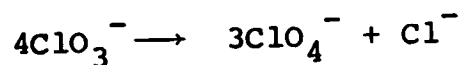
does not occur at an appreciable rate in the absence of oxide at this temperature; the addition of 250 mg of $KClO_3$ to a compartment containing approximately 5 g of fused $LiClO_4$ did not result in any chlorate decomposition at 260°C after six hours, as shown by analysis.

A peculiarity of fused $LiClO_4$ is that other than silver no metals could be anodized to form the corresponding ions. The fact that metals cannot be anodized into solution has also been found in the case of the nitrate melts. By addition of transition metal nitrates and chlorides to a nitrate melt a few metal ions could be brought into solution (39). This approach was not

possible in fused $LiClO_4$; all added transition metal nitrates or chlorides produced oxides immediately. Some of the metal-metal oxide couples are of relatively stable potential; for example Mg/MgO at -2.1 v with a fluctuation of 40 mv over a period of hours. Some typical potentials of metals in contact with $LiClO_4$ melt are listed in Table II.

Most metals form visible oxide layers with the exception of rhodium, iridium, and platinum which do not appear to form oxide layers even at high current densities. The behavior of the different metals tested is summarized in Table II. The behavior of thallium was unusual; the area of metal exposed to air formed black oxide as expected, while the area of metal exposed to the melt remained bright. On anodization, thallium was visibly lost from the wire, the surface remaining bright. Nernstian behavior was not observed; the potentials assumed after successive anodizations were stable but no reproducible Nernst slopes could be obtained, values of n ranging from 1.6 to 2.9. Analysis of the hydrolyzed melt for thallium (40) gave an e^-:Tl ratio of about 1:1. This behavior would suggest the formation of a thallium oxide soluble in fused lithium perchlorate.

The reason for this oxide formation with most

TABLE II

METAL BEHAVIOR IN FUSED LITHIUM PERCHLORATE

Metal	Potential against Ag(I)/Ag (volts)	Oxide Formation (without current)	Oxide Formation (with current)
Mg	-2.1	massive	massive
Al	-0.4	film	massive
Ti	unstable	film	film
V	unstable	film	massive
Fe	unstable	massive	massive
Co	+0.4	massive	massive
Ni	+0.4	massive	massive
Cu	unstable	massive	massive
Zn	-0.7	massive	massive
Zr	unstable	film	massive
Nb	unstable	film	massive
Mo	unstable	film	massive
Rh	unstable	none	noble
Pd	unstable	thin film	film
Ag	0.0(def.)	none	forms Ag^+
Cd	-0.5	massive	massive
W	unstable	film	film
Re	unstable	dissolves	dissolves
Ir	unstable	none	noble
Pt	unstable	none	noble
Au	unstable	none	thin film*
Hg	unstable	none	massive
Tl	-1.4	none	see text
Pd	-1.0	massive	massive
U	unstable	massive	massive

* only at high current density; otherwise noble.

metals could well be the lower solvation energy of
metal ions in fused perchlorates (and presumably also
fused nitrates) as compared with fused chlorides (41)
in which anodization of many metals is successful. To
gain stabilization which is not available from the
poorly-coordinating perchlorate anion, the metal cation
presumably adds oxygen by breaking Cl-O bonds in a
neighboring ClO_4^- anion.

C O N C L U S I O N

The electrochemical behavior of $LiClO_4$ is analogous to that of other molten salts containing oxyanions i.e., it showed in addition to the anodic and cathodic limiting reactions an additional cathodic peak. The reaction at this peak was shown to be

$$ClO_4^- + 2e^- \rightarrow ClO_3^- + O^{2-}$$
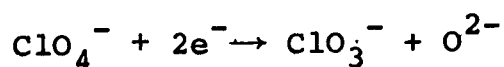
The generated oxide attacked the ClO_4^- anion, contrary to the stability of oxide ion in other oxyanion melts. A peroxide intermediate was proposed for the decomposition of ClO_4^- to chloride.

The cathodic peak reaction superimposed on the cathodic limiting reaction when the cathode was at the limiting potential. The lithium oxide produced shielded the simultaneously deposited lithium metal from solvent attack. Interruption of the current reduced the lithium oxide concentration in the immediate vicinity of the electrode and the lithium metal reacted vigorously with the solvent. Alloying with silver metal electrodes prevented this spontaneous reaction between lithium metal and the perchlorate ion.

No reversible metal ion/metal couples besides silver could be realized. This was explained by the poor coordination stabilization given by the perchlorate anion. The metal ions will break Cl-O bonds and become

stabilized by oxide ions. This behavior of metal ions greatly diminishes the usefulness of lithium perchlorate as a solvent in electrochemical investigations. Furthermore, oxide ions from the glass containers decomposed the melt slowly, which resulted in a continuous increase in the chloride concentration. This makes the solvent unfit even for a study of chloride complexes.

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PART II

THE ELECTROCHEMISTRY OF GROUP IB AND IIIA METALS IN

FUSED $AlCl_3$-NaCl-KCl EUTECTIC

A B S T R A C T

The electrochemistry of copper, silver, gold, gallium, indium, thallium and their ions, and of chlorine and bromine in fused $AlCl_3$-NaCl-KCl was investigated by e.m.f. and voltammetric techniques. Univalent oxidation states were observed for all of the metals. In addition, copper was further oxidized to the divalent species while gallium and indium were oxidized to trivalent species. The standard potentials for the above couples were established in the $AlCl_3$-NaCl-KCl eutectic at 135°C.

I N T R O D U C T I O N

Despite the fact that aluminum metal has been pro-
duced electrochemically for over 80 years little effort
has been directed towards a systematic study of the
haloaluminate melts. The understanding of the physical
chemistry and electrochemistry of the fluoroaluminates
and the chloroaluminates is far from being complete (1).
While the fused fluoroaluminates are of great importance
in the production of aluminum (1), it has recently been
found (2-12) that chloroaluminate melts have a surpris-
ingly strong tendency to stabilize low valence states
of metals.

This behavior will be the concern of this and the
following part of this thesis. Part II deals especi-
ally with the electrochemical generation and character-
ization of low valence states of group IB and IIIA metal
ions in the ternary $AlCl_3$-NaCl-KCl eutectic. The physical
data of this system have been summarized in detail
before (3) and will not be repeated here.

L. F. Yntema and coworkers (13-17) were the first
to investigate the possibilities of the ternary $AlCl_3$ -
NaCl-KCl eutectic as a solvent for metal ions 25 years
ago. The low melting point of this eutectic was first
found by Wasilewski, Kaczorowski and Dynkin in 1934 (18).

Yntema's first paper (13), however, led to

erroneous conclusions because of the reference electrode used. It consisted of a platinum wire inserted into the melt. It was argued that the sum of the potential drops from anode to reference electrode and reference electrode to cathode was equal to the potential difference between anode and cathode. Then the reference electrode to cathode potential drop, as extrapolated to zero current, was assumed to be determined by the reaction at the cathode.

While this argument is basically correct, a reference electrode of this type has severe practical disadvantages. The main objection comes from the undetermined potential at which the reference electrode is held. The potential determining species will be melt impurities and therefore probably be of low concentrations. An electrode of this type will be very susceptible to concentration polarization, even at very low current densities. A further disadvantage of a reference electrode of this type is that the reference electrode will not necessarily be stable even at negligible polarization from one experiment to the other nor will it be reproducible in another run. Consequently, the discrepancies between the deposition potentials quoted in the first paper (13) and the following (14), in which he used the now well-established Al(III)/ Al(O) (2,3) reference electrode, were quite large; e.g., for copper 0.85 V (13) and 0.66 V (14).

Yntema's interests apparently lay mainly in the electro-deposition of metals from their ions dissolved in chloroaluminate melts, and little attention was paid to other effects. In group IB he studied the deposition of copper from added CuCl (13,14) and of silver from added AgCl (14). In group IIIA gallium was deposited from a solution of Ga_2O_3 in the ternary eutectic (17). Although TlCl was dissolved in the bath (17) he observed neither oxidation nor reduction of the Tl(I) which led him to the erroneous conclusion that TlCl must be highly insoluble in the melt eutectic.

While this thesis agrees basically with Yntema's findings in the case of group IB, it was found that Yntema's interpretation concerning group IIIA metals and their ions were not correct. It was not known at this time that gallium has a stable plus one oxidation state. Accordingly, when Ga(III) was added to the melt and gallium deposited at the cathode the presence of Ga(I) as an intermediate was not recognized although the current voltage curve displayed one well-defined additional break at high current densities. It is now known that gallium metal reacts with gallium trichloride to form $Ga[GaCl_4]$, a complex containing equal amounts of Ga(I) and Ga(III). Excess gallium metal does not undergo further reaction with this complex unless aluminum trichloride is added (19); under these circumstances the $GaCl_4^-$ ion reacts until all Ga(III) is

reduced to Ga(I). The resulting complex has the formula $Ga[AlCl_4]$.

Thallous chloride, as will be shown later, is soluble in the melt contrary to Yntema's conclusions but it is not electrochemically active.

The metals investigated in this study were those of group IB and IIIA, thus extending the previous work in this field done by D. A. Hames and J. A. Plambeck (2, 3). The latter authors have shown (2,3) that in the ternary $AlCl_3$-NaCl-KCl zinc exists in the plus two oxidation state while cadmium and mercury exist in both the plus one and plus two oxidation states. The electrochemical techniques of potentionmetry, voltammetry and chronopotentiometry were used to study dilute solutions of these ions.

The numerical findings of Hames and Plambeck (2,3) were highly precise. But several disagreements between different investigators seem to exist. The value of the equilibrium constant for example of the reaction

$$Cd(II) + Cd(0) \rightleftharpoons 2Cd(I)$$
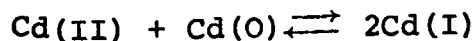
was reported by Hames and Plambeck as 3.6×10^4. Corbett and coworkers (7) found a value of 1.71 ± 0.11 on the basis of spectroscopic studies. However, solvent and temperatures used were not identical in the two studies. While Hames

and Plambeck used the ternary $AlCl_3$-NaCl-KCl eutectic (66 mole % $AlCl_3$, 20 mole % NaCl, and 14 mole % KCl) at 135°C, Corbett and his group used the system $NaAlCl_4$ - 7.7 mole % $AlCl_3$ at 350°C. A qualitative interpretation of the differences would have to invoke the concept of acid stabilization (3,20,21) which will be presented in detail in Part III. Furthermore, it would be expected that the temperature difference of 200°C would also decrease the equilibrium constant observed by Hames and Plambeck because the thermal energy would weaken the metal-metal bond.

Another point of discrepancy is the zinc ion/zinc electrode. T.C.F. Munday (5) and the author of this thesis observed drifting potentials when zinc ions were produced by coulometric oxidation of zinc into the melt. Munday used the $NaAlCl_4$ - 5 mole % $AlCl_3$ system. Contrary to this, Hames and Plambeck (2,3) found the couple to be well-behaved. Their Nernst plot resulted in a straight line with a slope of n = 2. Their current densities used for the anodization were comparable to those of this thesis.

Discrepancies in the potentiometric data of the silver ion/silver electrode were found between this thesis and the work of Hames and Plambeck (2,3) and Corbett's school (4,5). This was very unexpected since no deviating behavior for the reaction

$$Ag(I) + e^- \rightarrow Ag(0)$$
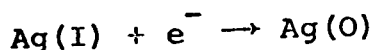
has been reported for   Ag(I)/Ag(0) before in fused salts or other solvents. Indeed the Ag(I)/Ag(0) couple was the only one which could be realized in the fused $LiClO_4$ system (22).

At this point the question of solvent purity and reproducibility arises. But as will be discussed later in detail it appears at the present time that melt impurities cannot be responsible for the observed behavior. Certain drifting potentials in molten chloroaluminates have been encountered by all workers (2-5) and in all cases this has had physical significance.

Corbett and his school (4) were the first to interpret the potential drifts in terms of complexation of the metal ions with one another. It has been shown that the $CdCl_2$/Cd system gave rise to subvalent cadmium species whose existence could be substantiated by magnetic (23), Henry's Law (24) and cryoscopic (25) studies as well as electrochemical methods (24,26). However, an uncertainty in the solute arises in all of these cases from the general inability to determine the amount of metal consumed in dilute solutions where ideal solution laws may be expected so apply. Only measurements concerning solute mobility (27,28) in this system suggest that the produced species is charged. On the other hand, a specific solute

is indicated by studies in the $CdCl_2$-$AlCl_3$ system. Besides, the introduction of $AlCl_3$ does not seem to alter the production of the subvalent species (4-6).

Reduction of divalent lead (4) resulted in a species Pb^+ (indistinguishable with the experimental methods from Pb_2^{3+}, Pb_3^{5+} etc.). In the case of tin the product of the reaction appeared to be Sn_2^+ (again indistinguishable from Sn_2^{3+}, Sn_4^{5+} etc.).

No rational explanation has so far been found for the drifting potentials in the case of the zinc electrode (5).

The bismuth ion has been studied extensively (6-12). The low valence states found corresponded to Bi^+, Bi_4^{4+}, Bi_5^{3+} and Bi_8^{2+}.

Austin, Vucick and Smith (29) suspected a Mn(I) species in a melt consisting of 80% $AlCl_3$, 10% NaCl and 10% KCl. It is, however, not clear from their text how the Mn(I) could have been generated from the added Mn(II). A reasonable interpretation might be that their anode consisted of aluminum metal which may then have reduced Mn(II) to Mn(I).

E X P E R I M E N T A L

The electronic instrumentation and electrochemical cell used have been described previously (2). The metals for the electrode were obtained in wire form from A. D. MacKay (New York, N.Y.) and were of 99.99% purity. Anhydrous $GaCl_3$ and $InCl_3$ were produced from the pure metals and chlorine gas (30). Anhydrous InCl was purchased from Alfa Inorganics (Beverly, Mass.). Reagent grade $AlCl_3$, NaCl and KCl (Fisher Scientific Co.) were used. The purification procedure used for the aluminum chloride in this investigation was less cumbersome than that previously reported (2) and allowed the preparation of a new melt for each experiment. In this procedure 250 g of aluminum chloride were placed in a closed-end Pyrex tube 40 cm long and 5 cm in diameter, which was fitted with a 6 cm O-ring joint. The aluminum chloride was covered with a 1 cm thick layer of granular aluminum metal (reagent grade 30 mesh, Fisher Scientific Co.). The tube was flushed with nitrogen and closed with a Pyrex cap which had a 4 mm stopcock on top; this was open to a mercury pressure relief valve during the sublimation. The vertical tube was heated by an external heating mantle and heating tape which extended to the height of the aluminum layer. A tubular ring with pin holes pointing inwards fitted loosely over the sublimation tube. Compressed air was blown through it to cool the tube and prevent condensation

of subliming aluminum chloride in the upper half of the tube. It was positioned approximately 10 cm down from the glass joint. The aluminum chloride condensed over a length of 7-10 cm as a colorless, crystalline solid. After nearly complete sublimation the closed tube was cooled and transferred into a glove box filled with dry nitrogen. The glass tube was then broken to obtain the solid aluminum chloride. The lower part of the crystal-lized aluminum chloride cylinder was generally discarded due to baked-in granular aluminum.

The aluminum chloride obtained by the above pro-cedure was a crystalline material pure white in color. It was ground, transferred into a tightly stoppered flask, removed from the glove box, weighed and returned to the glove box in which all further work was done. After addition of the appropriate amounts of sodium chloride and potassium chloride, the mixture was melted in a round bottomed flask and transferred into the electrochemical cell previously described (2). It was observed that the color of the melt varied from a faint yellow to light brown with the temperature employed during this initial melting process. The cause of the coloration in unknown. It has been suggested that it is due to carbon from organic material (31,32) or dissolved silicon compounds (33). The present author has observed,

however, that chlorine or hydrogen chloride also produce melt darkening, and for that reason these gases could not be used in the melt purification.

An aluminum wire spiral was added to the melt for one hour in order to reduce any metal ion impurities.

Reference Electrode

All potentials were measured with respect to an aluminum wire inserted into the melt. The use and non-polarizability of this reference electrode have been described (2). All measurements were made at $135° \pm 1°C$ rather than at $150°C$ (2), to keep evaporation of the aluminum chloride to a minimum during the experiments.

Metal-Metal Ion Electrodes

The compartments consisted of 10C sealing tubes (Ace Glass Inc., Vineland, N.J.) which were inserted into the melt and allowed to fill to the melt level. The metals were inserted as wires except in the case of gallium which is a liquid at this temperature. Here a spoon-like Pyrex cup was used which was attached to the end of a glass tube. A platinum wire which did not come in contact with the melt led to the bottom of the cup which was filled with liquid gallium metal and then inserted into the compartment.

Gas Electrodes

The chlorine electrode employed a compartment consisting of a 10D sealing tube extended to 20 cm and closed on top. A tungsten wire was sealed through the top and reached to the frit, parallel to a glass tube of 5 mm O.D. which served as a feed-in tube for chlorine gas and which also entered the compartment near the top. A second tube on top of this half cell was used as a gas outlet. The chlorine gas was dried over phosphorus pentoxide before being fed through Teflon tubing to the electrode.

Chlorine gas was first bubbled through the melt rapidly to saturate the melt and displace the nitrogen above it. Then time was allowed for the melt to reach thermal equilibrium, until the potential became stable within 1 mV. It was ascertained by several more small additions of chlorine and successive equilibrations that the melt was truly saturated with chlorine gas.

The bromine cell differed from the above by an additional 10/35 standard taper joint on top into which a small dropping funnel containing liquid bromine was fitted. At first a total of 5 ml of bromine were added in small portions to saturate the melt with bromine as well as to replace the nitrogen above it by bromine vapor. Bromide ion was produced by coulometric reduction of bromine in the compartment at a tungsten electrode operated at low current densities. The melt was occasionally

checked for bromine saturation by addition of small
amounts of bromine as described above for the chlorine
electrode.

R E S U L T S and D I S C U S S I O N

In order to report standard potentials the standard
states must be defined. The standard states used in this
work are: gases, 1 atm. pressure; elements and compounds,
pure element or compound in the most stable form at the
temperature used; species which are melt constituents (or
are linked to a melt constituent by a non-electrochemical
equilibrium, such as Al(III), the form in which they
actually exist in the pure melt; species which are not
melt constituents, unit concentration on a specified
concentration scale (e.g., one molar) but with the
properties of the species at infinite dilution in the
solvent melt. This definition agrees with those used for
other melts (34). Under these conditions the standard
and measured potentials of the Al(III)/Al(0) electrode
are the same, and all standard or measured potentials in
this paper are given with respect to this electrode.
These potentials, on the molar, molal, and mole fraction
concentration scales, are given in Table 1. All conform
to the IUPAC "Stockholm" sign convention, and all have
positive sign. tolerances given are standard deviations.

Chlorine

To establish the potential span of the melt in terms
of standard potentials the e.m.f. of the Cl_2/Cl^- couple
was measured precisely. Yntema and co-workers (13,14)
reported a value of 2.09 $\pm$ 0.04 V for this couple at 156°C.

TABLE I

Electromotive Force Series in $AlCl_3$-NaCl-KCl at 135°C

Couple	$E°_{molar}$	$E°_{molal}$	$E°_{m.f.}$	standard div.
Al(III)/Al(0)	0.000	0.000	0.000	defined[a]
Ga(I)/Ga(0)	0.199	0.222	0.276	0.002
Zn(II)/Zn(0)	0.254[b]	0.263[b]	0.304[b]	0.002
Ga(III)/Ga(0)	0.577[c]	0.585[c]	0.603[c]	0.002
Cu(I)/Cu(0)	0.689	0.710	0.745	0.002
Ag(I)/Ag(0)	0.695	0.719	0.802	0.001
Ag(I)/Ag(0)	0.740[b]	0.759[b]	0.832[b]	0.001
Ga(III)/Ga(I)	0.766	0.766	0.766	0.002
Hg(I)/Hg(0)	1.028[b]	1.037[b]	1.077[b]	0.001
In(III)/In(I)	1.1	1.1	1.1	0.15
Hg(II)/Hg(0)	1.22[b,c]	1.231[b,c]	1.271[b,c]	0.002
Cu(II)/Cu(0)	1.278[c]	1.288[c]	1.306[c]	0.002
Hg(II)/Hg(I)	1.415[b]	1.424[b]	1.464[b]	0.002
Br_2/Br^-	1.768	1.785	1.631	0.002
Cu(II)/Cu(I)	1.866	1.866	1.866	0.001
Au(I)/Au(0)	2.022	2.046	2.119	0.002
Cl_2/Cl^-	2.064	2.064	2.064	0.002

[a] defined as 0.000 at all temperatures in this melt.

[b] measured at 150°C; Ref. (2)

[c] calculated from free energies of experimentally measured couples.

Treadwell and Tereberi (35) found 2.062 V at 721 mm Hg

and 135°C in a slightly different ternary system (62

mole % $AlCl_3$, 26 mole % NaCl and 12 mole % KCl). The

temperature dependence, as measured vs. an Al(III)/Al(0)

reference electrode, at a platinum electrode was -0.72

mV/°C. Kher and Mene (36), in using the $NaAlCl_4$ system,

found the temperature dependence of the anodic decompo-

sition potential to be 0.982 mV/°C. The temperature

range extended from 200 to 660°C. Graphite anodes and

cathodes were used.

The present study reports a standard potential of

2.064 ± 0.002 V at 135°C and 1 atm. The standard and

measured potentials for the couple are the same under

the standard state definitions given above. The temper-

ature dependence of the electrode was measured from 120°

to 180°C as -0.65 ± 0.03 mV/°C. No hysteresis was observed.

The potential separation on a molal basis of the

Al(III)/Al(0) and Cl_2/Cl^- couples in the LiCl-KCl melt

is 2.073 V with a temperature dependence of the Cl_2/Cl^-

electrode vs. a Pt(II)/Pt(0) electrode of -0.334 ± 0.008

mV/°C (34,37). No direct comparison is possible between

the values for the two standard potentials, however, due

to the different definitions of the standard states of

the Al(III) ions.

Identical potentials were obtained for chlorine in

the $AlCl_3$-NaCl-KCl melt with carbon and tungsten electrodes.

It must be noted that the carbon electrodes disintegrated slowly upon contact with the melt to give carbon powder. This, however, did not give rise to an observable change in potential. Apparently this disintegration, which also occurs in the melt in the absence of chlorine, is due to the high content of aluminum trichloride since carbon electrodes have been used successfully in the $NaAlCl_4$ melt (4). However, Russian reports (38) do mention disintegration of graphite electrodes in $NaAlCl_4$.

The observation that a briefly shorted chlorine electrode would return to the previous equilibrium potential inside a few seconds led to a closer investigation of this phenomenon. The cell used was as described previously with a 1/8 inch O.D. graphite electrode. The temperature of the cell was maintained at 154 ± 1°C. Chlorine gas was passed over the electrode surface at an originally slow rate i.e., one bubble/5 seconds. The flow was speeded up to one bubble/second after 70 minutes when it became apparent that the gas flow could not keep up the potential (Figure 1). A 1 ohm resistor was connected across the cell and the voltage dropped across it was measured with a digital voltmeter. Figure 1 shows the current-time dependence of this cell.

The amount of electricity passed during this period was calculated as 187 coulomb. Using a value of 17.5 mA for an average current over the 3 hour period an average power dissipation of 0.3 mW results.
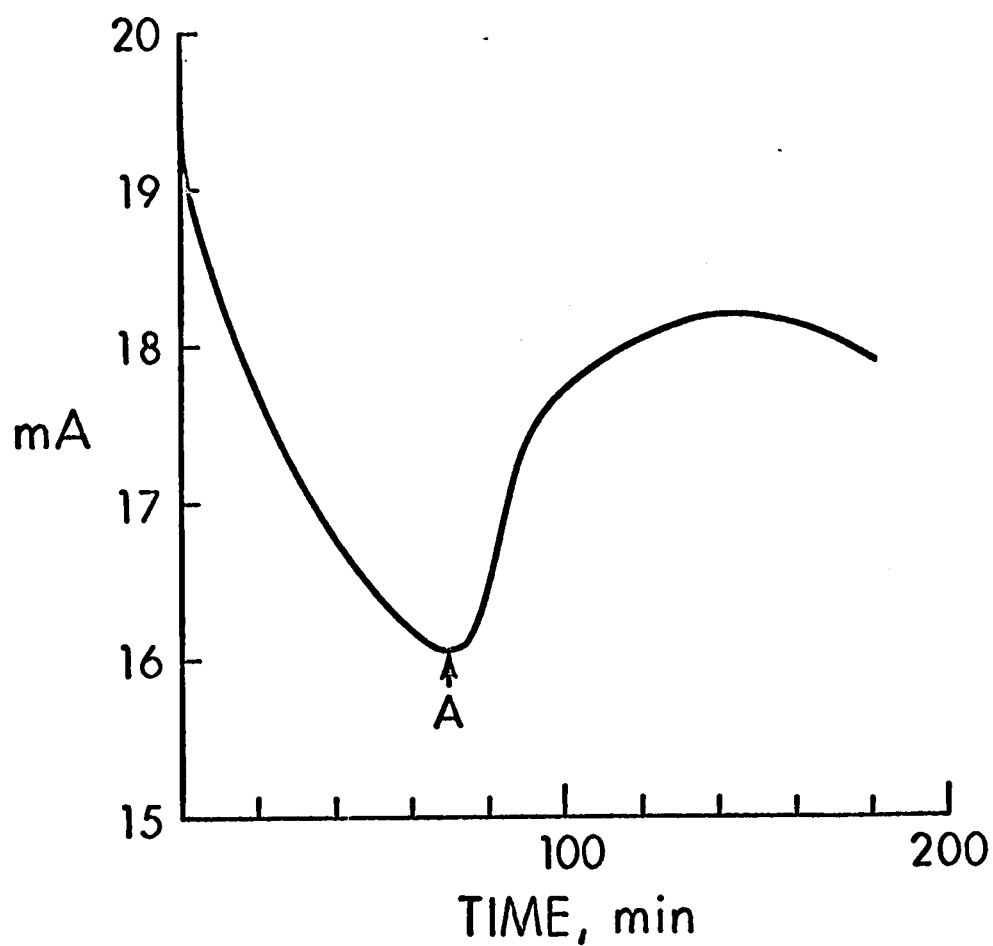
Figure 1.   Time-current dependence of the chlorine
fuel cell.   At A the chlorine flow was
increased fivefold.

The graphite electrode disintegrated nearly completely during the 3 hour period. It is for this reason that no exact current density can be given for the electrode. The original geometrical area was 3.6 cm^2 which results in an estimated initial average current density of 4.9 mA/cm^2.

The above data show that the chlorine electrode has features which make it promising as a fuel cell. Since the aluminum electrode which serves as a counter electrode is highly reversible and since the Al(III) concentration is very high no polarization occurs at this electrode. The only polarization this fuel cell experiences is concentration polarization at the chlorine electrode.

Bromine

The molal standard potential of the Br_2/Br^- couple was found to be 1.785 $\pm$ 0.002 V at 135°C and 1 atm. The temperature dependence of this couple was measured as -0.16 $\pm$ 0.03 mV/°C from 120° to 170°C. From the published data on the bromine electrode (34,37) one can calculate the separation between Al(III)/Al(O) and Br_2/Br^- in the LiCl-KCl melt to be 1.897 V. The temperature dependence of the bromine electrode has not been established in the LiCl-KCl melt.

Gallium

Gallium metal was anodized at low current densities to form Ga(I) (Fig. 2). The Nernst plot indicated a slope
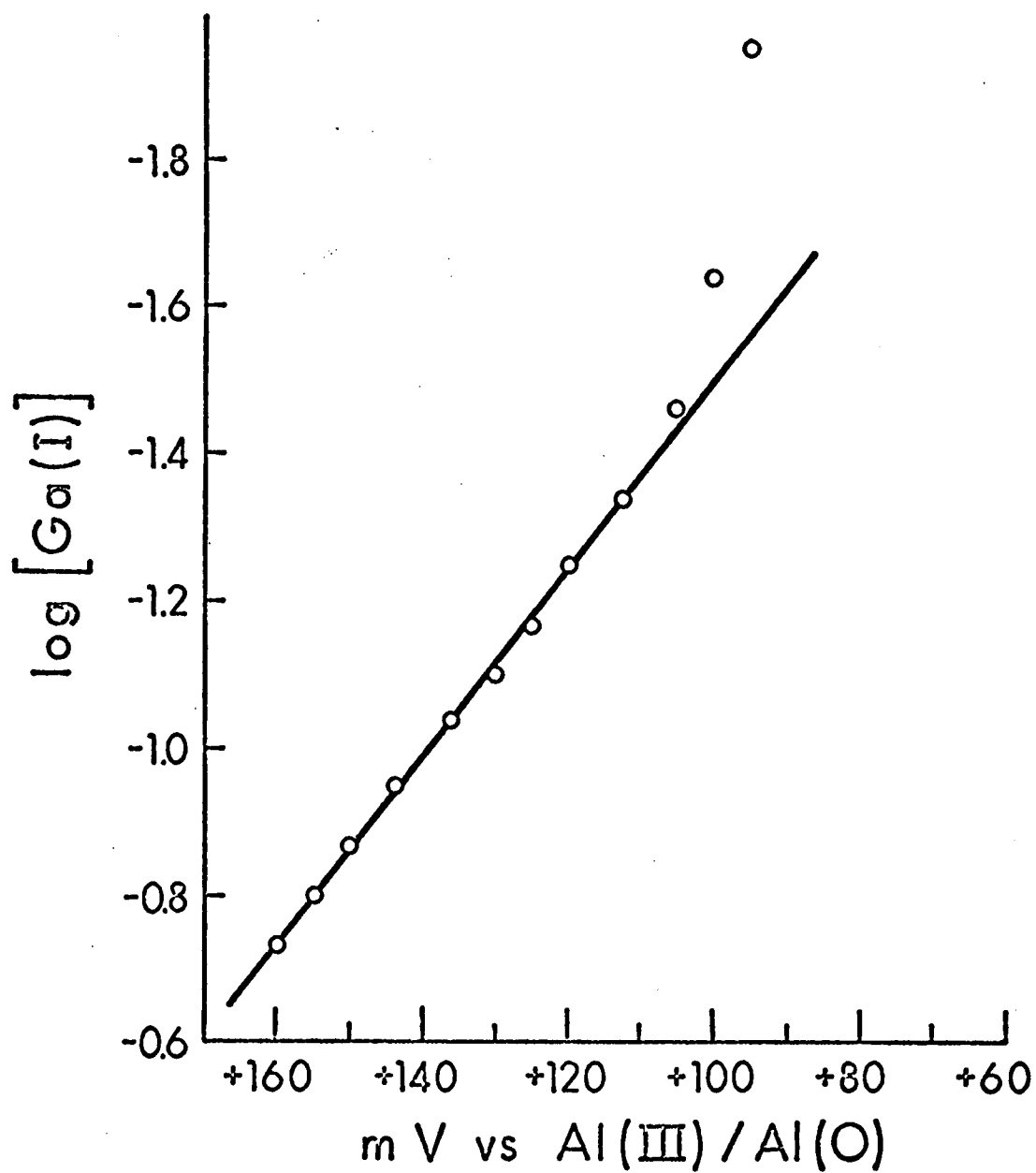
Figure 2.   Nernst plot for the Ga(I)/Ga(O) couple.
Typical run, concentration on molal
basis.

of 81 mV/log unit for this process, corresponding to
1.0 ± 0.1 electrons. The molal standard potential was
0.222 ± 0.002 V. Voltammetry with an inert tungsten
electrode indicated the presence of an anodic wave cor-
responding to the oxidation of Ga(I). Quantitative
coulometric oxidation at a platinum electrode at 5 mA/cm^2
showed this to be a two-electron process. The plot of
log [Ga(I)]/[Ga(III)] vs. e.m.f. (Fig. 3) resulted in a
straight line whose slope corresponded to 2.2 ± 0.1
electrons. A standard potential of 0.766 ± 0.002 V was
measured at equal concentrations of Ga(I) and Ga(III).

With these data it is possible to calculate the
equilibrium constant. If the equilibrium reaction is
defined as 1/2Ga(III) + Ga(0) $\rightleftharpoons$ 3/2Ga(I), which involves
a change of one electron, K = 5.0 x 10^6 (Table 2). The
equilibrium constant is in molal units and given by
K = [Ga(I)]$^{3/2}$/[Ga(III)]$^{1/2}$.

Figure 4 shows two voltammetric curves of gallium
solutions which were obtained with a tungsten microelect-
rode. Curve A represents the result of a scan of a
solution approximately 0.1 molal in Ga(I) while Curve B
was obtained at equal concentrations of Ga(I) and Ga(III),
about 0.5 molal.

Curve A, starting close to the Al(III)/Al(0)
potential and scanning towards more oxidizing potentials,
produces first a cathodic wave corresponding to the
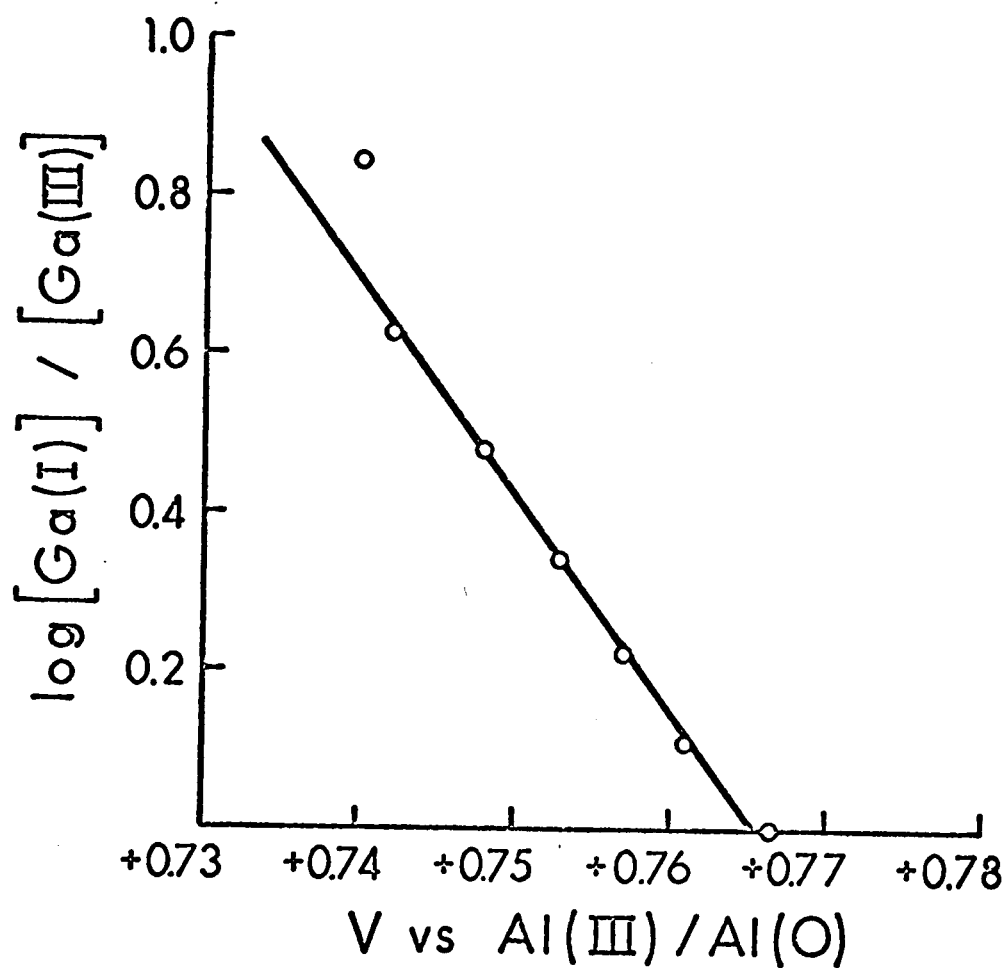
Figure 3. Nernst plot for the Ga(III)/Ga(I) couple. Typical run, concentration on molal basis, obtained by coulometric reduction of Ga(III) at platinum electrode.

TABLE II

Equilibrium Constants for Group IB, IIB and IIIA Elements

Equilibrium	$AlCl_3$-NaCl-KCl	LiCl-KCl 450°C (a)	H_2O, 25°C
Cu(II) + Cu(O) $\rightleftharpoons$ 2Cu(I)	2.1×10^{14}	7.1×10^{6}	5.9×10^{-7} c
Ag(II) + Ag(O) $\rightleftharpoons$ 2Ag(I)	$>3 \times 10^{12}$	$>3 \times 10^{7}$	1×10^{20} c
1/2Au(III) + Au(O) $\rightleftharpoons$ 3/2Au(I)	$>2 \times 10^{-20}$	$>4 \times 10^{-1}$	3.4×10^{-2} c
Zn(II) + Zn(O) $\rightleftharpoons$ 2Zn(I)	very small	very small	very small
Cd(II) + Cd(O) $\rightleftharpoons$ 2Cd(I)	2.6×10^{1}	very small	very small
Hg(II) + Hg(O) $\rightleftharpoons$ 2Hg(I)	3.6×10^{4}	–	1.6×10^{2} c
1/2Ga(III) + Ga(O) $\rightleftharpoons$ 3/2Ga(I)	5.0×10^{6}	–	3.0×10^{-10} b
1/2In(III) + In(O) $\rightleftharpoons$ 3/2In(I)	$>4 \times 10^{13}$	–	1.9×10^{-6} b
1/2Tl(III) + Tl(O) $\rightleftharpoons$ 3/2Tl(I)	$>4 \times 10^{25}$	–	2.3×10^{27} b

(a) Ref. (34)

(b) Ref. (40)

(c) Ref. (43)
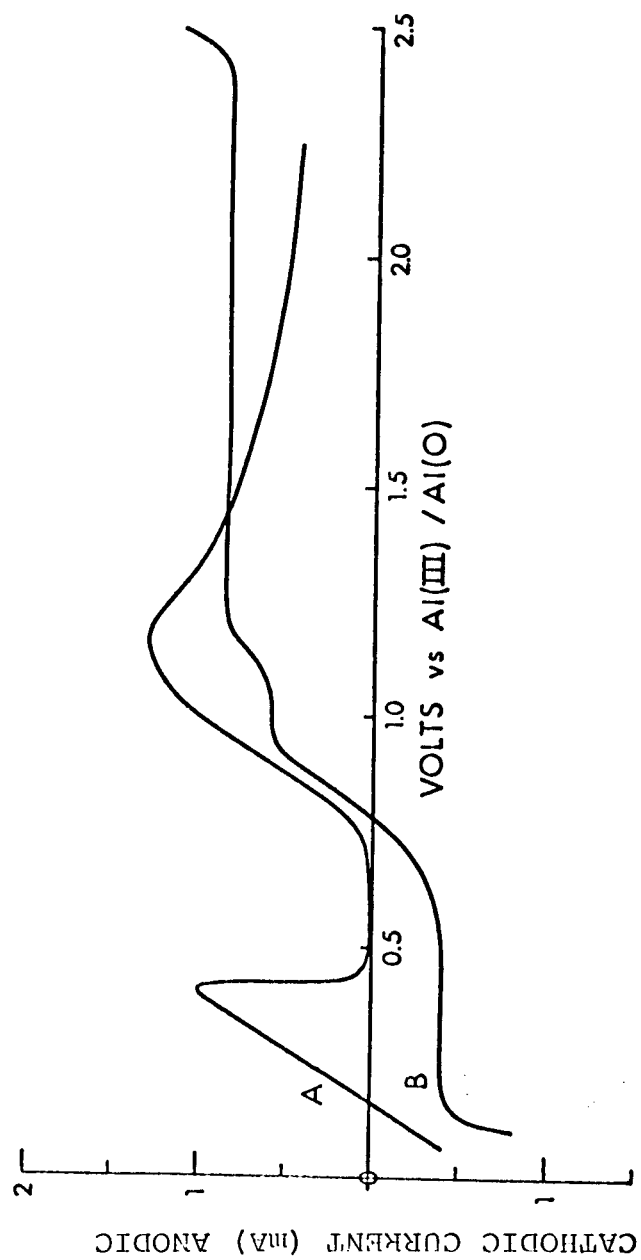
Figure 4. Voltammetry of gallium ions. A, 0.1 molal Ga(I),
0.04 V/sec; B, 0.05 molal Ga(I), 0.05 molal
Ga(III), 0.02 V/sec. Tungsten microelectrodes,
scan direction toward positive potential.

deposition of gallium metal at the tungsten electrode. The tungsten is covered rapidly with gallium and thereafter behaves like a gallium electrode. Curve A passes through the zero current axis at 0.16 ± 0.01 V which is in good agreement with the equilibrium potential of the Ga(I)/Ga(O) couple, 0.160 ± 0.002 V.

The deposited gallium metal is stripped off at potentials more oxidizing than this equilibrium value, giving rise to the observed anodic current. After the stripping is complete the current drops back to zero. The area under this anodic wave is equal to the area under the preceding cathodic wave because the amounts of gallium deposited and stripped off are equal. As shown by the coulometric oxidation mentioned above, Ga(I) is oxidizable to Ga(III); this oxidation begins at approximately 0.7 V on Curve A. This peak is slightly broader than those usually observed voltammetrically (39) but this is due primarily to the IR drop. As will be seen later Curve B shows waves rather than peaks.

Curve B of this figure shows a scan of a solution containing equal concentrations of Ga(I) and Ga(III). As with Curve A, gallium metal is deposited at the tungsten electrode:

$$Ga(I) + e^- \longrightarrow Ga(O) \tag{1}$$
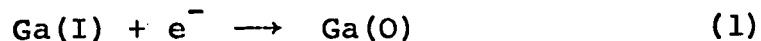
In the presence of Ga(III), a favorable equilibrium constant (Table 2) exists for the chemical reaction of this

gallium metal:

$$2Ga(0) + Ga(III) \longrightarrow 3Ga(I) \qquad (2)$$
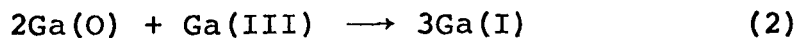
However, at the same time Ga(III) is also reduced

<u>electrochemically</u>:

$$Ga(III) + 2e^- \longrightarrow Ga(I) \qquad (3)$$

In scanning towards more oxidizing potentials, reaction
(1) will decrease and so will reaction (2). The retardation
of (2) will make more and more Ga(III) available for
reaction (3). The observed current will therefore drop
rapidly in the neighbourhood of the Ga(I)/Ga(0) couple
and then level off as reaction (3) takes over. Reaction
(3) will continue until the Ga(III)/Ga(I) equilibrium
potential at 0.766 ± 0.002 V is reached. The voltammetric
value obtained is 0.77 ± 0.02 V.

At more oxidizing potentials, Ga(I) is oxidized to
Ga(III) and thus gives rise to an anodic current as in
Curve A. After correction for the IR drop in the cell
(250 ohms, primarily in the frit of the compartment) it
can be seen that the first wave of Curve B corresponds
to the one in Curve A.

The first anodic wave in Curve B is followed by a
second, suggesting further oxidation of Ga(III). However,
a voltammetric scan of a solution of pure $GaCl_3$ shows no
such second anodic wave, and the cathodic wave observed
on attempted reduction of Ga(III) to Ga(I) appears at the

expected potential. The shapes of the second anodic wave (Curve B) and the cathodic reduction wave are not simple; the significance of this is not clearly understood and may be due to slow kinetic steps in the oxidations and reductions involved.

Indium

Indium metal in contact with the melt reacts with it completely to give aluminum metal. From the amount of indium metal put into the melt and, in the case of a complete reaction, of aluminum metal obtained, it is ascertained that In(I) was formed in solution by the reaction $Al(III) + 3In(0) \rightarrow Al(0) + 3In(I)$. The In(I)/In(0) couple must therefore be more negative in potential than the Al(III)/Al(0) couple. Inside the melt range In(I) can be oxidized; a voltammetric scan indicates oxidation at 1.2 ± 0.1 V. Likewise, the addition of $InCl_3$ and subsequent scanning results in a cathodic wave at 1.1 ± 0.1 V. More precise potentiometric measurements could not be made because $InCl_3$ scarcely dissolves into the melt even if the temperature is raised to 220°C while In(I) could not be quantitatively oxidized at higher In(I) concentrations. It is concluded that the waves seen in voltammetry correspond to the oxidation of In(I) to In(III) and reduction from In(III) to In(I).

The data obtained allow estimation of K for the reaction $1/2In(III) + In(0) \rightleftharpoons 3/2In(I)$. The value obtained (Table 2) is $>4 \times 10^{13}$.

Thallium

Thallium metal also reacts with the melt with pro-
duction of aluminum. It was shown, by the method described
above for indium, that thallium exists as Tl(I) in the
melt. It is, however, not possible to further oxidize
Tl(I) to Tl(III) inside the melt range. The equilibrium
constant K for the reaction $1/2Tl(III) + Tl(O) \rightleftharpoons 3/2Tl(I)$
is then $K > 4 \times 10^{25}$, which is comparable to the aqueous
value of $K = 2.3 \times 10^{27}$ (40).

The chemistry of the thallium/aluminum system has been
studied in detail by Palkin and Palyura (41). On the basis
of the results of differential thermographic and quantitative
chemical analysis the following ternary reciprocal displace-
ment system was established:

$$4TlCl + Al \longrightarrow Tl[AlCl_4] + 3Tl$$
$$4AlCl_3 + 3Tl \longrightarrow 3Tl[AlCl_4] + Al$$
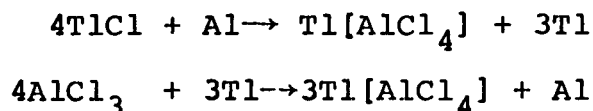
The driving force of the above reactions, in the opinion of
the Russian authors, arose from the formation of the highly
stabilized compound $Tl[AlCl_4]$.

Although the authors used a completely different solvent
system ($AlCl_3$ under pressure) their findings agree with
with this thesis. In this light Delimarskii's report (42)
in which he quotes a value of 0.3 V for thallium in $NaAlCl_4$
at 300°C seems to be doubtful. Unfortunately the way of
measurement and definition of these potentials are not known
since the original paper was not accessible. A further

uncertainty was his use of a platinum wire inserted into
the melt as a reference electrode. The shortcomings of a
reference electrode of this type have been discussed
earlier in this thesis. It may also be pointed out that
the other data (42) appear to be unreliable. This may be
due in part to a misprint in the English abstract (42).
Zinc and cadmium were reported in the text as having two
waves while the table quotes two waves for cadmium and tin.
Further, $BiCl_3$ was reported as having only one potential
(kind unspecified) while Yntema (15) had reported investi-
gations on bismuth 10 years earlier where he mentioned
the additional wave. Direct comparison of other work in
this field with Delimarskii's must therefore be done with
caution.

Copper

Yntema (13) measured the decomposition potential
of Cu(I) from which a value of $E° = 0.81 \pm 0.03$ V was
calculated (14) on the mole fraction scale. He made no
attempt to oxidize Cu(I) to Cu(II). In the present study
potentials of both the Cu(I)/Cu(0) and Cu(II)/Cu(I) couples
were measured accurately which allowed the determination
of their standard potentials and equilibrium constants. A
value of 0.710 ± 0.002 V was obtained for the molal standard
potential of the Cu(I)/Cu(0) couple. Cu(I) was then
oxidized coulometrically at inert electrodes in the same
manner as Ga(I).

Plotting the coulometric data as log[Cu(I)]/[Cu(II)] vs.

e.m.f. resulted in a straight line with a slope corres-
ponding to 1.0 ± 0.1 electrons. The standard potential
was measured at equal concentrations of Cu(I) and Cu(II)
as 1.866 ± 0.001 V. A voltammetric scan of a solution
containing equal concentrations of Cu(I) and Cu(II) is
shown in Fig. 5. The interpretation of these curves is
similar to that of the curves in Fig. 4.

The solution of Cu(II) in this melt is
green in color while the solution of Cu(I) is
colorless. The equilibrium value for
the reaction Cu(II) + Cu(0) $\rightleftharpoons$ Cu(I), with K defined using
molal concentrations, is K = 2.1 x 10^{14} which is much
larger than the aqueous value of 5.9 x 10^{-7} (43); the
equilibrium in acetonitrile, however, is favored by an
even larger constant of 2.5 x 10^{25} (44).

Silver

The Ag(I)/Ag(0) couple has been measured previously
(2) at 150°C and a value of 0.795 ± 0.001 V was reported.
In the present study the molal standard potential obtained
was 0.719 ± 0.001 V at 135°C with a temperature dependence
of -0.44 ± 0.03 mV/°C from 120 to 170°C (Figure 6). The
temperature vs. e.m.f. plot did not show any hysteresis.
The slope of the Nernst plot of the anodization corresponded
to 1.0 ± 0.1 electrons. Figure 7, Curve A, shows the first
seven points out of a total of ten which established the
slope.

Anodizing silver in another experiment at 150°C resulted
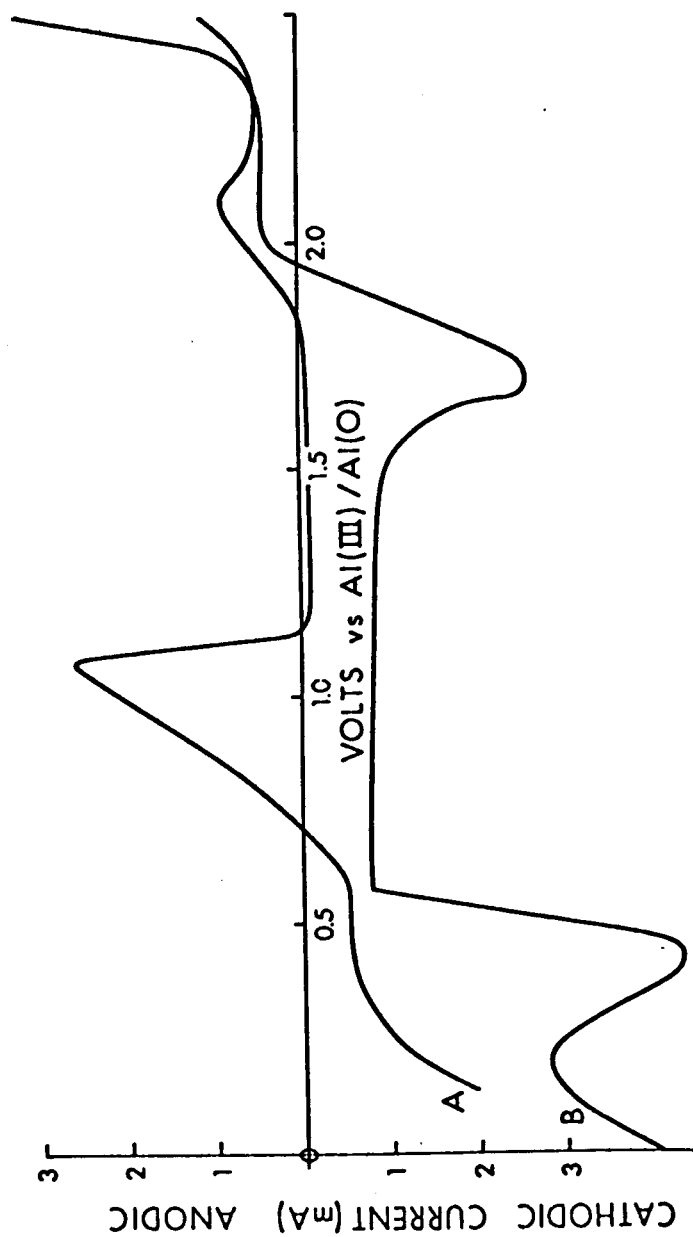
Figure 5. Voltammetry of a solution containing Cu(I) and Cu(II). Curve A scan in positive direction, Curve B scan in negative direction.
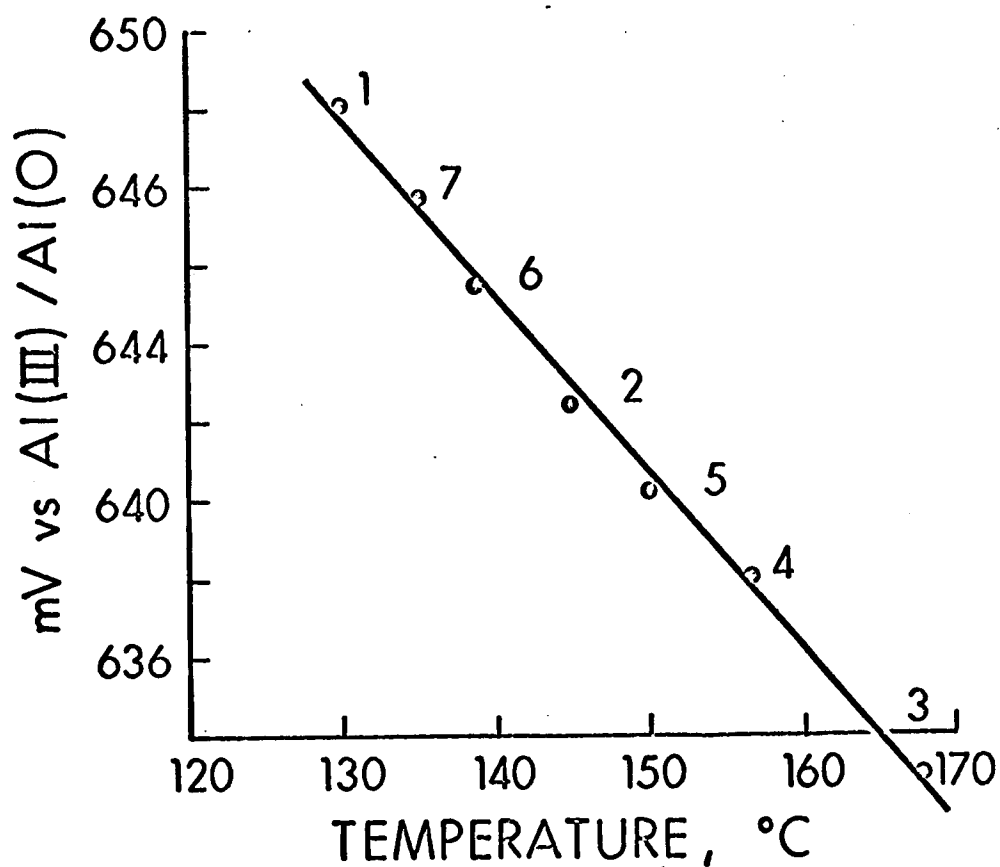
Figure 6. Temperature dependence of the
Ag(I)/Ag(O) couple vs. Al(III)/Al(O)
reference electrode. Numbers refer
to succession of points measured.
Ag(I) concentration approximately
10^{-1} moles/kg. Same experiment as
Figure 7, Curve A.
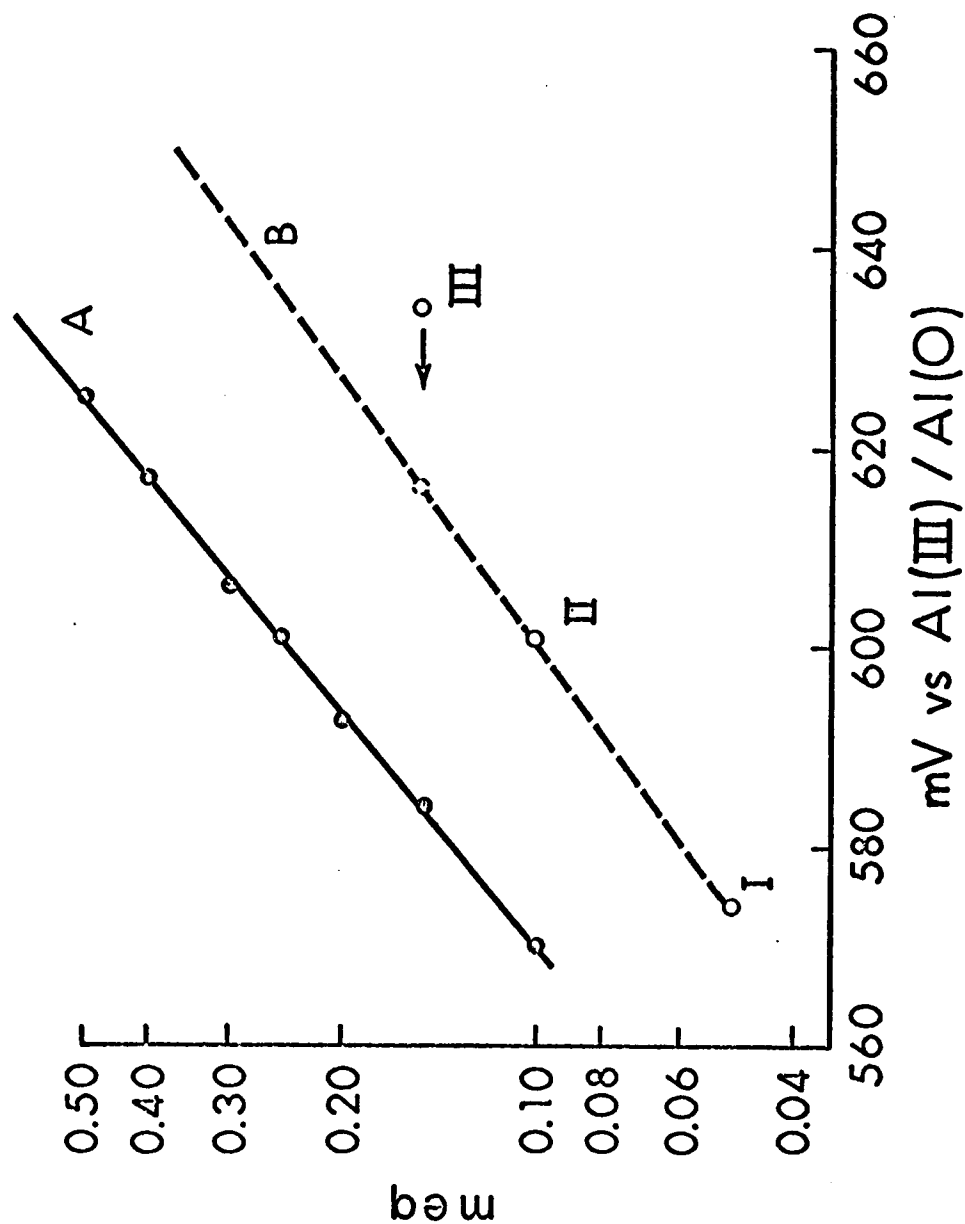
<u>Figure 7.</u> Nernst plot of Ag(I)/Ag(O) couple after coulometric anodization. Curve A, anodization current 10 mA; current density approximately 11 x 10^{-2}A/cm^2. Curve B, anodization current 50 mA; current density approximately 5.5 x 10^{-2} A/cm^2.

in a value of 0.729 V for the standard potential with n = 1.1. The experimental conditions such as concentration and current densities during anodization were identical to the ones of the previous runs at 135°C. However, weighing the silver wire before and after the experiment disclosed that more silver metal was lost than corresponded to the faradaic process.

Reducing the amount of melt inside the compartments as well as the current density (now 5 mA/cm^2, thus being comparable to (2)) in another run resulted in a molal standard potential of 0.736 V with n = 0.97. This value approached the reported value (2) of 0.795 V better than the previous ones but was still far from satisfactory agreement.

In Figure 7, Curve B, an anodization was performed at higher current density. The concentration of silver ion at point I was roughly 7 x 10^{-3} moles/kg, assuming a faradaic process with one electron. It can be seen in Figure 8, Curve I, that the potential stabilized inside a short time and remained stable. Using the data for point I a molal standard potential of 0.749 V can be calculated which is again far from the value of 0.795 V reported by Hames and Plambeck (2,3) but is in reasonable agreement with that of the previous experiment. A similar stability is observed for point II. The slope established by the two points (Figure 7, Curve B) is characteristic for n = 1.
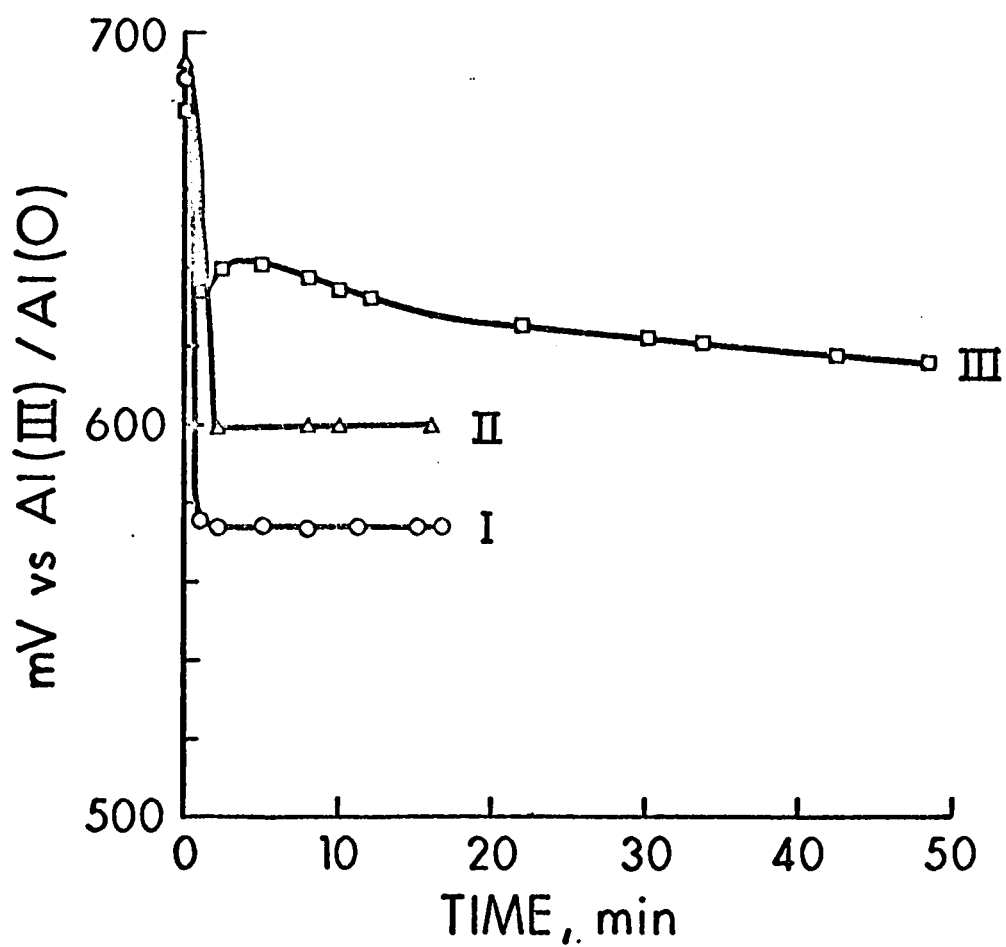
Figure 8. Time dependence of Ag(I)/Ag(O) vs. Al(III)/Al(O) reference electrode. Curves I, II, III refer to points I, II, III of Figure 7, Curve B.

Point III, however, is 20 mV from where it should be at the end of the anodization. It drifted slowly towards the line established by I and II which it reached after 45 minutes. The drift of the potential after 45 minutes had slowed down to 0.3 mV/min.

These data, especially those of Figure 8, show that the drift is not caused by combination of silver ions with melt impurities. At the lower concentrations of points I and II melt impurities would show a much more pronounced drifting than at higher concentrations. The reverse, however, is observed: there is no drift at low concentrations but a very strong initial drift at high concentrations. Also, the amount of silver lost was always significantly larger than corresponded to the faradaic process. The drifting of III in this light has to be explained as the production of polymeric silver species after the originally produced silver ion entity diffuses back to the electrode with which it will then react chemically. At low current densities and concentrations the polymeric species may be produced directly and stable potentials result.

This, together with the consistent value of one electron and each anodization, seems to suggest a complex silver species in solution e.g., Ag_q^{p+} with q and p depending on the experimental conditions.

In the case of bismuth, Bi^+, Bi_4^{4+}, Bi_5^{3+}, Bi_8^{2+} have been conclusively shown to exist in chloroaluminate melts (6-12). Yntema added Bi_2O_3 and observed one very

well-defined break in the current - voltage curve at low

current densities. He noticed the production of a reddish

brown compound at the cathode surface which could be

isolated by immersion of the electrode in 95% ethanol. The

substance decomposed in contact with water (17). This

compound may well be identical with one of the low valence

ions of bismuth mentioned before. It is reported (10) that

$Bi_5[AlCl_4]_3$ is of reddish color. Recently, Mamantov and

coworkers (45) reported preliminary electrochemical investi-

gations of the reduction of the Bi(III) ion by voltammetric

methods. They observed three reduction waves, one including

a two electron step.

It must be stated in conclusion that one cannot assume

that the potential of the silver ion/silver couple corres-

ponds to the simple reaction:

$$Ag^+ + e^- \longrightarrow Ag(0)$$
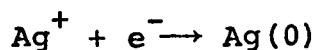
Gold

Gold was anodized into solution at low current

densities with a slope corresponding to 1.1 ± 0.1 electrons.

Several of the earlier anodization runs were unsuccessful

in that no stable potentials could be obtained. Inspection

of the gold wire after these experiments showed that

anodization had occurred only in a few spots where it had

resulted in the formation of deep pin holes. The holes

showed the crystalline structure of the metal wire. It

was found that remelting the wire before use tended to

prevent deep holes although dissolution was still not uniform. Stable potentials were thus obtained, however, and a molar standard potential of 2.046 ± 0.002 V was calculated for the Au(I)/Au(0) couple. This value is much higher than those for Cu(I)/Cu(0), 0.710 V, and Ag(I)/Ag(0), 0.719 V. The solution containing Au(I) is orange in color while those of Cu(I) and Ag(I) are colorless.

C O N C L U S I O N

It has now been shown electrochemically that low valence ionic species of group IB, IIB and IIIA exist in chloroaluminate melts. There are further indications that low valence states can be expected for many other elements such as bismuth and manganese. The species produced can be characterized by spectroscopic and/or electrochemical methods. It has been proven that the effects observed are not due to melt impurities.

The unambiguous characterization of low valence ions in the chloroaluminate melts makes a reconsideration of these and similar ions in other melts necessary. For example it appears from the published data that an unreported monovalent gallium species may well exist in the fused LiCl-KCl system.

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PART III

STRUCTURAL MELT UNITS AND SOME RELATED PROBLEMS

IN THE $AlCl_3$-NaCl-KCl EUTECTIC

A B S T R A C T

It is postulated that the ternary mixture composed of 66 mole % $AlCl_3$, 20 mole % NaCl, and 14 mole % KCl gives rise to a $Al_2Cl_7^-$ species in the molten and probably also in the solid state. Investigations by nuclear magnetic resonance of sodium-23, aluminum-27, and chlorine-35 nuclei as well as the available literature data suggest the formation of a large $Al_2Cl_7^-$ anion while the cations are assumed to occupy the holes left by the bulky anions.

The equilibrium constant for the observed thermal decomposition of the $Al_2Cl_7^-$ according to

$$Al_2Cl_7^- \rightleftharpoons AlCl_4^- + AlCl_3$$
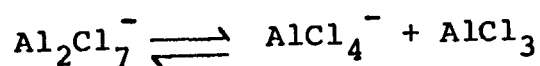
was calculated as 3×10^{-4}.

The behavior of oxide ion in the molten ternary $AlCl_3$-NaCl-KCl mixture is explained by the formation of anionic oxide-$AlCl_3$ complexes.

New evidence was found for the dissolution of a reducing aluminum species into the ternary melt.

I N T R O D U C T I O N

The observed low valence states of Group IB, IIB, and IIIA elements (1,2) as well as those of bismuth, tin, and lead (3-11) in chloroaluminate melts should be rationalized by, at least, a qualitative model. In order to do this, the physicochemical behavior of the melt and the entities comprising it must be understood. Most authors (3-14) have considered this system as consisting basically of $Na[AlCl_4]$ with varying amounts of dissolved $AlCl_3$. Corbett (3-6) used a system composed of $Na[AlCl_4]$ with 3 - 7 mole % $AlCl_3$.

It was realized that a characterization of the ternary system $AlCl_3$-NaCl-KCl could be done by its comparison with the similar systems $Na[AlCl_4]$ and $AlCl_3$ which have been investigated in detail in the past. Literature checks concerning the ternary mixture reveal that a surprising amount of unrelated information already exists. During the work of this thesis, the data were further augmented by NMR and X-ray measurements.

Solid $AlCl_3$ is known to have an ionic layer structure (15). On melting its volume increases 83% (16) which is caused by the formation of the molecular species Al_2Cl_6 (17). The structural units of this melt can be visualized as two distorted $AlCl_4$ tetrahedra sharing one edge (17). The equivalent conductance of $AlCl_3$ decreases at the melting point due to the formation of the molecular species and was determined as 1.9×10^{-5} cm^2/ohm equiv. at 200°C (18).

The reaction of $AlCl_3$ with an alkali metal chloride MCl in a 1:1 mole ratio results in the formation of $M[AlCl_4]$ (19,20). The crystal structure of $Na[AlCl_4]$ (21) shows a lattice made of nearly perfect tetrahedral $AlCl_4^-$ ions with Na^+ ions located in the empty spaces between the tetrahedra. The Al-Cl distance of 2.13 $\overset{o}{A}$ is shorter than the sum of the tetrahedral covalent radii, while the Cl-Cl distance is 3.48$\overset{o}{A}$. This was attributed to partial double bond character of the Al-Cl bond (21).

Sodium tetrachloroaluminate $Na[AlCl_4]$ melts at 151°C (20) and a clear liquid may be obtained. Conductance measurements by Kryagova (22), Moss (23), and Midorikawa (24) point to the formation of M^+ and $AlCl_4^-$ entities in molten $M[AlCl_4]$. Raman investigations of molten $M[AlCl_4]$ by Balasubrahmanyam and Nanis (25) and earlier by Gerding and Houtgraaf (26) showed that $AlCl_4^-$ is of tetrahedral symmetry. The Raman studies (25) established further the identity of spectra of liquid and solid $Na[AlCl_4]$ and $K[AlCl_4]$. The absence of Raman lines other than those due to $AlCl_4^-$ seemed to indicate purely electrostatic interactions between anions and cations. There can therefore be no doubt that M^+ and $AlCl_4^-$ are the typical structural units in alkali chloroaluminate melts within the time range of the spectral measurements i.e., $10^{-12} - 10^{-14}$ sec.

Reaction of $AlCl_3$ with MCl in a 2:1 mole ratio above 150°C results in the formation of a liquid with eutectic

points between 100 and 200°C, depending upon M (19,20, 27-29). The ternary system $AlCl_3$-NaCl-KCl is of particular interest due to its low melting point of 98°C. The $AlCl_3$: (Na,K)Cl ratio is approximately 2:1 (27-29).

The ternary $AlCl_3$-NaCl-KCl system was first mentioned by Kendall, Crittenden and Miller (19) in 1923. The phase diagram of the same system was originally investigated by Wasilewski and coworkers (27) in 1935. These authors dwelt repeatedly on the tendency of the ternary system towards supercooling. Temperature vs. time plots of the cooling curves showed a large amount of supercooling with the loss of the subsequent plateau which had degenerated to a mere maximum (27). This effect may explain why the published data for the melting point of the eutectic are widely different among different authors. Although Wasilewski estimated the error to be 2-3°C (27) his melting point of 70°C could not be confirmed. Midorikawa (29), who also commented on the high degree of supercooling in detail, quotes 93°C as a melting point. By using a mechanical stirrer he claimed to have partially overcome the super-cooling except in mixtures with a high KCl content. The composition for his eutectic was 60 mole % $AlCl_3$, 26 mole % NaCl and 14 mole % KCl. Although Treadwell's result (30) of 94°C agrees as far as the melting point is concerned, his composition was slightly different: 62 mole % $AlCl_3$, 26 mole % NaCl, and 12 mole % KCl.

Plotnikov (28) reported a melting point of 89°C for a
composition of 63.5 mole % $AlCl_3$, 20.0 mole % NaCl, and
16.5 mole % KCl. It appears from this that the super-
cooling, as well as the volatility of the $AlCl_3$ upon
which most of the above authors also commented, will give
rise to a difference of 5 to 10% in the composition.

E X P E R I M E N T A L

The purification of $AlCl_3$ and the other chemicals used has been described in detail in Part II of this thesis.

NMR and X-ray samples were prepared by melting the components in a round bottomed flask inside the glove box. In the case of the NMR samples the liquid melt was transferred into the NMR tubes with disposable pipets. For the X-ray samples some melt was poured into a cold mortar which prevented formation of large crystals, finely ground with a mortar and pestle after cooling, and transferred into quartz capillaries. The NMR tubes were removed from the glove box after solidifying and sealed off under 10 mm Hg pressure. The capillaries were also closed outside the glove box without special precautions.

For H^1-NMR normal medium wall tubes were used while tubes of 10 mm O.D. were used for all wideline experiments.

The H^1-NMR was observed at 100 MHz and a 12 inch magnet (Varian Assoc.). The temperature was varied from 120 to 170°C. The nuclear magnetic resonances of Na^{23} Al^{27} and Cl^{35} were done at 170 $\pm$ 2°C. A Model V-4200 B Wideline Spectrometer with a 12 inch magnet of approximately 14 Kg (Varian Assoc.) was used in conjunction with a Model 5100 B frequency synthesizer and Model 5110 B frequency synthesizer driver (Hewlett-Packard) which synchronized a Model V-4210A variable radiofrequency oscillator (Varian Assoc.). For audio frequency amplification a Parr JB-4

amplifier (Princeton Applied Research) was used which fed its output into a G-14 (Varian Assoc.) strip chart recorder.

A particular resonance frequency was found by first searching for it with the variable frequency oscillator. This frequency was then firmly synchronized by the frequency synthesizer through the use of a Model 140A oscilloscope (Hewlett-Packard).

The linewidths were recorded in the dispersion mode (31) and are given as peak-to-peak values. The linewidth calibration was performed with the frequency synthesizer in the following manner. With the magnetic field scanning one resonance was first recorded. The frequency was then altered on the frequency synthesizer and another resonance was recorded. The distance between the two resonances corresponded directly to the frequency change and was then used to measure the linewidth.

The X-ray powder patterns were obtained with molybdenum K_α irradiation on a Philips PW 1009/80 X-ray generator. The lines were recorded on photographic film by a Monius camera.

Raman spectroscopy was done in a quartz cell 1 inch long and of 2 mm I.D. which was heated from the outside through a layer of resistance wire. A LR-1 (Perkin-Elmer) laser excited instrument was used.

R E S U L T S

In order to gain insight into the ion-solvent inter-

action, nuclear magnetic resonance studies were done using

Na^{23}, Al^{27}, and Cl^{35}.

Aluminum-27 possesses   spin 5/2 and a quadrupole

moment of 0.149; the resonance frequency at 10 Kg is

11.262 MHz. (32). The high quadrupole moment gives rise to

line broadening which will decrease with increasing symmetry

around the nucleus under consideration. Aluminum resonance

has been used as early as 1957 (33-39) where Al(III) was

dissolved in aqueous as well as non-aqueous solvents. The

value for aqueous $AlCl_4^-$ was 15.1 $\pm$ 0.5 Hz (37), while AlI_4^-

was 42 Hz (37). This study reports a value of 42 $\pm$ 4 Hz for

a solution of $Al(NO_3)_3$ in water at 27°C. The Al^{27} resonance

of molten $Na[AlCl_4]$ at 14 Kg and 15.67 MHz resulted in a

linewidth of 90 $\pm$ 5 Hz (Table I).

With $(Na,K)[Al_2Cl_7]$ a linewidth of 700 $\pm$ 30 Hz was

obtained. Chemical shifts between this compound and

$Na[AlCl_4]$ could not be observed due to the broadness of

the former line.

Sodium contains 100% Na^{23} with spin 3/2. Its magnetic

moment is 2.22, the resonance frequency 11.262 MHz at 10 Kg.

The quadrupole moment is again fairly high, 0.1 (32); a high

symmetry environment is necessary to observe the resonance.

So far, Na^{23} resonance has been studied only in water and

TABLE I

RESULTS OF NMR MEASUREMENTS

Nucleus	Compound	Linewidth Hz
Al^{27}	$Al_2Cl_7^-$	700 ± 30
	$AlCl_3:NaCl$ 1.4:1	550 ± 20
	$AlCl_4^-$	90 ± 5
	$Al(III),aq$	42 ± 4
Na^{23}	$Al_2Cl_7^-$	8.8 ± 0.5
	$AlCl_4^-$	8.8 ± 0.5
H^1	NH_4^+ in $Al_2Cl_7^-$	54.1 ± 0.2*
	NH_4^+ in $AlCl_4^-$	54.1 ± 0.2*
Cl^{35}	$Al_2Cl_7^-$	7000 ± 500
	$AlCl_4^-$	5000 ± 500

*N-H coupling

water-acetone solution (40,41). It has been observed that sodium must be highly ionic in order to obtain sharp resonance lines (42).

The linewidth of sodium in molten $(Na,K)[Al_2Cl_7]$ measured at 15.87 MHz, was 8.8 ± 0.5 Hz (Table I). The reported value for aqueous solution is 11.5 Hz (40).

Samples containing NH_4^+ as a cation were prepared by replacing some of the NaCl in the ternary mixture by NH_4Cl without otherwise changing the melt composition. Proton resonance of the NH_4^+ ion in $(Na,K)[Al_2Cl_7]$ and $Na[AlCl_4]$ resulted in a well-defined triplet with an N-H coupling constant of 54.1 ± 0.2 Hz. The value for NH_4^+ in water at 25°C was measured as 53.5 ± 0.2 Hz (43).

Nuclear magnetic resonance of Cl^{35} resulted in very broad lines. The linewidth in $(Na,K)[Al_2Cl_7]$ was approximately 7000 Hz while $Na[AlCl_4]$ showed a linewidth of approximately 5000 Hz.

An attempt was also made to use Tl^{205} nuclear magnetic resonance. The Tl^{205} species with spin 1/2 has a magnetic moment of 1.61 (32,44) and resonates at 24.57 MHz at a field of 10 Kg. This nucleus was the first to be investigated in molten salt systems (45,46). More recent investigations show the sharp linewidth of Tl^{205} even in solid samples (47).

The resonance frequency is higher than those available from the frequency synthesizer, and an attempt was made to use a 56.4 MHz oscillator with a corresponding increase in

field strength to 22.9 Kg. However, the experiments were not successful because of large inhomogeneities in the magnetic field which greatly reduced the sensitivity of the detection.

As part of the present study, the generation of an $Al_2Cl_7^-$ species was demonstrated by electrochemical methods in addition to reported vapor pressure studies (48,49). Addition of $AlCl_3$ to a compartment containing an Al(III)/Al(O) electrode in $Na[AlCl_4]$ resulted in an increase in the electromotive force as measured versus an Al(III)/Al(O) reference electrode in $Na[AlCl_4]$ (Figure 1). The positive sign of the emf is evidence for spontaneous formation of the $Al_2Cl_7^-$ entity. Due to a large junction potential it is not possible to give an exact figure for ΔG. It can however be estimated to be in the 10 - 20 Kcal/mole range. The curve peaks at a ratio of $AlCl_3$:NaCl of approximately 2:1 which corresponds to $Na[Al_2Cl_7]$. The ΔG value is in agreement with the ΔH value for the reaction

$$AlCl_3 + NH_4Cl \longrightarrow NH_4[AlCl_4]$$
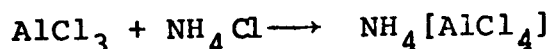
which was reported (50) as +13.3 Kcal/mole, if the TΔS term is small.

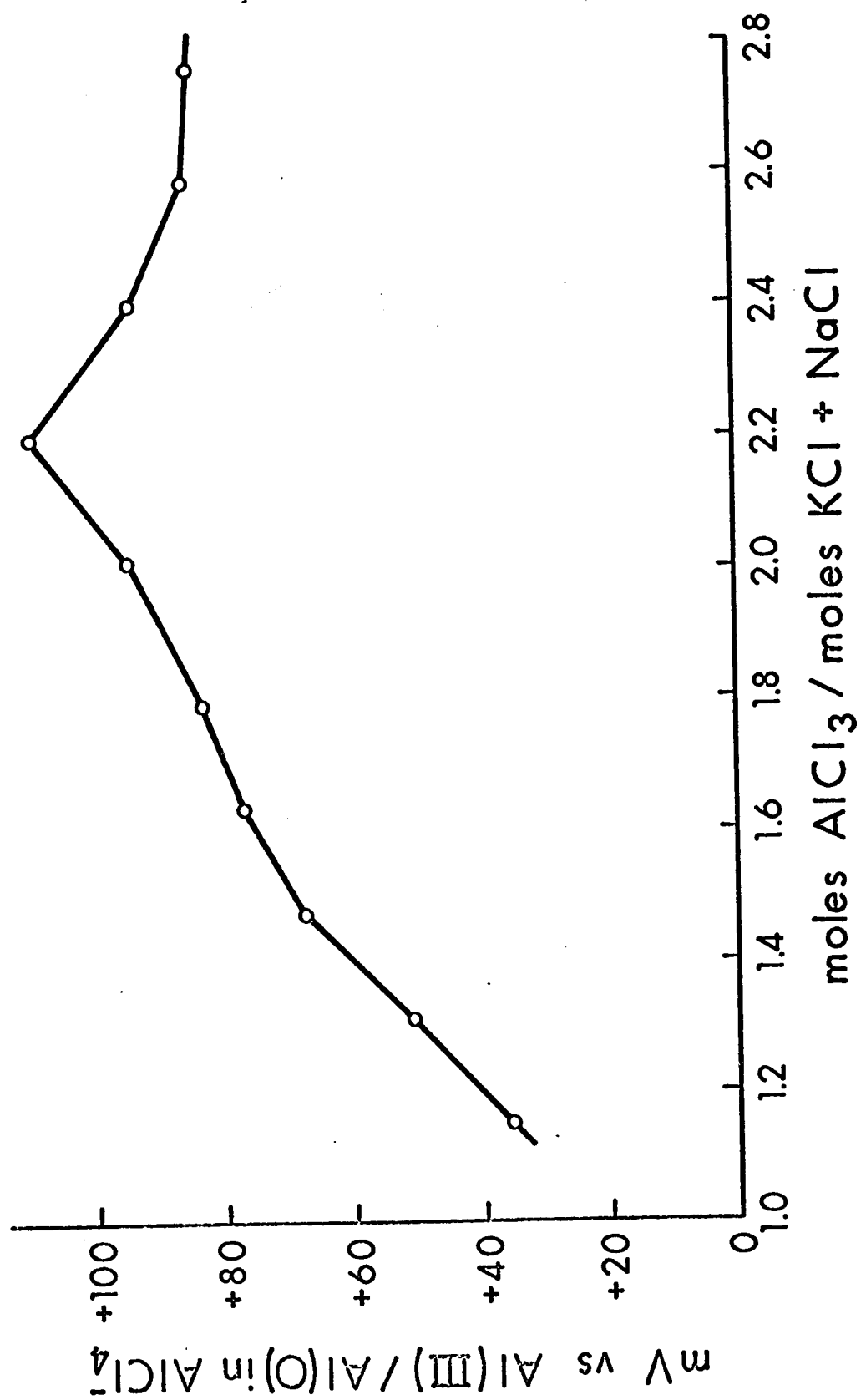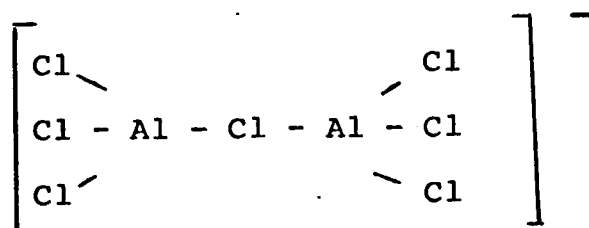**Figure 1.** Change of the Al(III)/Al(O) potential upon addition of AlCl$_3$.

D I S C U S S I O N

(A)   Structural Units in the Eutectic Melt.

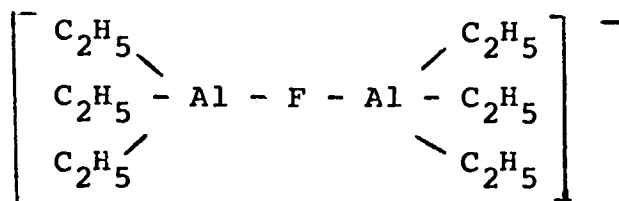A simple calculation shows that the $AlCl_3$-NaCl-KCl eutectic with 66:20:14 mole %, respectively, corresponds approximately to $(Na,K)[Al_2Cl_7]$. Species corresponding to $Al_2Cl_7^-$ have been recognized before. Complications in Friedel-Crafts alkylations and acylations have been traced to the formation of protonated arenes like $[ArH_2^+][AlCl_4^-]$ and $[ArH_2^+][Al_2Cl_7^-]$ (51) which are the main cause of the observed intense red to orange colors (52). Moore and Morrey (48,49) were the first to propose $Al_2Cl_7^-$ in a melt system. The basis for this proposal was vapor pressure studies of $AlCl_3$ over $AlCl_3$-MCl systems in the Al:M range from 1:1 to 2:1. However, no comments were made about the $Al_2Cl_7^-$ species as such. Gruen (53) was the first to suggest the following structure for $Al_2Cl_7^-$:

$$\left[\begin{array}{c} Cl\diagdown \qquad\qquad\qquad \diagup Cl \\ Cl - Al - Cl - Al - Cl \\ Cl\diagup \qquad\qquad\qquad \diagdown Cl \end{array} \right]^-$$

The only unambiguous proof of the above structure would come through Raman spectroscopy. In his paper Gruen (53) quoted work in progress at his laboratories in this direction but no later publication has appeared in the open literature. Raman spectroscopy by the author of this thesis did not give results

due to unremovable turbidity of the samples which caused too large an amount of scattering.

The only indication for the correctness of the above structure as proposed by Gruen (apparently unknown to him, although published somewhat earlier) comes from the field of organometallic aluminum chemistry. Ziegler (54) observed that AlR_3 reacted with alkali halides MX to form complexes in 1:1 and 2:1 ratios. Subsequent X-ray analysis of $K[Al_2(C_2H_5)_6F]$ by Natta and coworkers (55) resulted in the structure

$$\left[\begin{array}{c} C_2H_5 \diagdown \qquad\qquad \diagup C_2H_5 \\ C_2H_5 - Al - F - Al - C_2H_5 \\ C_2H_5 \diagup \qquad\qquad \diagdown C_2H_5 \end{array}\right]^{-}$$

The main result, with respect to the present problem, was the establishment of tetrahedral symmetry around the aluminum atoms. Further information from the X-ray analysis of $K[Al_2(C_2H_5)_6F]$ was an Al-F distance of 1.80 ± 0.06 Å which is close to that observed in $Na_3[AlF_6]$ (56). The bonding in the organometallic aluminum anion was explained by the authors by assuming sp hybridization of the fluorine for the σ-bond, with partial π-bond character arising from overlap of the filled $2p_y$ and $2p_z$ orbitals of fluorine with the empty 3d orbitals of the aluminum. A similar type of structure and bonding mechanism can easily be visualized for $Al_2Cl_7^{-}$. One would expect the 3p - 3d overlap

to be weaker which would result in a weaker Al-Cl-Al bond. This has indeed been observed qualitatively: while $K[Al_2(C_2H_5)_6F]$ can be dissolved in a weak base like ether, attempts to isolate $Al_2Cl_7^-$ from the $(Na,K)[Al_2Cl_7]$ eutectic in the same manner have so far failed (53).

The reaction of Cl^- with $AlCl_3$ (13,48,49,53,57) results in the primary formation of $Al_2Cl_7^-$:

$$2AlCl_3 + Cl^- \rightleftharpoons Al_2Cl_7^- \qquad (1) \qquad K'$$
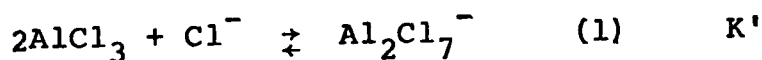
Further addition of Cl^- will result in the formation of $AlCl_4^-$:

$$Al_2Cl_7^- + Cl^- \rightleftharpoons 2AlCl_4^- \qquad (2) \qquad K''$$
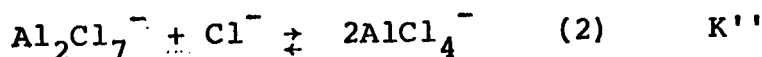
The values of K' and K'' at 728°C are approximately 10^{13} and 10^3, respectively (48,49). These data apply to systems with K^+ as a cation. Smith (58) reported a value of 10^5 for K'' at 600°C with Cs^+ as the cation while Trémillon (13) gives 10^6 at 175°C with Na^+ and K^+ as cations. The differences in the equilibrium constants display the influence of the cations upon the anion as well as the temperature dependence of this interaction. Trémillon's value was chosen for the calculation of K''' since his system and temperature approached the ones used in the present system most closely.

Combining reactions (1) and (2) one obtains

$$Al_2Cl_7^- \rightleftharpoons AlCl_4^- + AlCl_3 \qquad (3) \quad K'''$$
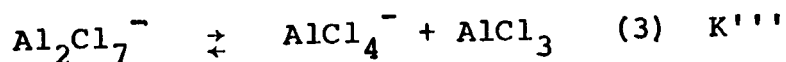
Reaction (3) describes the observed physical decomposition
of the $Al_2Cl_7^-$ species. K''' can be calculated from K' and
K'' as approximately 3×10^{-4}. The tendency to break into
$AlCl_4^-$ and $AlCl_3$ is therefore not very large, a fact which
is displayed directly in the low vapor pressure of $AlCl_3$ over
these melts. At 135°C the vapor pressure is 11.5 mm Hg (30).

From the foregoing discussion it can therefore be
assumed that the eutectic is composed mainly of (Na,K) $[Al_2Cl_7]$.
It would be a contradiction, however, to state that the
definitely observed eutectic corresponded to (Na,K) $[Al_2Cl_7]$.
Compound formation always corresponds to a maximum in the
phase diagram while a eutectic forms a minimum. Wasilewski
(27) and Midorikawa (29) had, as was described earlier, great
difficulties with the system, especially in the neighborhood
of the eutectic point. Recently van Spronsen (59,60) published
very careful investigations on mixtures of $AlBr_3$ with KBr. He
found the formation of a defined compound $K[Al_2Br_7]$, corres-
ponding to a maximum in the phase diagram and a eutectic
minimum of this compound with a 10 mole % increase of $AlBr_3$
content. What can be suspected for the chloride system has
thus been proven to exist for the bromide system. Early
electrochemical investigations by Yntema (61-65) have shown
that there appears to be no major differences in the sol-
vation mechanism for other ions between the chloro- and
bromoaluminate melts: the deposition potentials for most of

the investigated ions was nearly identical in the two solvents. This fact makes the extension of van Spronsen's results to the chlorides a reasonable one. It can therefore be assumed that the $AlCl_3$-NaCl-KCl system is a true eutectic, consisting mainly of $(Na,K)[Al_2Cl_7]$ with probably a small excess of $AlCl_3$. This would make the eutectic a binary one, and not a ternary one as quoted since Wasilewski. Macroscopic as well as microscopic evidence therefore points to $Al_2Cl_7^-$ as the anionic melt entity.

Solid $Na[AlCl_4]$ and $(Na,K)[Al_2Cl_7]$ showed different line patterns in the X-ray powder spectra. $Na[AlCl_4]$ is known to exist in the solid lattice as Na^+ and $AlCl_4^-$ (21) and a possible break-up of $Al_2Cl_7^-$ on freezing according to reaction (3) must be excluded since no lines corresponding to $AlCl_4^-$ were seen. This suggests that a $Al_2Cl_7^-$ anion is crystallizing as such without decomposition which is also demonstrated clearly by the maximum in the phase diagram in the case of the bromide system (59,60).

With the knowledge of the melt entities it is now possible to go one step further and examine the ion-solvent interaction. The linewidth studies with nuclear magnetic resonance which have been reported earlier in the result section were done with the hope of gaining insight into the symmetry environment of the different nuclei.

The tetracoordinated $AlCl_4^-$ showed a linewidth of 90 ± 5 Hz while a solution of aqueous Al(III) which is hexacoordinated (66) by water molecules showed a linewidth of

42 $\pm$ 4 Hz. Unfortunately, a direct quantitative comparison between the two linewidths is not possible due to the different parameters which influence linewidth, such as temperature, viscosity, and susceptibility, in the two media.

Although it appeared at first that the broad line of (Na,K)[Al$_2$Cl$_7$] indicated a drastic reduction of symmetry around the aluminum, later experiments showed that this is not the case. A sample composed of two separate tubes, one containing Na[AlCl$_4$] and the other (Na,K)[Al$_2$Cl$_7$], displayed both the narrow and the wide line. On the other hand, a sample with an AlCl$_3$:NaCl ratio of 1.4:1 in a single tube gave only a comparatively small reduction in linewidth to 550 $\pm$ 20 Hz. It did not show two lines which would have corresponded to AlCl$_4^-$ and Al$_2$Cl$_7^-$ and the broadening is interpreted as exchange corresponding to reaction (3).

The three measured linewidths for the chloroaluminates (Table I) allow a reevaluation of K'''. The observed linewidth $\Delta\nu_{obs}$ of the mixture AlCl$_3$:NaCl = 1.4:1 is related to those of AlCl$_4^-$ and Al$_2$Cl$_7^-$ by (36, 67):

$$\Delta\nu_{obs} = P_{Al}\, \Delta\nu_{AlCl_4^-} + P_{Al2}\, \Delta\nu_{Al_2Cl_7^-}$$

where $\Delta\nu_{AlCl_4^-}$ and $\Delta\nu_{Al_2Cl_7^-}$ are the linewidths of AlCl$_4^-$ and Al$_2$Cl$_7^-$, respectively, while P_{Al} and P_{Al2} are mole fractions, defined as usual by

$$P_{Al} = \frac{[Al]_{AlCl_4^-}}{[Al]_t} \qquad P_{Al2} = \frac{[Al]_{Al_2Cl_7^-}}{[Al]_t}$$

The total aluminum concentration $[Al]_t$, according to reaction (3), is given by

$$[Al]_t = [Al]_{AlCl_4^-} + [Al]_{Al_2Cl_7^-} + [Al]_{AlCl_3}$$

The last term in the last equation is considered to be small and will be neglected in the first approximation. Using the numerical values of $\Delta\nu_{obs} = 550$ Hz, $\Delta\nu_{AlCl_4^-} = 90$ Hz, $\Delta\nu_{Al_2Cl_7^-} = 700$ Hz, $[Al]_t = 7.3$ molal (in the 1.4:1 mixture) one can solve the two simultaneous equations and obtains $[Al]_{AlCl_4^-} = 1.8$ molal which corresponds to a $AlCl_4^-$ concentration of $[AlCl_4^-] = 1.8$ molal, and $[Al]_{Al_2Cl_7^-} = 5.5$ molal or $[Al_2Cl_7^-] = 2.8$ molal.

Since equilibrium constant for reaction (3) is given by

$$K''' = \frac{[AlCl_4^-][AlCl_3]}{[Al_2Cl_7^-]}$$

a numerical value is needed for the concentration of the $AlCl_3$. It can be obtained through the following relation:

$$[Cl^-]_t = [Cl^-]_{AlCl_4^-} + [Cl^-]_{Al_2Cl_7^-} + [Cl^-]_{AlCl_3} =$$

$$= 4 [AlCl_4^-] + 7 [Al_2Cl_7^-] + 3 [AlCl_3] .$$

Insertion of $[Cl]_t = 27.1$ molal, $[Cl^-]_{AlCl_4^-} = 7.2$ molal, $[Cl^-]_{Al_2Cl_7^-} = 19.6$ molal yields an $AlCl_3$ concentration of 0.1 molal. From this one obtains $K''' = 6.2 \times 10^{-2}$. The discrepancy of this value with the one of 3×10^{-4} calculated earlier can be due to a variety of effects. The thermo-dynamic value for K' used in the previous calculation of

K''' was measured at 728°C. At lower temperatures K' would be expected to decrease which would result in an increase of K'''. The temperature dependence of K' has not been reported. Furthermore, the value for K' was difficult to obtain experimentally (48,49) and must be considered as approximate only. On the other hand, several assumptions had also to be made in the calculation of K''' from the linewidth: equality of concentration and activity, negligible amounts of $AlCl_3$ present, and no formation of chloroaluminate polymers.

It is felt that the value of K''' = 6.2 x 10^{-2}, calculated from NMR measurements is somewhat too large due to the use of concentration instead of activity while the thermodynamic one is too low because K' was measured at 728°C. The present calculations therefore indicate 10^{-4}<K'''<10^{-2}.

Further evidence for the exchange according to (3) comes from another observation. The addition of one mole of $AlBr_3$ to one mole (Na,K) [$AlCl_4$] will produce $Al_2Br_3Cl_4^-$. The aluminum halide subliming out of the melt under equilibrium conditions is pure $AlCl_3$; only a fast nitrogen purging will liberate some bromide. The addition of $AlBr_3$ and the subsequent sublimation of $AlCl_3$ show at least a halogen exchange and most likely also point to a complete (AlX_3) - exchange.

The Cl^{35} nuclear magnetic resonance of Na[AlCl$_4$] and (Na,K)[Al$_2$Cl$_7$] yield linewidths of 5000 and 7000 Hz, respectively (Table I). Their interpretation can be put on a semi-quantitative basis.

The relation governing the nuclear quadrupole relaxation in liquids (36, 67-70) is

$$\frac{1}{T_2} = \frac{3\pi^2}{10} \frac{2I+3}{I^2(2I-1)} (1 - \frac{\varepsilon^3}{3}) \ (\frac{eQ}{h} \frac{\delta^2 V}{\delta z^2})^2 \ \tau_c$$

where $1/T_2 = \pi\Delta\nu$ with $\Delta\nu$ being the peak to peak linewidth of the derivative in Hz, I is the spin of the nucleus under consideration, ε is the assymmetry factor ($0<\varepsilon<1$), e is the electric charge, Q is the electric quadrupole moment, h is Planck's constant and $\delta^2 V/\delta_z^2$ is the gradient of the electric field at the nucleus. τ_c is given by Debye's formula

$$\tau_c = \frac{4\pi\eta a^3}{3kT}$$

where a is the effective molecular radius, η is the viscosity, k is Boltzmann's constant and T is the absolute temperature. τ_c is known as the correlation time and can be visualized as being the order of the time a molecule takes to turn through a radian or to move over a distance comparable with its dimensions (69). The term $\frac{eQ}{h} \frac{\delta^2 V}{\delta z^2}$, known as the quadrupole coupling constant, can be obtained directly from nuclear quadrupole resonance (71,72). The quadrupole coupling constant for Cl^{35} in Na[AlCl$_4$] was -22.6 MHz. This information together with the linewidth, allows the calculation

of the correlation time, if ε is set equal to zero in

the first approximation (73). Using $\Delta\nu = 5000$ Hz one

obtains $\tau_c = 3 \times 10^{-10}$ sec, as compared to $10^{-12} < \tau_c < 10^{-11}$

for water (69). The correlation time for $Al_2Cl_7^-$ can be

calculated as $\tau_c = 4.2 \times 10^{-10}$ sec. The longer

correlation time for $Al_2Cl_7^-$ as compared to $AlCl_4^-$ is

most likely indicative for the larger size of the molecule

as displayed by a in Debye's formula, assuming negligible

change in the viscosity.

As mentioned earlier, τ_c is characteristic for the

whole molecule as such. This allows in turn the calculation

of the quadrupole coupling constant of the Al^{27} nucleus in

$AlCl_4^-$ and $Al_2Cl_7^-$. For $AlCl_4^-$ one obtains 1.7 MHz while

the value obtained for $Al_2CL_7^-$ is 8.4 MHz. Reported values

are 470 MHz for solid $AlCl_3$ (74) and approximately 10 MHz

for a solution containing the $Al(C_2H_5)_3$ dimer (36) which

is known to be in a rapid exchange equilibrium with its

monomer. This equilibrium is therefore similar to that of

the bridged $Al_2CL_7^-$ species. Due to the higher covalency

in the organometallic aluminum species a somewhat larger

coupling constant is encountered there. The coupling

constant for solid $AlCl_3$ was found to be representative

for a bond which was 2/3 ionic and 1/3 covalent (74)

which gave the aluminum a charge of +2. In the light

of this interpretation the higher coupling constant in

$AlCl_4^-$ would mean an increase in the covalency of the

Al-Cl bond and further lowering of the charge on the

aluminum. This is in agreement with the general concept

of coordination chemistry.

With regard to the cations one noticed immediately

the extremely sharp line of the Na^{23} resonance of 8.8 $\pm$ 0.5

Hz (Table I). No chemical shift was observed between the

sodium resonance in $Na[AlCl_4]$ and $(Na,K)[Al_2CL_7]$. The

sharpness of the sodium line in the two melts is attributed

to a high symmetry around the sodium ion with, at the same

time, a very weak interaction with the surrounding chloride

ions. This agrees with what has been found for the $Na[AlCl_4]$

by Raman spectroscopy (25,26) and shows again the similarity

between the $Na[AlCl_4]$ and $(Na,K)[Al_2Cl_7]$ melts.

Nuclear magnetic resonance of H^1 in NH_4^+ showed an

N-H coupling of 54.1 $\pm$ 0.2 Hz (Table I) which was close

to that observed in aqueous solution (43). One interpre-

tation of this result is that the N-H angles remain the

same in both solvents. This is, however, not too surprising

because of the fairly rigid structure of the NH_4^+ molecule.

The N-H coupling must therefore be regarded as a much cruder

measure of the environment of the cation than is the line-

width in the case of sodium.

Gruen, as mentioned already, has proposed a solvation

model where the ion, in his case a transition metal ion, is

surrounded by two $Al_2CL_7^-$ anions and where 3 terminal

chlorides of each anion give rise to an octahedral coordination

(53). This applied for liquid Al_2Cl_6 as a medium. Looking at the Na^{23} resonance in the ternary molten mixture a similar interpretation seems plausible. The sodium is likewise surrounded octahedrally by the chloride atoms of two $Al_2Cl_7^-$ molecules. The Al-Cl bond is much more covalent than the Na-Cl bond and the interaction of the sodium with the chloride atoms must be purely electrostatic. In other words, the sodium ion is in an extremely ionic state. Other cations will remain similarly isolated in the holes left by the bulky $Al_2Cl_7^-$ anions. This, by the way, explains why all eutectics containing $Al_2Cl_7^-$, but with different cations, melt in the fairly close range from 100 - 200°C.

A deeper understanding into the behavior of cations other than the alkalis may be obtained through a discussion of the probable solvation process. This may be illustrated by a specific example. The Fe(III) ion is not stable in any medium as an ion of charge +3. It will interact with its coordinating molecules, e.g., chloride ions, and lower its high positive charge by the attraction of electron density to somewhere in the range of +0.4 (75). If, on the other hand, the Fe(III) ion is surrounded by $Al_2Cl_7^-$ anions, the available electron density on a chloride is reduced since part of the electron density will be drawn towards the aluminum ion as well.

The Fe(II) ion, however, will need less stabilization from coordination in a pure chloride medium (e.g. LiCl-KCl) as well as in the $Al_2Cl_7^-$ medium. This is due to its lower formal positive charge.

Therefore, Fe(III) is destablized with respect to Fe(II) in the chloroaluminate melts. This statement is equivalent to that saying Fe(II) is stabilized with respect to Fe(III). The formation of Fe(II) is therefore thermodynamically more favored in the chloroaluminate system. Although the above example has not been investigated during the work of this thesis there is definite evidence for this in the equilibrium constants, Part II, Table 2. The lower oxidation state is always more favored in chloroaluminates.

Another way of lowering the stabilization needs (solvation energy) of an ion would be the reaction with a neutral metal atom, e.g., the electrode. This has been observed for silver, tin, lead and bismuth (3-11). Part II of this thesis concluded that Ag(I) reacts with the silver metal of the electrode to form species of the type Ag_q^{p+} An extreme example would be a species like Ag_2^+ where the positive charge is now spread out over two silver atoms. Since the charge is no longer an integer Smith (58) has coined the term "fractional charge" where no implication is made as to the actual number of atoms in a cluster. A typical and well characterized entity in this class is Bi_5^{3+} which can readily be prepared in form of the compound $Bi_5[AlCl_4]_3$ (5).

Hames and Plambeck (1,2) and Corbett (6) have shown that Cd(I) is much more stable than Cd(II) in chloroaluminates. This agrees with the expected destabilization of

Cd(II) with respect to Cd(I). The dimerization of Cd(I) to Cd_2^{2+} (6) need not be explained on the basis of ion-solvent interaction. The $d^{10}s^1$ state of the univalent ions of this group is apparently unstable and dimerization going to $d^{10}s^2$ occurs through the formation of metal-metal bonds.

It was observed during the electrochemical work (Part II) that at low concentrations $(10^{-3}$ molal) the Nernst plot showed deviations from the expected straight line. It could be argued that there is a different amount of catenation at low concentrations than at high ones. From 10^{-2} to 10^{-1} molal no deviations were observed which in this light would indicate formation of a cluster of constant fractional charge.

(B)   The Oxide Ion.

The O_2/O^{2-} electrode could not be realized in this study in the $(Na,K)[Al_2Cl_7]$ melt despite several attempts with tungsten and platinum as electrode materials. The addition of oxide ion did not produce the expected Nernstian behavior either. Similarly, the addition of small amounts of Li_2O did not give rise to changes beyond a few millivolts in the case of the Al(III)/Al(O) and Ag(I)/Ag(O) couples. It appeared as if oxide ions disappeared in the melt.

It has been argued earlier that the formation of $Al_2Cl_7^-$ is due to the high Lewis acidity of $AlCl_4^-$. The

high basicity of O^{2-} will cleave $Al_2Cl_7^-$ by acting upon the equilibrium of (3), thus resulting in the formation of $AlCl_4^-$ and $AlCl_3$-oxide complexes. However, no confirmation of such a species was attempted.

Some interesting facts regarding the oxide ion problem arise from the comparison of Yntema's work on gallium (65) with this thesis. Yntema added gallium as Ga_2O_3 to the melt. His results agree with the ones of this thesis where gallium ions were produced by coulometric oxidation of gallium metal. It must be assumed that the Ga-O bond was destroyed and Ga(III) produced. This case is not an isolated one. Yntema observed that K_2WCl_6 and WO_3 gave the same deposition curve (65). Recent investigations of Russian workers (76) showed a eutectic of the system $AlCl_3$-$WOCl_4$ in a 3:1 mole ratio. Although this result can at the present time not be rationalized in terms of a compound there seems to be no doubt that the formation of Al-O containing species occurs.

A similar oxide-dissolving mechanism was proposed by Fremont and coworkers (12) for their system containing 60 mole % $AlCl_3$, 26 mole % NaCl, and 14 mole % KCl:

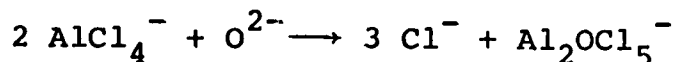$$AlCl_4^- + O^{2-} \rightarrow M^{2+} + AlO^+/,nCl^-$$
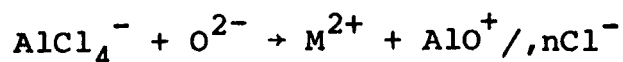
It may be noticed, however, that the authors did not recognize $Al_2Cl_7^-$ as the anionic melt species. The reaction as written may be of some merit in melts containing $AlCl_4^-$.

Trémillon proposed in a recent paper (14) the formation of AlOCl and/or $Al_2OCl_5^-$ in the $Na[AlCl_4]$ system through the following reactions

$$AlCl_4^- + O^{2-} \longrightarrow 3\ Cl^- + AlOCl$$

and

$$2\ AlCl_4^- + O^{2-} \longrightarrow 3\ Cl^- + Al_2OCl_5^-$$
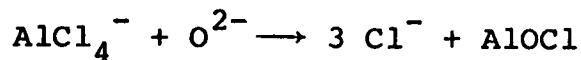
The $Al_2OCl_5^-$ is presumed to have the Al_2Cl_6 structure.

(C) The Problem of Dissolved or Low Valence Aluminum in the Molten $(Na,K)[Al_2Cl_7]$ System.

Hames and Plambeck (1,2) have shown that the Al(III)/Al(O) couple is essentially nonpolarizable in the $AlCl_3$ - NaCl-KCl eutectic. Earlier investigators (77,78) came to the same conclusion when trying to establish Tafel plots for the Al(III)/Al(O) electrode in molten salts. Hames (1) explained this on the basis of the high (approximately 6 molal) concentration of Al(III) in the melt.

On the other hand considerable evidence exists that some complications do arise. There can be little doubt that aluminum either dissolves into the melt as an uncharged species or it reacts with the melt with the formation of Al(I). For instance, it was observed that when a Au(I) solution in a compartment with a C-porosity frit was placed inside the melt over aluminum metal, gold was precipitated within the glass frit. The two diffusing

species (gold and aluminum) presumably met inside the frit
where the redox reaction then took place. Similar obser-
vations were made when the compartment contained Cu(I) ions.
Smith (58) has observed dark coloration when aluminum
metal was in contact with molten Al_2Cl_6. Munday (3) dis-
cussed in detail the formation of low valence aluminum
species in the melt although he lacked chemical evidence.
When aluminum metal was in contact with $(Na,K)[Al_2Cl_7]$ a
dark substance was observed to sublime out of the melt and
condense at the cooler parts of the cell.

The existence of AlCl and AlF is well established in
the vapor phase (79-81). AlCl can be prepared by the
reaction

$$2 \ Al(\ell) \ + \ AlCl_3(g) \longrightarrow 3 \ AlCl(g)$$
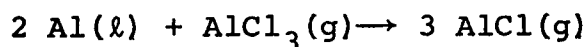
at temperatures above 700°C (73). The equilibrium constant
lies at approximately 10^{-9} atm^2 at 900°C. The $\Delta H^\circ_{f,298}$ was
found to be -13.3 ± 0.4 kcal/mole. If it is attempted to
extrapolate the temperature dependence of the equilibrium
constant to 200°C, a value of approximately 10^{-28} is
obtained. Clearly, another mechanism, most likely solvation,
must be assumed if Al(I) is to be considered as the produced
entity.

Although this thesis cites direct evidence for a
reducing aluminum species in solution, no quantitative
results could be ascertained. It appears at the present

time that the high exchange current which causes the
nonpolarizability of the Al(III)/Al(O) electrode may
well be due to an unknown intermediate species.

C O N C L U S I O N

This thesis attempted to show the existence of $Al_2Cl_7^-$ in the melt system used and to explain the destabilization of the higher valence states of metal ions in terms of the great covalent strength of the terminal Al-Cl bond. It was further argued that the overall charge on a metal ion can also be lowered by the reaction with neutral metal atoms thus giving rise to cluster formation.

Several problems, however, which are common to all molten salt system remain. The ions $AlCl_4^-$ and $Al_2Cl_7^-$ can be shown to exist by various methods. Conductance measurements show that these anions, together with the cations, are the current carriers. But if an electrolysis is done the species reacting at the electrodes are Al(III) and Cl^-, according to the Al(III)/Al(0) and Cl_2/Cl^- couples which can also be realized. It is especially this problem which makes the evaluation of the processes at the Al(III)/Al(0) electrode conceptually difficult.

No precise ideas can be formed as to the type of the cluster ions. If they fill the empty spaces between the large $Al_2Cl_7^-$ anions the question arises as to whether their complexity is defined by the available space or not. This space in itself may not be constant should further polymerization of the $Al_2Cl_7^-$ species occur.

Although several points concerning the ternary $AlCl_3^-$

NaCl-KCl have been clarified it is felt that much more work needs to be done before a complete understanding of this system is obtained.

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