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"Electrochemical Studies in Aluminum Chloride Melts"
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SUMMARY

A melt purification system has been developed which produces a final melt far superior electrochemically than previous reports in the literature. A residual current of less than 2 \( \mu \text{amp/mm}^2 \) at a sweep rate of 0.5 V/sec was used as the criteria for a pure melt. The use of a second purified bulk melt and a heated pipette permitted the rapid exchange of working electrode compartments while retaining the same reference electrode system. The major portion of the work was carried out in the 1:1 AlCl\(_3\):NaCl melt at 175 and 200°C. Several measurements were made in the 2:1 melt and a few on the silver systems in intermediate compositions.

Programs for PDP-8I and PDP-12 digital computers and the required electronic circuitry systems were developed to carry out various electrochemical measurements in the melt. A pair of 50 yard transmission lines were used to connect the computer to the experiment. Ensemble averaging and digital, least squares smoothing are used within the programs to improve the signal-to-noise ratio by at least an order of magnitude. Some of the computerized electrochemical techniques used to examine the different systems were pulse polarography, double pulse polarography, staircase voltammetry, kinetic double potential step chronoamperometry and double potential step chronocoulometry.

The silver, iron and copper systems constituted the major portion of our work on metal ions in the aluminum chloride melts. Some of the other systems briefly examined were the hydrogen chloride, lead and
cadmium systems. The AgCl, CuCl, FeCl$_3$, and CdCl$_2$ salts were found to be completely soluble (~20-30 mM) in the 1:1 melt at 175°C, whereas the FeCl$_2$, PbCl$_2$, and CuCl$_2$ were only sparingly soluble. All of these metal chloride salts are soluble in the chloride ion deficient 2:1 melt. Only a single dissolution peak was observed for most of the metals at low current densities in the 1:1 melt. At higher dissolution rates, a second anodic peak corresponding to a secondary electrode reaction was recorded. The second peak was enhanced by both an increase in the dissolution rate and a decrease in the temperature. The second peak was not observed in the 2:1 melts, indicating once again the importance of the chloride ion activity in these melts.

Nernst plots, cyclic voltammograms and pulse polarograms were used to determine the $E^\circ_M$ values for most of the metal redox couples in the 1:1 melt. The $E^\circ_M$ for silver was found to be almost invariant ($\pm$ 20 mV) with respect to the AlCl$_3$ concentration between 50 and 66 mole % AlCl$_3$. This indicates that the Ag(I)/Ag electrode is a far superior reference for this system than the aluminum electrode since the latter undergoes a 467 mV change over the same AlCl$_3$ concentration range. All of our $E^\circ$ values have been tabulated in Appendix I, along with a few literature values. 467 mV were added to all of the literature values for the 2:1 melt in order to report all of the electrode potentials vs the aluminum electrode in a 1:1 melt. All of our results are in agreement with the available literature values for the 2:1 melt and they form the most comprehensive list to date for the 1:1 melt.
In dilute solutions the electrode couples were found to be reversible and involved the expected number of electrons. The Cd$_2^{2+}$ ion is not stabilized in the AlCl$_3$ deficient melt (1:1) to the same degree as it is in the AlCl$_3$ rich melt (2:1). The degree of stabilization previously reported for low valency states in these melts appears to be directly proportional to the amount of free AlCl$_3$, while the metal chloride solubilities are inversely proportional to the Cl$^-$ concentration.

The low diffusion coefficients ($< 10^{-5}$ cm$^2$/sec) for these metals indicate that they are complexed with the bulky AlCl$_4^-$ or Al$_2$Cl$_7^-$ ions in the melt. The size of these complexes retards their mobilities, hence the low diffusion coefficient. From the sparse values in the literature for the 2:1 melt, it appears that the D values for these ions increase with the AlCl$_3$ content. This may be due to a dilution effect of the neutral AlCl$_3$ and Al$_2$Cl$_6$ molecules in the melt.

Hydrogen chloride gas, which had been bubbled through the 1:1 melt, produced an irreversible reduction peak at about 1.15 V vs Al. The potential of this peak is a direct function of the Cl$^-$ ion concentration in the melt in a similar fashion to that observed for the aluminum electrode. The position of the reduction peak is in the same position as those reported for water and impurities found in the unpurified aluminum chloride melts.

Electrode reactions of several classes of aromatic compounds in 1:1 and 2:1 AlCl$_3$:NaCl melts were investigated using cyclic voltammetry. Ferrocene and triphenylamine were found to undergo reversible
one electron oxidations. The radical cations formed from triphenylamine, diphenylamine and \text{N,N'-dime}
ylaniline are stabilized in AlCl\text{3} melts when compared to other aprotic solvents. \text{N,N',N'-tetramethylbenzidine} and \text{N,N'-diphenylbenzidine} appeared to undergo two closely spaced one electron oxidations, the potentials of these couples being extremely solvent composition dependent. \text{N,N,N',N'-tetraphenylphenyl}esediamine was found to undergo the expected two one electron oxidation steps. The results for the oxidation of three aromatic hydrocarbons differ substantially from those reported earlier. Hydroquinone appears to undergo an acid-base reaction prior to its electrode reaction. Reductions of organic compounds so far studied have been found to be complex.
INTRODUCTION

This is the Final Report on a program for studying electrochemistry in aluminum chloride melts. When this activity was initiated, funding for one year was obtained, with the intention that this activity could be step-funded over a four year period. Due to problems in obtaining suitable personnel, a one-year extension without additional funds was obtained. Hence, although the period covered is a two-year interval, only one year's funding was expended. Also, the step-funding initially anticipated did not materialize. However, in carrying out the research activity, a long-term view was taken. Extensive development of computer controlled electrochemical experimentation was undertaken. A good deal of effort was expended in attempting to obtain electrochemically pure melts and develop reproducible solid electrodes for studies in the melt. Since one of the goals of the work was eventually to study electrode kinetics, some effort was invested on considerations of the methods which might ultimately be employed.

The experimental work had as its long-term goals the study of various solute species across the entire accessible composition range of the NaCl-AlCl₃ system. Several months ago an effort was initiated on looking at organic, as well as inorganic, solutes in these melts. A detailed literature review was undertaken and has been submitted in a previous report. The experimental work on the organic system indicates, however, that perhaps an entirely new area of organic electrochemistry may be achieved. The inorganic solute species were chosen
on the basis of previous studies—to have something with which to compare our work—and on the basis of confusion in the literature of importance to the area.

In effect, while this is a Final Report on the NASA funded activity, it must be regarded as an interim report on a continuing investigation into the electrochemistry in aluminum halide melts. Thus, some of the work summarized here is necessarily fragmentary and incomplete.
I

EQUIPMENT DESIGN AND EXPERIMENTAL PROCEDURES

All of the experimental work was carried out in a nitrogen-filled dry box to protect the melt from moisture and oxygen.

Previous methods of melt purification in the literature involved one or a combination of the following steps:

(1) Preparation of AlCl₃ from Al and HCl
(2) Sublimation of the AlCl₃
(3) Electrolysis using Pt electrodes
(4) Adding Al or Mg metal
(5) Filtration

Anders and Plambeck¹ report that after using steps 2-5 (cited above) a faint yellow to light brown color remained in the melt.

The fusion of Fluka (A.G., anhydrous, iron free) aluminum chloride and Fluka (A.G.) sodium chloride produced a faintly yellow-colored melt which would slowly turn grey in color on standing for a period of several days. Rather than use a pair of Pt electrodes¹ (which produce Cl₂ at the anode during electrolysis), a pair of aluminum electrodes were used. The net result during the electrolysis in the current procedure is either the replacement of impurities in the melt with the aluminum ion or the transfer of Al from one electrode to the other. The simple displacement of the impurities using Al metal failed due to the coating of the metal surface by a film formed by the displaced metal impurities which effectively stopped further displacement. The transfer of Al metal in the
electrolysis procedure continually replenishes the Al surface and prevents the passivication of the aluminum. The normal procedure is to electrolyze the melt at 250°C for ten to twelve hours at a current density of 1.5 ma cm⁻².

All of the glassware and electrodes were heated to 500°C for several hours and then allowed to cool in the evacuated antechamber of the dry box to prevent any contamination of the melt.

An experimental cell was designed and several new furnaces were built to facilitate the ease and rate at which new electrode cells could be set up. The cell (Figure 1) consists of a Teflon biscuit (¼" x 3") sealed to the top of a glass cell by means of a tight fitting groove in the Teflon. Several holes were drilled in the Teflon top and various sizes of ground joints were press-fitted in these holes. The typical cell top contained a 6 mm hole for a thermocouple well, a 10/18 joint for a counter electrode, a 14/20 joint for the reference electrode compartment and a 1" hole with an O-ring groove around the top for the working electrode compartment.

The normal procedure was to prepare a 100 ml melt in a cell placed in a furnace containing a window so that the bottom of the cell could be seen. After purification, the 7 mm fine-porosity sintered-glass fritted reference electrode compartment was placed into the melt. The aluminum reference electrode consisted of a spiral of aluminum wire connected to a short piece of tungsten wire sealed in the glass plug in the top of the reference compartment.
The counter electrode consisted of a large tungsten wire spiral sealed into a 10/18 glass plug.

A second melt of about 250 ml was prepared in a second furnace. About 10 ml of this melt was transferred by means of a preheated pipette to a working electrode compartment in the smaller cell. This electrode compartment consisted of a 20 mm medium-porosity sintered glass frit at one end, a 1" piece of glass tubing in the middle and a 14/20 ground joint at the top. A tightly fitting O-ring around the 1" glass barrel of the compartment both supported and sealed it to the Teflon top. Teflon adapters were used to seal the electrodes into the compartment as well as adjust the level of the electrode in the compartment. All of the compartments were adjusted so that all of the melt levels in the cell were equal. It was necessary to blow a small hole 2 to 3 inches above the melt level in each of the cell compartments to equalize any differences in the vapor pressures above the various melts.

Small ring furnaces were built to fit around the Teflon tops. By maintaining the tops between 175 and 200°C, the build-up of AlCl₃ in the cooler portions of the cell was eliminated. This feature is of utmost importance when measurements are made in the AlCl₃ rich melts. Two temperature controllers purchased from ThermoElectric, Model 32422, were used to control the temperatures of the melts to ± 0.5°C.

A white salt-like precipitate often remained in the bottom of the cell after the purification process if the process had been
carried out at temperatures below 200°C. Analysis showed that the melt contained the same mole percent of AlCl₃ regardless of whether there was a solid at the bottom of the cell or not. These results indicated that the precipitate must have the same composition as the NaAlCl₄ melt and not NaCl as previously suspected. The potential of the Al reference in the small electrochemical cell never varied by more than 5 mV from an aluminum electrode immersed in the melt which had been pipetted from the large bulk melt storage cell. This provided another piece of evidence in support of the results from the aluminum analysis. The precipitate appears to be a sparingly soluble phase of NaAlCl₄ which is nucleated by some species which is not completely eliminated from the melt by electrolysis at temperatures below 250°C.

Chemical analysis of the NaCl and AlCl₃ found their purity to be better than 99.5%. The NaCl was further dried at 450°C under vacuum for 3 hr before it was transferred to the dry box and weighed out into the cells. The AlCl₃ was stored at all times in the dry box to prevent any contamination.

Several different electrodes were used in the experimental measurements. A pyrolite carbon button electrode (area = 0.0985 cm²) was prepared by press-fitting a short piece of carbon rod into a piece of ½" Teflon rod. This electrode proved to be useful for potentials in excess of 1.5 V vs the aluminum reference electrode. The tungsten electrodes tended to become fouled at these excessively anodic potentials.
The background cyclic voltammogram using a platinum button electrode (area = 3.63 x 10^{-3} \text{ cm}^2) exhibited two anodic and two cathodic waves between +0.5 and +1.3 V; however, at potentials more anodic than +1.3 V the electrode appeared to be well behaved. Continued cyclic sweeps caused one peak couple to grow and the other to decrease in height. As the sweep rate was increased, the growth phenomenon shifted from the couple at 1.1 V to the one at 0.75 V. The fact that stirring had no effect on the voltammogram and that none of the other electrode materials exhibited peaks in this region suggested one of two things: (1) the peaks may arise from some surface reaction involving a platinum chloride film, or (2) some impurity is strongly adsorbed and the reaction is catalyzed on the platinum surface. For these reasons the platinum electrode received only limited use as an indicator electrode in the aluminum chloride melts.

Several tungsten button electrodes and a tungsten wire electrode were used for most of the experimental measurements. The useful potential range of these electrodes was from 0.3 to 1.7 V. Beyond this range it appeared as if the electrode increased in area resulting in a background current of about 4 to 5 times the magnitude of the original values. No significant changes were observed in the shape of these enhanced voltammograms except for the increase in magnitude by a constant factor. If the tungsten wire was found to be very splintery due to longitudinal holes in the wire, it was not used in the manufacture of the electrodes. The wire was sealed into 5 mm Pyrex glass tubing using a bead of uranium glass. The button electrodes
were ground flat on an emery wheel and then polished with fine emery paper. All the tungsten electrodes were then electrolyzed for 15 sec at 4–5 V AC in a 25% sodium hydroxide solution. After rinsing with water, the electrodes were dried under vacuum at 110°C for several hours. It was necessary to cycle the electrode from +0.5 to +1.5 V in the melt for several minutes to remove the final traces of the oxide film on the metal electrode surface. This electrolysis procedure produced a reasonably reproducible indicator electrode.

Measurements were made in the chloroaluminate melt using a Brinkman hanging mercury drop electrode (area = 4.18 x 10⁻² cm²). Cycles varying in sweep rate from 0.05 V/sec to 100 V/sec exhibited a useful working range from +0.1 V to +1.0 V vs Al for the mercury electrode. Shifting the cathodic gate from +0.10 V to +0.05 V produced an anodic peak at +0.55 V which disappeared as soon as the cathodic gate was returned to +0.10 V. The useful working range for the mercury electrode does not change in the AlCl₃ rich melts when measured against an Al reference electrode in the same AlCl₃ rich melt. The approximate E°ₘ values of the Hg(I)/Hg couple at 175°C in the 1:1 and the 2:1 melts are 1.0 and 1.5 V vs Al in NaAlCl₄, respectively. This is in good agreement with the published value of 1.50 V for Hg in the 2:1 melt at 218°C.² The main disadvantages of this electrode are the mechanical problems and the fact that most of the metals of interest are electroactive at potentials in excess of 1.0 V. The advantages are the use of a non-solid electrode and the observed capacitance is about 1/10 that observed for the tungsten electrodes.
Cyclic voltammetry was used to determine the current-voltage characteristics of the melt before (Figure 2a) and after (Figure 2b) purification. The final melt was completely colorless and exhibited no irregularities in the current-voltage curves using a tungsten or mercury indicator electrode. After a week's storage of the melt open to the atmosphere in the dry box, no detectable changes were observed.

The background current reported by G. Torsi and G. Mamantov is about 10 times that which we obtained for similar experimental conditions. The backgrounds obtained by Giner and Holleck are likewise considerably larger than ours, as shown in Figure 3. Unfortunately, most of the other workers have not published their background currents; hence, many of the discrepancies in the literature may be due to impure melts.

The capacity current, \( i_c \), for the system in the absence of a faradaic reaction is given by:

\[
i_c = AC_d v
\]

where \( A \) is the indicator electrode area in cm\(^2\), \( v \) is the sweep rate in V/sec and \( C_d \) is the differential capacity of the double layer in farads/cm\(^2\) at the potential at which \( i_c \) is measured.

Plots of \( i \), measured at various potentials, versus the sweep rate (0.05 to 100 V/sec) gave consistent capacitance values of 14.3 \( \mu \)F cm\(^{-2}\) for the mercury electrode in the NaAlCl\(_4\) melt at 175°C. The plots for the tungsten electrodes at sweep rates greater than 1 V/sec gave consistent \( C_d \) values with respect to sweep rate; however, the \( C_d \)
values increased as the applied potential decreased. The $C_d$ values increased from 50–80 $\mu$F cm$^{-2}$ at 1.0 V to 160–200 $\mu$F cm$^{-2}$ at 0.3 V which is consistent with the 350 $\mu$F cm$^{-2}$ reported for the aluminum electrode at 0 V vs Al. Slow sweep rates (0.05–0.5 V/sec) produced observed capacitances which were abnormally high and very dependent upon the preparation of the electrode. At slow sweep rates any faradaic reaction, such as filming or alloying, makes an appreciable contribution to the observed current. The degree of roughness of the solid electrode will change the effective capacitance area of the tungsten electrodes and, hence, the calculated $C_d$ value. These difficulties do not appear to be as prevalent in the case of the mercury electrode, in which case the 14.3 $\mu$F cm$^{-2}$ obtained for the mercury electrode is far more reliable than those obtained using the solid electrode.
II

SYSTEM FOR COMPUTERIZATION OF ELECTROCHEMICAL MEASUREMENTS
IN FUSED SALTS

Many of the modern electrochemical techniques involve the output of a complex time-based potential waveform to a potentiostat followed by rapid measurement of the resulting current at specific points in time. In order for the experimental parameters to be optimized, complex analysis of the raw data is often required before the experimental data can be interpreted. The use of a 12 bit A/D converter gives a resolution of one part in four thousand which is better by a factor of 40 than that which can be expected from an oscillographic trace. The use of RC timing circuits in analog systems is a much more tedious process than merely typing a numerical time value into the computer program.

The experiment may be performed several times, using either point repetition as with pulse polarography or repetition of the entire experiment as with staircase voltammetry. The results are then averaged to increase the signal-to-noise ratio. This is known as ensemble averaging or cross-correlation.\(^6,7\)

To increase the signal-to-noise ratio still further, digital smoothing of the type recommended by Savitzky and Golay\(^8\) is employed. Peaks are detected and determined by a method similar to that described in their paper.

Published results obtained on aqueous chemical solutions using an earlier version of our system describe its capabilities and
limitations.\textsuperscript{9} Response obtained on $4 \times 10^{-8} \text{ M Cd(II)}$ solution indicates that usable data can be obtained at this level while a precision of 10\% is indicated on $4 \times 10^{-7} \text{ M Cd(II)}$.

The current computer system is built around a PDP-12 digital computer. An extra interface panel was designed and built to enhance the resolution in the analog-digital interconversions and to drive an X-Y point plotter. Figure 4 illustrates all of the main features of our computer system. An overall schematic of the electronics used to communicate between the experimental cell and the computer is given in Figure 5. A system consisting of line drivers and a line receiver were used to drive two 50 yard coaxial cables connecting the computer to the experiment. The common mode signal (4V, 60 cps) picked up by the transmission line is eliminated by the use of a differential amplifier in the line receiver. The use of additional lines, so that the relays on the computer can be used to activate various switches in the potentiostat, greatly enhanced the versatility of the computer data acquisition programs.

The original pulse polarography program\textsuperscript{9} has been modified for the PDP-12 as well as adding base line correction features and correcting some timing errors which became significant at short pulse times. To enable the use of a DME, a birth detector for the pulse polarography system which synchronized the computer with the DME was developed.

The reversibility of an electrode can be characterized by the use of reverse scan pulse polarography.\textsuperscript{10} A Double Pulse Program
(DPLS) was developed to compensate for some of the assumptions used in the reverse scan technique. The voltage waveform in Figure 6 illustrates how this new technique insures a set of identical conditions for each pulse sequence. The necessary equations for testing reversibility at a solid electrode have been previously reported. The study of unstable species which can be generated electrochemically can be accomplished by this technique. The species is generated in situ during the delay time and then examined by pulsing back towards the rest potential to produce a conventional pulse polarogram.

The description and operating procedure of the chronoamperometric program used to determine diffusion coefficients has been discussed fully in a previous report.
III
SILVER SYSTEM

The silver(I) was generated coulometrically with 100% current efficiency in a fritted compartment at a current density of 30 mA cm$^{-2}$. The polarization of the silver wire never exceeded 200 mV during the electrolysis. The $E^0_M$ values vs the Al reference electrode in the 1:1 melt from the Nernst plots (Figure 7) for silver in the 1:1 and 2:1 melts at 175°C are 1.143 V and 1.167 V, respectively. The $dE^0_M/dT$ for silver between 175 and 225°C in the 1:1 melt is 0.63 mV deg$^{-1}$. This value is in accord with the -0.44 mV deg$^{-1}$ reported for silver in the ternary melt.\textsuperscript{1} The $E^0$ value determined from a Nernst plot for silver in the 1:1 melt at 200°C (experimental n = 0.98) is in agreement with these results as well.

Plambeck has reported $E^0_M$ values of 0.712 V and 0.748 V for silver in the ternary melt at 150°C.\textsuperscript{1,12} The former paper reports the temperature coefficient from which a $E^0_M$ of 0.701 V for the Ag(I)/Ag couple in the ternary melt at 175°C was calculated. The difference between the silver electrode potential vs Al in the ternary melt (66% AlCl$_3$, 20% NaCl, 14% KCl) and that in the 2:1 melt should be negligible; hence, this value can be compared with our value for silver in the 2:1 melt. The 0.696 V for the ternary or 2:1 melt is in good agreement with the 0.700 V (1.167-0.467) that was measured in the present study.

The response of the silver standard electrode potential to change in the melt's AlCl$_3$ content (Figure 8) was studied at 175°C using the
The $\text{AlCl}_3$ mole % was varied from 66% to 49% by adding known alliquots of NaCl to a 2:1 melt. The two $E^0$ values determined from the Nernst plots are also in accord with these experimental values (Figure 8).

These results verify the previous postulation that the Ag(I)/Ag couple is virtually unaffected by the chloride ion activity change going from the 2:1 to the 1:1 melt. The difference of 20 mV in the $E^0_{\text{Ag}}$ between the two melts is almost negligible compared to the 467 mV observed for the aluminum electrode. The silver ion is either very weakly complexed with the chloride species in this melt or the formation constants for $\text{Ag(AlCl}_n^-)_m$ and $\text{Ag(Al}_2\text{Cl}_7^-)_m$ must be almost equal. The behavior of Ag(I) in nitrate melts doped with chloride ion indicates that the first possibility is not the case. A more pronounced chloride activity effect on the silver electrode may be observed in the chloride rich melts where the chloride mole fraction becomes significant compared to that of the $\text{AlCl}_4^-$ ion. This possible response is supported by the increase in curvature in Figure 8 as the $\text{AlCl}_3$ mole % approaches 50%. It is quite evident that the silver electrode is a far superior reference electrode for these melts than is the aluminum electrode.

The observed currents from pulse polarography and cyclic voltammetry in the silver system at 200°C on tungsten indicates the electrodes behaved ideally with respect to pulse width, sweep rates and the Ag(I)
concentration. At 175°C several electrochemical complications are observed. Both the pulse polarograms (Figure 9) and cyclic voltamograms (Figure 10) exhibit a prewave or peak about 200 mV anodic of the reduction wave. The magnitude of the prewave in the pulse polarography increased in magnitude as the rest potential is shifted anodically and as the delay time between pulses is increased. An increase in the Ag(I) concentration appears to enhance the prewave as well. The sweep rate and switching potential in cyclic voltammetry determines the nature of the prewave. A small break in the cathodic portion of the chronopotentiogram (Figure 11) for this system corresponds to this prewave. A sharp anodic peak appears positive to the main anodic stripping peak. The peak does not appear at 175°C until the Ag(I) concentration exceeds \( \approx 0.8 \) mM on a continuous sweep. If the sweep is held momentarily at 0.5 V, the anodic peak can be observed at lower Ag(I) concentrations. Regardless of the Ag(I) concentration, no anodic peak could be observed without a prior silver deposition and dissolution. The position of this peak shifts more anodically with a decrease in temperature and to a lesser degree with an increase in the Ag(I) concentration. At temperatures of 200°C and above, this peak collapses completely into the main stripping peaks. A small break can be seen in the chronopotentiogram which corresponds to this peak (Figure 11). Cyclic voltacoulograms show that the area under the small anodic peak corresponds to the quantity of silver on the electrode surface ranging from less than half a monolayer to several layers. The size of the peak is directly
proportional to the amount of silver being stripped off the electrode. Cyclic voltammograms in the 2:1 melt exhibit only the single large anodic stripping peak regardless of the Ag(I) concentrations or switching potential.

This anodic behavior suggests that there may be two different electrode reactions by which the silver metal is stripped from the indicator electrode.

\[
\begin{align*}
\text{Ag} + n\text{Cl}^- - e^- &= \text{AgCl}^{1-n} & \text{E}_1 \\
\text{Ag} - e^- &= \text{Ag(I)} & \text{E}_2 < \text{E}_1 \\
\text{AgCl}^{1-n} &\stackrel{k_f}{\longrightarrow} \frac{k_r}{k_f} \text{Ag(I)} + n\text{Cl}^- & k_f \ll k_r
\end{align*}
\]

The reaction is not Cl\(^-\) diffusion limited when small amounts of silver is anodized; however, at a higher rate of silver anodization, the local Cl\(^-\) concentration is depleted and the electrode reaction shifts to the less favored reaction at a more anodic potential. The product from the second reaction then reacts in the solution to form a single dominate silver species in solution, hence a single deposition peak. The secondary electrode reaction may involve the AlCl\(_4^-\) species.

\[
\text{Ag} + m\text{AlCl}_4^- - e^- = \text{Ag(AlCl}_4\}_{m}^{1-m}
\]

rather than the Ag(I) ion, but the same argument holds in that the AlCl\(_4^-\) concentration is so high that there will not be a diffusion limit. In the 2:1 melt only the formation of the Ag(Al\(_2\)Cl\(_7\))\(_n\)\(^{n-1}\) or Ag(AlCl\(_4\))\(_m\)\(^{m-1}\) since the Cl\(^-\) concentration is approximately zero. The plot of the silver E\(^0\) vs AlCl\(_3\) concentration (Figure 8) shows that
the formation constants for the AlCl$_4^-$ and Al$_2$Cl$_7^-$ complexes are approximately equivalent and it is only the Cl$^-$ complex which shows an increased stability. If there is a small peak due to Cl$^-$ in the 2:1 melt, it is lost in either the main Al or Ag stripping peaks since only a single anodic silver peak can be observed.

Elevated temperatures increase both the Cl$^-$ concentration (by a factor of 4 at 250°C) and the Cl$^-$ diffusion coefficient (by a factor of $\approx 1.6$ at 250°C) to assist the primary electrode reaction. The decrease in peak separation with a temperature increase seems to indicate that the formation constant for the AlCl$_4^-$ complex has a smaller temperature coefficient than that for the Cl$^-$ complex.

The cathodic peak in the anodic sweep portion of the cyclic voltammogram at high Ag(I) concentrations along with the irregularities on the back portion of the deposition peak (Figure 12) indicate even further electrode complications such as metal alloying. There is about a 50 mV nucleation overpotential for the initial deposition of silver onto tungsten metal (Figure 11). The silver system appears to be a reversible and well behaved system above 200°C while below this temperature, several kinetic complications develop at Ag(I) concentrations in excess of 1 mM. The electrochemical properties measured in the silver system are summarized in the Table below.
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<th>Melt composition</th>
<th>1:1</th>
<th>1:1</th>
<th>2:1</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature °C</td>
<td>175</td>
<td>200</td>
<td>175</td>
</tr>
<tr>
<td>$E^0_M$ V (vs Al in 1:1)</td>
<td>1.143</td>
<td>1.127</td>
<td>1.163, 1.168&lt;sup&gt;1&lt;/sup&gt;</td>
</tr>
<tr>
<td>$dE^0_M/dT$ mV/°C</td>
<td>-0.63</td>
<td>-0.63</td>
<td>-0.44&lt;sup&gt;1&lt;/sup&gt;</td>
</tr>
<tr>
<td>$E^0_{1/2}$ at 1 M V</td>
<td>1.120</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$D \times 10^6$ cm&lt;sup&gt;2&lt;/sup&gt; sec&lt;sup&gt;-1&lt;/sup&gt;</td>
<td>3.01</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
IV
IRON SYSTEM

The electrochemistry of iron in the NaAlCl₃ melts is of primary importance as it has been argued that the common impurity in the melt is iron, organic materials or dissolved silicon compounds. Giner and Hollek, using cyclic voltammetry, reported the following reactions in a 66 mole % AlCl₃ melt at 120°C.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>E vs Al in 1:1 Melt</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe³⁺ → Fe²⁺</td>
<td>1.47 V</td>
</tr>
<tr>
<td>Fe²⁺ → Fe⁺</td>
<td>0.77 V</td>
</tr>
<tr>
<td>Fe⁺ → Fe⁻</td>
<td>&lt; 0.57 V</td>
</tr>
<tr>
<td>Fe → Fe²⁺</td>
<td>0.97 V</td>
</tr>
<tr>
<td>Fe²⁺ → Fe³⁺</td>
<td>1.57</td>
</tr>
</tbody>
</table>

They report the formation of a passive film (Fe²⁺-salt?) in the electrode during the reoxidation of the iron. Yntema et al. reports that in the ternary melt (66% AlCl₃) at 156°C only iron is deposited from 1.02 to 0.82 V vs Al in the 1:1 melt, whereas at 0.60 V, a co-deposit of Fe and Al is formed.

A typical cyclic voltammogram is given in Figure 13 for a NaAlCl₄ system at 175°C after FeCl₃ has been added. An attempt was made to anodize a piece of iron wire (0.2 cm²) in the melt. At currents as low as 0.5 mamp, the iron wire rapidly became polarized and evolved...
Cl₂ at about 2 V. A steady current of about 100 µamp could be realized by potentiostating the iron wire at +1.6 V vs the aluminum reference electrode. The electrochemical results appeared to be independent of the method of addition. The behavior of the double anodic peak at 0.78 and 0.74 V with increasing sweep rate (Figure 14) is similar to the type of behavior exhibited by silver. Increasing the sweep rate decreases the amount of Fe²⁺ that is reduced during the cathodic portion of the sweep; consequently, a greater portion of the total reoxidation of the Fe (at 0.74 V) is the result of the first electrode reaction and there is a decreasing amount left to react in the second electrode process. Increasing the sweep rate from 0.125 V/sec to 0.5 V/sec caused the two relative peak heights to be reversed.

The effect of increased Fe²⁺ concentration can be simulated on the voltammogram by repeated scanning between 0.63 and 0.3 V (Figure 15). The rapid switching back to the cathodic scan just after the iron metal has been stripped from the electrode causes a local concentrating effect. Both the cathodic and anodic peaks exhibit an increase in magnitude with preference given to the more anodic peak of each doublet. The slow growth of the anodic peak during continuous cycling about the Fe³⁺/Fe²⁺ couple along with the observed polarization of the iron wire during anodization indicates that Fe²⁺ is only very sparingly soluble in the 1:1 melt. Solid FeCl₂ doesn't appear to dissolve in the melt to any appreciable degree.

The dependency of peak heights on the Fe²⁺ solubility makes the correlation of peak current with concentration almost useless for all
the peaks except the Fe$^{3+}$ to Fe$^{2+}$ reduction at 1.42 V (Figure 16). The peak separation of 100 mV is slightly greater than the 84 mV for a completely reversible couple at 175°C. This increase in peak separation may be due to some irreversibility in the system or distortion of the anodic peak by insoluble species. The $E_1^c$ for the ferric-ferrous couple by cyclic voltammetry is 1.47 V and the $E_1^a$ for the reduction of ferrous to iron metal is 0.59 V.

The pulse polarogram wave height for the Fe$^{2+}$ → Fe reduction (0.577 V) is twice that for the Fe$^{3+}$ → Fe$^{2+}$ reduction (1.472 V) in Figure 17. The slope from the $i_d$ versus concentration plot for the Fe$^{2+}$ → Fe reaction is twice that for the Fe$^{3+}$ → Fe$^{2+}$ reduction. Due to the limited solubility of Fe$^{2+}$, the currents for the reoxidation of Fe$^{2+}$ → Fe$^{3+}$ are slightly larger than those observed for the reverse reaction.

The cathodic and reverse anodic scans for the Fe$^{3+}$/Fe$^{2+}$ couple are presented in Figure 18. The cathodic $E_1^c$ differ by only 9 mV and the average $i_{d}^c / i_{d}^a$ ratio over a range of concentrations is 0.91 where the theoretical values for completely reversible system are 0 mV and 0.962 mV, respectively. The good fit of the experimental polarogram to the theoretical polarogram in Figure 18 further indicates a high degree of reversibility in the Fe$^{3+}$/Fe$^{2+}$ couple.

Several current reversal chronopotentiograms were recorded in an attempt to confirm our results. The irreproducibility of the current data obtained did not warrant interpretation except that there is an
apparent couple between 0.4 and 0.3 V. This may be due to a co-deposition of iron and aluminum on the electrode which is in keeping with the results of Yntema, et al.\textsuperscript{16}

An it\textsuperscript{1/2} curve from chronoamperometry was also used to calculate a value for the diffusion coefficient for comparison with those obtained from the other electrochemical methods. Only the reduction of ferric ion to ferrous ion gave reproducible results. The results for the other scans were dependent upon the length of time between initial potential application and pulse application. This behavior was to be expected since the starting at any potential other than on the anodic side of the Fe\textsuperscript{3+}/Fe\textsuperscript{2+} couple results in the electrolysis of a non-uniform solution rather than a uniform solution. For a similar reason, D values cannot be calculated from the pulse data for the other scans and the cyclic voltammetric data at the other areas of interest are too scattered to warrant their use. The Fe\textsuperscript{3+} D values calculated from the three electrochemical methods are summarized in Table IV-2 along with the measured E\textsubscript{1/2} values.

### Table IV-2

**ELECTROCHEMICAL CONSTANTS FOR THE IRON SYSTEM IN NaAlCl\textsubscript{4} SELLS AT 175°C**

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Redox Couple</th>
<th>Method</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Integral Pulse</td>
<td>Chronoamperometry</td>
</tr>
<tr>
<td>$E_{1/2}$ (V, 8.58 mM)</td>
<td>Fe\textsuperscript{3+}/Fe\textsuperscript{2+}</td>
<td>1.476</td>
</tr>
<tr>
<td></td>
<td>Fe\textsuperscript{2+}/Fe</td>
<td>0.579</td>
</tr>
<tr>
<td>$E^0$ (V)</td>
<td>Fe\textsuperscript{3+}/Fe\textsuperscript{2+}</td>
<td>1.689</td>
</tr>
<tr>
<td></td>
<td>Fe\textsuperscript{2+}/Fe</td>
<td>0.703</td>
</tr>
<tr>
<td>D (cm\textsuperscript{2}/sec)</td>
<td>Fe\textsuperscript{3+}</td>
<td>$9.9 \times 10^{-6}$</td>
</tr>
</tbody>
</table>
Of the three methods used to determine D, the cyclic voltammetry method is the least reliable.\(^{17}\) The average D value from the other two methods is \(8.8 \times 10^{-6}\) cm\(^2\)/sec.

The Fe\(^{2+}\) species was found to be soluble in the 2:1 melt at 175°C and an overpotential of only 150 mV resulted when the iron wire was anodized at a current density of 5 ma cm\(^{-2}\). The separation between the two anodic stripping peaks (0.76 and 0.93 V) is considerably greater in the 2:1 melt than in the 1:1 melt (Figure 19). No peaks corresponding to the Fe\(^{3+}/Fe^{2+}\) couple were observed for potentials cathodic of +2.2 V. The small anodic peak at +1.14 V and the cathodic prewave at \(<1 V\) are present in the background sweeps and are not due to the iron in the melt. The distortion of the reduction peak is due in part to other small pre-aluminum deposition waves which can be observed in the background.

The Nernst plot for the Fe\(^{2+}/Fe\) couple had a slope of 0.0371 V compared to the theoretical value of 0.0444 V for a two-electron process. The \(E^0_M\) for Fe\(^{2+}/Fe\) at 175°C in the 2:1 melt is 1.04 V with a temperature coefficient of -0.77 mV deg\(^{-1}\) over a temperature range of 175° to 225°C. Our \(E^0_M\) value of 1.01 V at 218°C is in good agreement with the published value of 1.00 V.\(^2\)

There is no apparent reason why we could not observe the Fe\(^{3+}/Fe^{2+}\) couple previously reported in the 66% AlCl\(_3\), 14% KCl, 20% NaCl melt.\(^4\) The partial replacement of sodium ions with potassium ions should have very little effect on the system if the shift in the \(E_M\) for the Fe\(^{3+}/Fe^{2+}\) couple is the same as that for the Fe\(^{2+}/Fe\) couple in going from the 1:1
to the 2:1 melt. The $E^0_M$ for the 3/2 couple should be about 2.0 V vs Al in the 1:1 melt.
COPPER SYSTEM

Copper ions were added to the 1:1 melt by three different methods:

1. Anodization of copper wire to Cu(I)—a current density of 10 ma cm$^{-2}$ polarized the copper wire about 200 mV anodic of its equilibrium potential;

2. Addition of CuCl—the CuCl dissolved slowly in the melt to give a similar electrochemical response as did the anodized copper wire; the melt became pale yellow in color due to unknown impurities in the salt;

3. Addition of CuBr$_2$—this salt would not dissolve and produced very little electrochemical response to cyclic voltammetry.

It is recommended that due to its ease and purity, anodization of copper wire should be used exclusively to add copper to the 1:1 melt. Also, the results of any attempt to anodize Cu(I) to Cu(II) quantitatively are unreliable due to the limited solubility of CuCl$_2$ in the 1:1 melt at 175°C. At a Cu(I) concentration of about 8 mM, the melt became slightly milky in color and the reduction peak for Cu(II) to Cu(I) (on cyclic voltammograms) became more peaked in nature and resembled a stripping peak. The solubility of CuCl$_2$ appears to be slightly less than 8 mM and considerably greater than that for CuBr$_2$ in the 1:1 melt at 175°C. No apparent problems were encountered in oxidizing Cu(I) to Cu(II) in the 2:1 melt. This may be due to the lower Cl$^{-}$ concentration in the 2:1 melt and/or the unspecified copper concentration used in the experiments.
The Nernst plot for the electrode reaction, $\text{Cu}^+ + e^- = \text{Cu}$, from the results of two independent experiments is given in Figure 20. The $n$ value of 0.765 from the experimental Nernst slope requires further verification. When the calculation of the standard molarity electrode potential is based on the experimental Nernst $n$ of 0.765, it is 1.228 V; when based on $n = 1$, it is 1.150 V. The value of 1.06 V for $E^0$, which we calculated from cyclic voltammetry, is in rough agreement with our Nernst values. Francini, et al.,\textsuperscript{19} using a D.M.E. in a 53 AlCl$_3$ mole % melt report an $E^0$ value of 0.63 V which corresponds to 0.93 V vs our reference electrode. This result as well as ours are in accord with the 0.689 V reported\textsuperscript{1} for copper in the 2:1 melt at 135°C. The temperature coefficients were reported for the literature $E^0$ values, thus it is not possible to adjust the reported values to 175°C.

The series of cyclic voltammograms (Figures 21-24) for Cu(I) concentrations ranging from 2.1-12.28 mM, show the limited solubility of CuCl$_2$ and that the presence of Cu(I) suppresses the evolution of Cl$_2$. At low Cu(I) concentrations ($< 2.1$ mM), the normal Cl$_2$ evolution is observed at potentials in excess of 1.8 V, whereas at higher Cu(I) concentrations ($> 3.7$ mM), no excessive Cl$_2$ evolution occurs until 2.2-2.3 V is reached. The shift in the Cl$_2$ evolution potential is probably due to the local depletion of Cl$^-$ caused by the formation of CuCl$_2$. A similar behavior is observed when switching from the 1:1 melt to the Cl$^-$ deficient 2:1 melt. The enhancement of the anodic peak, with respect to the reverse cathodic peak for the Cu$^{+2}$/Cu$^+$
couple (Figure 22), indicates that there is some irreversible oxidation of Cl\(^-\) at 2 V; this concurs with the net 6\% gain in anodic products per cycle in the cyclic voltacoulogram for both copper electrode couples (Figure 25). The cyclic voltacoulogram for the Cu\(^+\)/Cu couple only (Figure 26) shows that there is quantitative reoxidation of all the reduction products of this process. The cathodic peak current for the Cu\(^+\)/Cu couple is linear with the Cu\(^+\) concentration (Figure 27) and the ip/v\(^1/2\) at a given concentration was found to be constant for v from 0.05-1.0 V sec\(^{-1}\). The shift in the E\(_p\) peak of copper deposition is 0.087 V per decade change in concentration compared to the theoretical value of 0.0889 V for a one-electron process at 175° C.

Evolution of Cl distorts the peak for the Cu\(^+\) - e = Cu\(^+2\) reaction and makes measurement of the anodic peak potential somewhat arbitrary; however, the peak separation of 100 mV (Figure 22) is still in reasonable agreement with the theoretical value of 85.5 mV for a reversible one-electron process. The cathodic peak potential shifts from 1.88 V to 1.80 V when the solubility of the CuCl\(_2\) is exceeded. At Cu(I) concentrations less than 8 mM, the cathodic E\(_p\) for the Cu\(^+2\)/Cu\(^+\) couple is independent of sweep rate for v from 0.05-1.0 V sec\(^{-1}\).

No unanticipated irregularities were observed in the chronopotentiogram of the copper system (Figure 28) except for a small nucleation peak for the deposition of Cu(I) on tungsten. This peak is considerably smaller than the one observed for the deposition of silver on tungsten.

Pulse polarograms were recorded for the Cu(I) reduction (Figure 29). No satisfactory plots could be obtained for the oxidation of
Cu(I); however, the double potential step pulse polarogram (Figure 30) illustrates the reduction of both the Cu(II) and Cu(I) species in the melt. A constant $i_t^b$ value of $2.57 \times 10^{-6}$ amp sec$^{-1/2}$ and a $E_{1/2}$ of 0.833 V were recorded for the reduction of Cu(I) with pulse widths from 10-100 m sec.

The $E^0$ and $D$ values calculated from the various techniques are compared to literature values in Table V-1.

The copper system in the 1:1 melt consists of two reversible electrode couples, Cu$/\text{Cu}^+$ and Cu$^{+2}$/Cu$^+$, with $E^0_M$ values of 1.10 and 1.95 V vs Al, respectively. The limited solubility of CuCl$_2$ ($\approx 8$ mM) may provide the basis for a usable electrode system for the NaAlCl$_4$ melts.
### TABLE V-1

ELECTROCHEMICAL PROPERTIES FOR COPPER IN A NaAlCl₄ MELT AT 175°C

<table>
<thead>
<tr>
<th>Source</th>
<th>$D \times 10^6$ cm²/sec⁻¹ (for Cu⁺)</th>
<th>$E_M^{0}$ V Cu⁺/Cu</th>
<th>$E_P^{0}$ V Cu⁺+/Cu</th>
<th>$E_F^{0}$ V Cu⁺+/Cu</th>
<th>$E_M^{0}$ Cu⁺²/Cu⁺</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pulse Polarography</td>
<td>6.90</td>
<td>1.077</td>
<td></td>
<td>0.833*</td>
<td>1.98</td>
</tr>
<tr>
<td>Cyclic Voltammetry</td>
<td>9.88</td>
<td>1.056</td>
<td>0.815**</td>
<td></td>
<td>1.92</td>
</tr>
<tr>
<td>Nernst Plot ($n = 1$)</td>
<td></td>
<td>1.150</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Nernst Plot ($n = 0.765$)</td>
<td></td>
<td>1.228</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Reference 19 on Hg (vs Al in 1:1 melt)</td>
<td></td>
<td></td>
<td>0.90†</td>
<td>0.93†</td>
<td></td>
</tr>
<tr>
<td>Reference 1, 135°C, in Ternary Melt</td>
<td>6.01</td>
<td>0.689</td>
<td></td>
<td></td>
<td>1.866</td>
</tr>
<tr>
<td>Reference 1, +0.467 V (1:1 melt)</td>
<td></td>
<td>1.156</td>
<td></td>
<td></td>
<td>2.333</td>
</tr>
</tbody>
</table>

* 3.50 mM Cu⁺
** 2.11 mM Cu⁺
† 0.1 to 1 mM Cu, 150°C, 53 mole % AlCl₃
VI

LEAD SYSTEM

The Pb(II) was generated coulometrically in the melt at a current density of 10 mamp cm$^{-2}$ with an overpotential of 100 to 200 mV. For lead concentrations between 0.5 and 22 mM, the experimental lead Nernst plot exhibited a fair proximity with the theoretical slope for n = 2 at 200°C. At higher lead concentrations, the emf potentials were abnormally high and a white crystalline solid formed in the fritted compartment. The Nernst plot does not indicate that the solid is PbCl$_3$. However, the abnormal behavior may be due to a marked increase in the lead activity coefficient. A $E^0_M$ value of 0.906 V was calculated from the Nernst plot for lead at 200°C. A $E^\text{Al}_\text{AlCl}_3$ value of +0.44 V has been reported for lead in a 53 mole % AlCl$_3$ melt at 170°C using a DME. This value is equivalent to 0.86 V vs Al in NaAlCl$_4$ which differs from our $E^0_M$ value by only 46 mV.

A plot of $i$ peak from cyclic voltammetry vs lead concentration indicates that the solubility of lead chloride in the NaAlCl$_4$ melt at 200°C is about 11 mM. The lead electrode couple appears to be reasonably well behaved in dilute solutions (< 10 mM). However, the formation of an unidentified solid at higher concentrations interferes with the various electrochemical measurements.
A cursory examination of the cadmium electrode system in the 1:1 melt was carried out because of a report that Cd\(^{2+}\) is stabilized in the 2:1 melt.\(^{12}\) Cadmium was added to the melt by the anodization of a piece of cadmium wire. The cyclic voltammograms (Figure 31) of the low cadmium concentrations (0.3-10 mM) exhibited no unusual behavior; however, at the higher concentrations (> 20 mM) several additional peaks were observed (Figure 32). The cathodic peak potential of 0.47 V was invariant with sweep rate (0.1-50 V/sec) in a 5.83 mM solution and compares well with the 0.468 V observed for cadmium on mercury.\(^{19}\) The two overlapping cathodic peaks indicated that the possible formation of a Cd\(^{2+}\) intermediate becomes more predominate with an increase in cadmium concentration. The equilibrium constant for the reaction,

\[
Cd^{2+} + Cd \rightarrow Cd_{2}^{2+}
\]

is 26 in the 2:1 melt\(^{12}\) which indicates the Cd\(^{2+}\) ion is stabilized by the higher concentration of AlCl\(_3\) or Al\(_2\)Cl\(_7\) in the 2:1 melt. These observations are consistent with those reported for the bismuth system in these melts.\(^{3}\) It has been reported that oscillopolarographic measurements of Cd\(^{2+}\) (0.1-1.0 mM) in a 52 mole % AlCl\(_3\) melt using a D.M.E. produced no evidence for Cd\(_2^{2+}\).\(^{19}\)

The Nernst plot for cadmium (Figure 33) verifies a two-electron process and the \(E^0_M\) is 0.664 V vs Al in the 1:1 melt at 200°C. A \(E^0_M\)
value of 0.592 V was calculated from our cyclic voltammograms, while a decomposition potential of 0.63 V was reported for cadmium in the 1:1 melt at 300°C.\textsuperscript{20}

A $E^0$ value of +0.35 V has been reported for cadmium in the 2:1 melt at 150°C\textsuperscript{12} which is equivalent to +0.82 V vs the Al electrode in the 1:1 melt. The cadmium electrode potential shifts about 190 mV cathodically when the AlCl\textsubscript{3} concentration in the melt is decreased from 66 mole % to 50 mole %. Even though this shift is less than half that for the aluminum electrode, the cadmium electrode is not a useful reference electrode. The shift in potential may be due to the change in chloride concentration, as it is for the aluminum electrode, or a change in predominate electrode reaction, i.e., \( \text{Cd}^{2+} + 2e = \text{Cd} \) (in the 1:1 melt) to \( \text{Cd}_2^{2+} + 2e = 2\text{Cd} \) (in the 2:1 melt).

A typical pulse polarogram is given in Figure 34; however, a considerable deviation from the linear relationship between the limiting diffusion current and cadmium concentration was observed at concentrations above 2 mM (Figure 35). The diffusion coefficient calculated from a point on the straight line in Figure 35 is 3.18 \( \times 10^{-6} \) cm\textsuperscript{2} sec\textsuperscript{-1} which compares well with 2.66 \( \times 10^{-6} \) cm\textsuperscript{2} sec\textsuperscript{-1} calculated from the cyclic voltammogram and the reported value of 3.30 \( \times 10^{-6} \) cm\textsuperscript{2} sec\textsuperscript{-1}.\textsuperscript{19}
Moisture reacts with the melt according to the following reaction.\textsuperscript{21}

$$2\text{AlCl}_4^- + \text{H}_2\text{O} \rightarrow 2\text{HCl} + \text{Al}_2\text{OCl}_5^- + \text{Cl}^-$$

Figure 36 shows the voltammogram which was recorded at 175°C on a tungsten button (area = $6.28 \times 10^{-3}$ cm$^2$) immediately after bubbling dry HCl gas through the melt for 5 min. The large nondescript peak at +0.55 V decayed rapidly with time to give a steady state voltammogram in about 10 min (Figure 36). The first cyclic sweep produces a trace which is considerably larger than the steady state trace which is reached after about 5 cycles. Stirring the melt had no appreciable effect on the shape or magnitude of the recording.

No anodic wave could be detected on the reverse sweep using the tungsten electrode. Bubbling nitrogen through the melt for about 5 min reduced the peak height by about a factor of 5. This is consistent with the efficiency that has been reported for the removal of HCl from the organic AlCl$_3$ systems. Without knowing the concentration of the active species, it is not possible to relate the peak potential of 950 mV to the $E^0$ value. If a nominal value of 200 mV is used for the shift from $E^0$ to $E_p$, the estimated $E^0$ value of 1.15 V is in agreement with the 1.1 V obtained for HCl in the 1:1 melt.\textsuperscript{21}

In order to observe an oxidation peak for H$_2$, it is necessary to maintain a good three-phase contact at the electrode as well as a reasonably large solubility product for H$_2$ in the melt. Most gases are only
sparingly soluble in fused salts at the best of times. The absence of any irregularities in the region 0.9–1.0 V is a reasonable diagnostic for the absence of moisture in these melts.
In any investigation of electrochemical reactions, it is necessary to have some knowledge of the possible homogeneous reactions. This is especially true in reactive solvents such as our AlCl₃ solvent system or anhydrous hydrogen fluoride. Therefore, a thorough literature review on the reactions of organic compounds in AlCl₃ solvent systems was carried out. This review is summarized below while a complete account can be found in the third semi-annual report of this contract.

Many different organic reactions are found to proceed in AlCl₃ containing solvent systems. Three major types of reactions, namely condensation-addition, rearrangement and isomerization and dehydrogenation-addition reactions have been studied extensively. Other types of reactions which have been found to occur in these solvents are dehydration, exchange and reduction-chlorination reactions. AlCl₃ solvent systems containing an organic compound as a component have been studied. Only two reports have appeared on the electrochemical behavior of organic compounds in AlCl₃ solvent systems.

In the general category of condensation-addition reactions, mono- and dibasic carboxylic acids, acid anhydrides and lactones were found to react with a variety of aromatic and heterocyclic compounds, most of which are activated by hydroxyl, amino and/or alkyl substituents. The reactions are carried out in the temperature range of 100-220°C with reaction times ranging from 2 min to hours. In the case of
monobasic acids only keto products are obtained. With dibasic acids and acid anhydrides keto-acids are the initial products; however, if the reaction conditions are severe enough, ring closure of the keto-acid occurs yielding quinones. Lactones give rise to ring closed ketones. Intramolecular ring closure has been found in the case of aryl substituted aliphatic acids. In some cases, isomerization was observed to play an important role.

Numerous molecular rearrangements and isomerizations are found to occur in AlCl₃ solvent systems. In a few cases, these reactions allow the synthesis of compounds which cannot be prepared by any other method. Of the rearrangements which have been studied, the Fries rearrangement is the most common. Phenolic esters and arylsulfonates undergo rearrangement to the respective hydroxy ketones and sulfones. Isomerization of alkyl groups is found to occur in some cases. ß-Aroyl-acrylic acids and aryl vinyl ketones are found to rearrange to ring closed ketones, the acid function remaining intact in the former case. Heterocyclic compounds such as chromanones and coumarins also rearrange to cyclic aromatic ketones. A thorough study was carried out by Baddeley and his co-workers of the isomerizations in aromatic ketones and sulfones and in alkylated phenols and benzenes. The migration of an alkyl and/or acyl or sulfonyl group depends mainly on the relative rates of deacylation or desulfonation followed by reacylation or resulfonation respectively and also on the intermolecular migration of the ð-alkyl group to the adjacent meta-position. Sufficient AlCl₃ together with some HCl is necessary for
the reaction to occur. Steric factors were also found to be of importance.

The dehydrogenation-addition reaction which is generally known as the Scholl reaction has mainly been carried out mainly with two classes of organic compounds—unsubstituted and substituted polynuclear hydrocarbons and diaryl ketones. Both intra- and intermolecular reactions have been observed. Hydrogen chloride is claimed to be needed as a catalyst for the reaction. The by-product of these reactions is assumed to be hydrogen gas the fate of this material has been considered. In a few cases, reducible groups within the starting materials have been found to be reduced during the course of the reaction and this was offered as evidence for the existence and fate of the hydrogen gas.

Several other types of organic reactions have been observed in AlCl₃ solvent systems. Dehydration reactions have been carried out, one example is the formation of benzonitriles from benzamides. The ring closure dehydration of 1-arylamino-anthraquinones to ceramidonines has been extensively studied.

Exchange reactions involving a variety of starting materials have been reported. Of technical importance are the exchange reaction of the hydrogens attached to silicon for chlorines and the exchange reaction forming methylmetal compounds from methyl chloride and the metal chlorides. Fluorine in certain ethers has also been found to exchange with the chlorine of AlCl₃ solvent systems.
One final reaction of interest reported to occur in AlCl₃ solvent systems, is that involving aromatic nitro compounds. In two instances it has been reported that nitro-substituted aromatics undergo simultaneous reduction of the nitro group and chlorination of the aromatic nucleus. The hydrogen necessary for the reduction probably comes from hydrogen chloride which is either added to the reaction mixture or formed during the course of the reaction.

AlCl₃ solvent systems with an organic compound as a component have been used as organic reaction media. Similar reactions occur in fused AlCl₃-pyridine system reactions and in AlCl₃. Reactions have been reported to occur in which the organic component also acts as a reactant, e.g., the formation of benzamide from benzene in an AlCl₃-urea melt.

Only two reports on the electrochemical reactions of organic compounds in AlCl₃ solvent systems have appeared. In one case, Fleischmann and Fletcher²² studied the electro-oxidation of several aromatic hydrocarbons. They found that the larger polynuclear hydrocarbons show a series of electron transfers while the simple hydrocarbons show a single wave. Their cyclic voltammetric results also appeared to indicate that these oxidations were electrochemically reversible. The second report²³ of organic electrode reactions in AlCl₃ solvent systems was concerned with the electro-initiated polymerization of several aromatic compounds. The system to be electrolyzed consisted of a ternary complex of an aromatic hydrocarbon, a hydrohalogen acid and an aluminum halide. Among the interesting products formed were poly(p-phenylene) from benzene and p-sexipheny from biphenyl. The mechanism of these processes
were found to be very complex.

For our initial investigation of organic electrochemistry in AlCl₃ solvent systems we wanted a simple molecule that would undergo a reversible one electron change in order that other molecules could be compared with it. One molecule which has been found to undergo a reversible one electron change in several aprotic solvents is ferrocene.²¹ We established that ferrocene is stable in 50:50 mole % AlCl₃:NaCl melt at 175°C. The cyclic voltammogram for the anodic oxidation of ferrocene at a W button electrode is shown in Figure 37. The shape of the curve is characteristic of a reversible reaction and the measured electrochemical parameters such as $i_p/\nu^k$ (where the symbols have their usual meaning) are consistent with a reversible one electron oxidation. A calculated cyclic voltammogram is almost identical with the experimental curve (some deviation after $E_p$). Controlled potential electrolysis (cpe) causes the original orange ferrocene solution to change to blue in color. This is similar to what is observed in aprotic solvents. All the above observations are consistent with a reversible one electron oxidation of ferrocene.

To extend our studies of organic electrochemical reactions in AlCl₃ solvent systems we required organic compounds which were both stable in the solvent and were known to undergo anodic oxidations in a potential range similar to that of ferrocene. Aromatic amines were found to be such a class of compounds. A number of amines in this class have been studied and have also been found to undergo a variety
of electrochemical reactions depending upon the substituents of the nitrogen atom.

Triphenylamine (TPA) in aprotic solvents such as acetonitrile has been shown to undergo anodic oxidation at a platinum electrode to yield the corresponding radical cation which reacts further by dimerizing to $\text{N}_2\text{N}_2\text{N}',\text{N}'\text{-tetraphenylbenzidine}$ with a rate constant of $2.4 \times 10^3 \text{ mole}^{-1} \text{ sec}^{-1}$. As would be expected, the cyclic voltammogram (with sweep rates in the range of 0.1-1.0 V/sec) for this oxidation show no cathodic current corresponding to the reduction of the initially formed radical cation. The cyclic voltammogram for TPA in a 50:50 mole % $\text{AlCl}_3:\text{NaCl}$ melt at $175^\circ\text{C}$ is shown in Figure 38 with $E_\text{p}^\text{anodic}$ at 1155 mV and $E_\text{p}^\text{cathodic}$ at 1060 mV. The observed $i_p$ curve is characteristic of a reversible one electron oxidation (compare with that obtained for ferrocene, Figure 37). This is a remarkable result! At temperatures 150° higher, the product of the electrode reaction, TPA radical cation, is stable. In other words, the $\text{AlCl}_3$ solvent system stabilizes the TPA radical cation much more than other aprotic solvents. This result is also substantiated by the fact that $E_\text{p}^\text{anodic}$ is virtually constant over a $10^3$ change in sweep rate and that $i_\text{p}^\text{cathodic}$ shows little change with switching potential. Controlled potential electrolysis (cpe) gives a blue solution which is stable for at least 24 hr (the TPA radical cation gives blue solutions in aprotic solvents). Cyclic voltammograms of the electrolyzed solution indicate the presence of another species which we have not yet identified. Changing the solvent to a 66:34 mole % $\text{AlCl}_3:\text{NaCl}$ melt
(10^7 change in acidity) gave identical cyclic voltammograms (peak potentials were identical) as were the voltammograms recorded at higher temperature.

The surprising stabilization of the TPA radical cation in AlCl_3 solvent systems led us to look for other amines where this stabilization might occur. In aprotic solvents DMA is reported to undergo anodic oxidation to form a radical cation which undergoes very rapid follow up chemical reactions.\(^{25}\) It is stated that the radical cation has not been detected as such in electrochemical experiments. The cyclic voltammogram for DMA in a 50:50 mole % AlCl_3:NaCl melt is shown in Figure 39. This voltammogram has the classic shape for an ECE type mechanism. The cathodic peak which occurs on sweep reversal together with the anodic peak which occurs on the second anodic sweep constitute a redox couple which corresponds to that for \(\text{N}_2\text{N}_2\text{N}_1\text{N}_1\) tetramethylbenzidine (peak position and separation are identical, see below) which is the expected dimerization product. The shoulder prior to the cathodic peak is approximately 100 mV cathodic of the main oxidation peak and no doubt corresponds to the reduction of the DMA radical cation. At faster sweep rates this shoulder becomes a well defined peak, the peak separation being in the vicinity of 100 mV. Plots of \(E_p\) (anodic) versus sweep rate (at fast sweep rates \(E_p\) approaches a constant value) are indicative of an ECE type mechanism. The fact that we can observe the DMA radical cation is again indicative of stabilization of the radical cation by AlCl_3 solvent systems.
In a similar manner we have studied the anodic oxidation of diphenylamine (DPAmine). The cyclic voltammograms are very similar to that for DMA. When the sweep rate is increased from 0.5 V/sec to 100 V/sec two distinct redox processes are observed. The redox couple for the electroactive product corresponds very closely with that for N,N'diphenylbenzidine (see below), one of the possible products from the reactions of the initial electrode reaction product. This couple certainly does not correspond to that for carbazole (see below). From the anodic and cathodic peak separation for the main oxidation peak, we again conclude that we are observing the reduction of the DPAmine radical cation and that this radical cation is stabilized in the AlCl₃ melt. From the peak positions we again conclude that the radical cation from the oxidation of DPA is stabilized in the AlCl₃ melt. The DPA radical cation has not been observed electrochemically in other aprotic solvents. The formation of a single electroactive product is in contrast to the results in aprotic solvents where at least two products are formed; this is again indicative of stabilization of the radical cation.

A number of other aromatic amines were also studied primarily because they have been shown to undergo reversible two one-electron oxidations in aprotic solvents. Secondly, they were possible products of other electrode reactions (see above). When the cyclic voltammograms of N,N,N',N'-tetramethylbenzidine (TMB) were run in 50:50 mole % AlCl₃:NaCl melts, only a single apparent redox couple (Eₚ (anodic) = 1050 mV) was observed within the potential limits of the melt. The
peak separations at 0.5 V/sec was 60-70 mV, the separation becoming
greater at higher sweep rates. Values of $i_{p}/\nu^{1/2}$ decrease a fair amount
when the sweep rate is varied between 0.05 and 0.5 V/sec. However,
$i_{c}$ (cathodic) is not dependent upon the switching potential. From
these observations it is not clear whether we are observing a two
electron oxidation or two closely spaced one-electron oxidations.
Controlled potential electrolysis gives an orange solution which does
not change over a long period of time even when open to the atmosphere.
It is interesting to note that in aprotic solvents, one obtains an
orange solution only after two electrons have been removed from TMB,
the color of solution when only one electron has been removed being
blue-green. This may indicate that we are indeed observing a two
electron change.

Furthermore, when the cyclic voltammograms were obtained for TMB
in 66:34 mole % AlCl$_3$:NaCl melts, the results were surprising. An
anodic peak was observed at 2070 mV while a cathodic peak was observed
at 1170 mV. However, these widely separated peaks do constitute a
redox couple as the cathodic peak is only observed after sweeping
through the anodic peak. Cpe again gives rise to an orange solution
in which the only electroactive species corresponds to the redox
couple observed in cyclic voltammetry. A possible explanation for
the large change (approx. 1 V) in the anodic peak potential with a
change in melt composition is that we are observing an acid-base reac-
tion between TMB and AlCl$_3$ (the acidity of the AlCl$_3$ solvent changes
by a factor of $10^7$ for the range of composition studied) which makes
it much more difficult to oxidize the amine in the 2:1 melt. The fact that the cathodic peak potentials differ by only 200 mV and that the cpe results are similar would indicate that we are reducing the same species.

Cyclic voltammetric results have also been recorded for N,N'-diphenyl-benzidine (DPB) which was expected to undergo two one-electron oxidation steps. Again as the case of TMB, DPB in a 1:1 melt, gave only one apparent redox couple with a peak separation of 120 mV which is substantially larger than the theoretical value of 89 mV for a one electron change of 175°C. The values for $E_p$ did not change significantly with increasing sweep rates. Plots of $E$ vs log $i_{d^{-1}}/i$ from pulse polarography had a slope of 120 mV. Values of $i_{p}^{1/2}$ and $i_{p}^{1/2}$ were also constant. These observations are best explained by describing the electrode reaction as two closely spaced one-electron oxidation steps. Cyclic voltammograms of DPB in a 2:1 melt again showed unusual results. At certain sweep rates (0.01-0.5 V/sec) a redox couple is observed ($E_{p}$ (anodic) = 1600 mV at 0.05 V/sec) with a peak separation of 110 mV. $E_{p}$ (anodic) increases while $E_{p}$ (cathodic) decreases with increasing sweep rates. At very low sweep rates, one obtains what looks like a normal polarogram, very little of any cathodic current flowing on sweep reversal. At sweep rates greater than 0.5 V/sec, the anodic peak again shows a limiting behavior with the wave becoming ill defined at sweep rates greater than 5 V/sec. Comparing these results with those for TMB, we again see a shift in the anodic peak (wave) and cathodic peak toward more anodic potentials when the solvent
is changed from a 1:1 to a 2:1 mixture, this shift being nowhere as large as that for TMB. However, the behavior of the anodic portion of the voltammogram suggests that we are again observing some form of a kinetic effect, possibly a slow acid-base reaction or slow electrode kinetics.

\(\text{N}_2\text{N}_2\text{N'},\text{N'}\)-tetraphenylphenylenediamine (TPPD) was also expected to undergo two one-electron oxidations and indeed the cyclic voltammograms of TPPD in a 1:1 melt consisted of two redox couples: \(E_p^{\text{anodic}}\) = 860 and 1315 mV with peak separations of 70-90 mV. \(E_p^{\text{anodic}}\) for the first peak increased with increasing sweep rate while \(E_p^{\text{anodic}}\) of the second peak remained constant. These preliminary results appear to indicate that TPPD probably undergoes two reversible one-electron oxidations.

Preliminary cyclic voltammetric investigations of the oxidations of several other amines was also carried out. Of particular interest was the oxidation of carbazole which is a possible product from the oxidation of diphenylamine (see above). The cyclic voltammograms for carbazole show on anodic sweep a well defined peak with \(E_p^{\text{anodic}}\) = 1540 mV which shifts to higher potentials with increasing sweep rate. The cathodic sweep shows at least two ill defined waves. The second anodic gives an indication of a wave between 1200 and 1400 mV. There appeared to be filming of the electrode during the course of these experiments. Also of interest was the primary amine \(p\)-toluidine. The cyclic voltammograms for this material again gave, on anodic sweep, a well defined peak at 1600 mV (0.5 V/sec) which increased in potential
with increasing sweep rate. On cathodic sweep a well defined peak was found at 1140 mV. The second anodic showed no other peaks. These results for carbazole and p-toluidine again indicate that we are observing follow up chemical reactions in these anodic oxidations. It is interesting to note that the simple amine, p-toluidine, appears to undergo simple follow up chemical reactions as only one electroactive product is observed. This is not the case in other solvents.

We have also carried out a cyclic voltammetric study of a number of aromatic hydrocarbons in order to compare our results with those of Fleischmann and Fletcher. The first compound which we studied was anthracene. If the cyclic voltammograms were run immediately after dissolving this compound in a 1:1 melt, a redox couple is observed with \( E^p_{(anodic)} = 1450 \text{ mV} \) and a peak separation of 90-100 mV. On cathodic sweep a wave is also observed at 800 mV which comes from the redox couple. However, after a short period of time, more cathodic peaks (waves) which continue to increase in size are observed. These results indicate that anthracene is undergoing chemical reactions and are much different than those obtained by Fleischmann and Fletcher who observed four redox couples.

The contrasting results for anthracene led us to study two other hydrocarbons, namely diphenylanthracene and pyrene. Under the proper conditions (sweep rate greater than 0.2 V/sec, anodic potential limit of 1500 mV) the cyclic voltammograms for diphenylanthracene consist of a single redox couple with \( E^p_{(anodic)} = 1320 \text{ mV} \) and a peak separation of 80-90 mV. The redox couple did not change significantly after
many sweeps nor did the peak potentials change with sweep rate. At sweep rates below 0.2 V/sec the anodic peak was drawn out while the cathodic peak was well defined. When the anodic limit was increased, the cyclic voltammograms became very complex. Although the initial anodic sweep was normal, at switching potentials greater than 1600 mV a second sharp cathodic peak was observed at 1400 mV. On the second anodic sweep at least two other sharp anodic peaks are observed which, like the new cathodic peak, increase during continuous cycling. Holding at 1500 mV after the first cycle also causes these new peaks to appear.

In a similar manner, when the anodic limit was less than 1700 mV, the cyclic voltammograms for pyrene contained a redox couple with $E_p$ (anodic) = 1490 mV and a peak separation of 90-100 mV together a cathodic wave at 800 mV. On continuous sweep a second cathodic peak at 1270 mV builds with time. When the anodic limit was extended to 1800 mV, new anodic and cathodic peaks appeared in a manner identical to that for diphenylantracene. The results for diphenylantracene and pyrene are certainly very different from those described by Fleischmann and Fletcher.\textsuperscript{22} It seems obvious that we are observing complex follow up chemical reactions after the initial electron transfer. The shape of the peaks possibly indicate that there is filming of the electrode. These results together with those for anthracene point out the fact that one must be aware of the homogeneous chemical reactions that can occur. Also, it should be noted that another group of workers\textsuperscript{26} have been unable to reproduce Fleischmann and Fletcher's results.
The electrochemical oxidation of one hydrocyclic compound has been studied briefly. This was hydroquinone (H$_2$Q) which is of interest because it has been used extensively as a reactant in AlCl$_3$ melts and its electrochemistry has been investigated in several solvents. The observed cyclic voltammogram for H$_2$Q is shown in Figure 40. Although the anodic wave is not well resolved (because of solvent background), it becomes sharper after several sweeps. The first reduction peak on sweep reversal is obviously the reverse of the oxidation process while the reduction wave at approximately 700 mV is attributed to the reduction of H$^+$. A possible explanation for this is as follows. When H$_2$Q dissolves in an AlCl$_3$ melt, the reactions shown below may take place:

\[
\text{H}_2\text{Q} + \text{AlCl}_3 \leftrightarrow \text{HQAlCl}^+ + \text{H}^+
\]

\[
\text{HQAlCl}^- + \text{AlCl}_3 \leftrightarrow \text{Q(AlCl}_3)_2^{2-} + \text{H}^+
\]

The electrochemical reactions are the oxidation of the AlCl$_3$ complex of either the mono- or di-anion of hydroquinone, its subsequent reduction and the reduction of the proton (reduction of HCl occurs at approximately the same potential).

A brief study of the reduction of dinitrobenzene and chloranil in a 50:50 mole % AlCl$_3$:NaCl melt indicated that reaction occurs; however, it appears irreversible with complex follow up chemical reactions.

The results of our studies on organic electrode reactions in AlCl$_3$ solvent systems can be summarized as follows:

1) ferrocene and triphenylamine undergo reversible one electron oxidations;

2) the radical cations formed from triphenylamine, diphenylamine
and dimethylaniline are stabilized in AlCl₃ solvent systems when compared to other aprotic solvents; the voltammograms for DMA and DPamine indicate that these materials are reacting by an ECE type mechanism;

3) although TMB and DPB were expected to undergo two one-electron oxidations only one redox couple which was solvent composition dependent was observed; from the peak separations for both materials it is possible to conclude that these couples constitute two closely spaced one-electron oxidations; the solvent composition dependence could be attributed to some form of slow kinetics either heterogeneous or homogeneous;

4) the expected two one-electron oxidations were observed for TPPD;

5) the electrode reactions of carbazole and p-toluidine appear to be of the ECE type;

6) our results for the anodic oxidation of three aromatic hydrocarbons differ substantially from those of Fleischmann and Fletcher,²² the reactions being much more complex than reported; further work is certainly necessary;

7) hydroquinone undergoes an acid-base reaction when it dissolves in a 1:1 melt, the anodic reaction being attributed to the AlCl₃ complex of the mono- or di-anion of H₂Q;

8) reductions of organic compounds so far studied have been found to be complex.
REFERENCES


(26) Bauer, D., private communication.

APPENDIX I

Combined EMF Series in AlCl₃:NaCl Melts

<table>
<thead>
<tr>
<th>Couple</th>
<th>$E^°_M$</th>
<th>T°C</th>
<th>Solvent</th>
<th>Reference</th>
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</thead>
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<td>Al(III)/Al</td>
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<td>120-220</td>
<td>1:1</td>
<td>Defined</td>
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<td>Al(III)/Al</td>
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<td>175</td>
<td>2:1</td>
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<td>R+/Ferrocene</td>
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<td>175</td>
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<td>Cd(II)/Cd</td>
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<tr>
<td>Fe(II)/Fe</td>
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<td>175</td>
<td>1:1</td>
<td></td>
</tr>
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</tr>
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<td>53:47</td>
<td>(19)</td>
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<tr>
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<td>1:1</td>
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<td>(1)</td>
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*Listed value agrees with previously reported values.
FIGURE TITLES

Figure
1 Experimental Electrochemical Cell
   A - Thermocouple well
   B - 19/22 ground joint for reference electrode
   C - 25 mm hole for working electrode compartment
   D - 14/20 ground joint for counter electrode
   E - Working electrode
   F - Teflon adaptor
   G - Working electrode compartment
   H - O-ring
   I - Teflon cell top
   J - Ring furnace
   K - Glass cell
   L - Furnace
   M - Melt
   N - Reference electrode compartment and Al electrode
   P - Tungsten counter electrode

2 Current Density vs Voltage Curves for NaAlCl₄ Melt at 175°C
3 Current Density vs Voltage Curves for 1:1 and 2:1 AlCl₃-NaCl Melts
4 Block Diagram for PDP-12 Computer System
5 Block Diagram for Electrochemical Data Acquisition System
6 Double Pulse Polarography Voltage Function
7 Nernest Plot for Silver in the 1:1 and 2:1 AlCl₃-NaCl Melts at 175°C
8 Standard Electrode Potentials for Aluminum and Silver as a Function of AlCl₃ Concentration
9 Integral Pulse Polarogram of 0.7 mM AgCl in a NaAlCl₄ Melt at 175°C
10 Cyclic Voltammogram of AgCl in a NaAlCl₄ Melt at 175 and 225°C
11 Chronopotentiogram of AgCl in a NaAlCl₄ Melt at 175°C
12 Cyclic Voltammograms of AgCl in a NaAlCl₄ Melt at 175°C
13 Cyclic Voltammograms of FeCl₃ in a NaAlCl₄ Melt at 175°C
14 Anodic Portion of Cyclic Voltammogram of FeCl₃ in a NaAlCl₄ Melt at 175°C
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15 Cyclic Voltammogram of the Fe(II)/Fe Couple in a NaAlCl₄ Melt at 175°C

16 Cyclic Voltammetry Peak Currents vs FeCl₃ Concentration in a NaAlCl₄ Melt at 175°C

17 Integral Pulse Polarogram of FeCl₃ in a NaAlCl₄ Melt at 175°C

18 Integral Pulse Polarogram of the Fe(III)/Fe(II) Couple in a NaAlCl₄ Melt at 175°C

19 Cyclic Voltammogram of FeCl₃ in a 2AlCl₃, NaCl Melt at 175°C

20 Nernst Plot for CuCl in a NaAlCl₄ Melt at 175°C

21 Cyclic Voltammogram of 2.10 mM CuCl in a NaAlCl₄ Melt at 175°C

22 Cyclic Voltammogram of 3.70 mM CuCl in a NaAlCl₄ Melt at 175°C

23 Cyclic Voltammogram of 7.51 mM CuCl in a NaAlCl₄ Melt at 175°C

24 Cyclic Voltammogram of 12.28 mM CuCl in a NaAlCl₄ Melt at 175°C

25 Cyclic Voltacoulogram of CuCl in a NaAlCl₄ Melt at 175°C

26 Cyclic Voltacoulogram of CuCl in a NaAlCl₄ Melt at 175°C

27 Cyclic Voltammetry Peak Currents vs CuCl Concentration in a NaAlCl₄ Melt at 175°C

28 Chronopotentiogram of CuCl in a NaAlCl₄ Melt at 175°C

29 Integral Pulse Polarogram of CuCl in a NaAlCl₄ Melt at 175°C

30 Double Pulse Polarogram of CuCl in a NaAlCl₄ Melt at 175°C

31 Cyclic Voltammogram of 5.83 mM CdCl₂ in a NaAlCl₄ Melt at 200°C

32 Cyclic Voltammogram of 25.35 mM CdCl₂ in a NaAlCl₄ Melt at 200°C

33 Nernst Plot for CdCl₂ in a NaAlCl₄ Melt at 200°C

34 Integral Pulse Polarogram of CdCl₂ in a NaAlCl₄ Melt at 200°C

35 Integral Pulse Diffusion Currents vs CdCl₂ Concentration in a NaAlCl₄ Melt at 200°C
Figure

36 Cyclic Voltammogram of HCl in a NaAlCl\textsubscript{4} Melt at 175°C

37 Cyclic Voltammogram of Ferrocene in a NaAlCl\textsubscript{4} Melt at 175°C

38 Cyclic Voltammogram of Triphenylamine in a NaAlCl\textsubscript{4} Melt at 175°C

39 Cyclic Voltammogram of Dimethylaniline in a NaAlCl\textsubscript{4} Melt at 175°C

40 Cyclic Voltammogram of Hydroquinone in a NaAlCl\textsubscript{4} Melt at 175°C
Cyclic Voltammetry

NaAlCl₄ Background on W
200°C, v = 0.5 V/sec

Figure 2
Nernst Plot for Ag(I) vs. Al in NaAlCl₄

175°C
+ Ag(I) in NaAl₂Cl₇
○ Ag(I) in NaAlCl₄

$E^0 = 1.163 \text{ V}$
$E^0 = 1.143 \text{ V}$

Figure 7
AlCl₃ Titration Curve at 175°C

Reference = Al in NaAlCl₄

\[ E_{Ag} = E_{Ag} - 1.0 \text{ V} \]

X from Ag Nernst Plots

Figure 8
Figure 6

40°C

Area of W = 0.785 mm²

60.4% of AU, 5 UMP

PLS 260/26

0.7 mm HS IN 1:2 MELT

JULY 7/74
Cyclic Voltammetry

2.25 molar AgCl in NaCl, 175°C, Area of W = 0.695 mm²

V = 0.05 V/sec
I = 2 V/sec/div

Figure 12
5.28 m molar PdCl₃ in NaACL₄
175°C, Area of W = 0.508 mm²
v = 0.5 V/sec
Anodic Stripping peak scan - 1.7 → 0.3 → 1.7 V vs. Al
8.38 mMolar FeCl₃
Area of W = 5.08 x 10⁻³ cm²
175°C

Figure 14
Cyclic Voltammetry

$[\text{FeCl}_3] = 8.58 \text{ m molar in NaAlCl}_4$

$175^\circ\text{C}$

Area of W = 0.508 mm$^2$

$v = 0.5 \text{ V/sec}$

Fe(II)/Fe couple

Figure 15
Cyclic Voltammetry
FeCl$_3$ in NaAlCl$_4$
$175^\circ$C, Area $W = 0.508 \text{ mm}^2$
$v = 0.5 \text{ V/sec}$

- Cathodic Fe(III) $\rightarrow$ Fe(II)
- Anodic Fe(II) $\rightarrow$ Fe(III)
- Cathodic Fe(II) $\rightarrow$ Fe

Figure 16
Figure 17

Volts vs Al

Pulse delay = 250 msec
Pulse width = 500 msec
175°C, area of W = 0.508 mm²
14 M alkali pept in NaCl
Inertial pulse

amp 0
100
200
Integral Pulse
FeCl₃ in NaAlCl₄
175°C, Area W = 0.508 mm²
Pulse width = 50 msec
Pulse delay = 250 msec

Voltage Scans
C 1.7 + 1.0 V
A 1.1 + 1.8 V

\[ E = E_1 + \frac{RT}{F} \ln \left( \frac{i_d - i}{i} \right) \]

Figure 18
Cyclic Voltammetry

0.98 mMolar FeCl₃ in 2AlCl₃, NaCl
Area of W = 1.79 mm²
v = 0.05 V/sec 175°C
H 15 sec hold

Figure 19
Figure 20

NERNST PLOT FOR CuCl IN NaAlCl₄
Reference = Al in NaAlCl₄
175°C

E° = 1.150 V (n=1)
E° = 1.228 V (n=0.765)

n = 0.765
n = 1

Log [CuCl] molar
Cyclic Voltammetry
12.08 molal CuCl2 in NaAlCl4
Area of W = 0.609 mm2
V = 0.5 V/sec 175°C

Figure 24
CYCLIC VOLTACOULOGRAM

3.70 Molar CuCl in NaAlCl₄
Area of W = 0.508 \text{ cm}²
v = 0.5 V/sec, 175°C

Q \mu\text{coul.}

V vs Al in NaAlCl₄

10/71

Figure 26
CYCLIC VOLTAMMETRY

Deposition peak current vs [CuCl]
Area of W = 0.609 mm²
175°C, NaAlCl₄ solvent

\[ v = 0.5 \text{ V/sec} \]
\[ v = 0.05 \text{ V/sec} \]

Figure 27
CYCLIC VOLTAMMETRY

5.83 mMolar CdCl₂ in NaAlCl₄
v = 1 V/sec, 200°C
Area of W = 0.817 mm²

0.75 0.50 0.25

V vs Al in NaAlCl₄

Figure 31

CYCLIC VOLTAMMETRY

25.35 mMolar CdCl₂ in NaAlCl₄
v = 0.25 V/sec, 200°C
Area of W = 0.817 mm²

1.5 1.0 0.5

V vs Al in NaAlCl₄

Figure 32
NERNST PLOT FOR CdCl$_2$ IN NaAlCl$_4$

Reference = Al in NaAlCl$_4$

200°C

$E^0 = 0.664$ V

$n = 2$

Figure 33
Figure 35

DIFFUSION CURRENT VS [CdCl₂]

Integral Pulse

Delay = 250 mSec
Pulse = 10 mSec
Solvent = NaAlCl₄
200°C, Area of W = 0.817 mm²
CYCLIC VOLTAMMOGRAM OF HCl in NaAlCl₄

Area of W = 6.28 x 10⁻³ cm²
v = 0.5 V/sec, 175°C

Immediately after bubbling HCl through the melt

10 minutes later

V vs Al in NaAlCl₄

Figure 36
Cyclic Voltammetry

1.75 m molar Ferrocene in NaAlCl$_4$

0.25 Volts/sec

Area of W = 0.628 mm$^2$

+ Calculated Values
Figure 38

Voites vs AV

Area of W = 0.628 mm²
0.5 Völt vs sec
5.53 mm Triphenylamine in NACl4

Cyclic Voltammetry
Figure 39

Cyclic Voltammetry
Dimethylamine in NaAlCl
d
Area of W = 0.628 mm²

Volts vs Al

-40 -30 -20 -10 0 10 20

0.4 0.6 0.8 1.0 1.2 1.4 1.6

IR 2P 2P 1P 1P AL

START
Figure 40

Volts vs AV

Area of W = 0.628 mm²
0.5 Volts/sec
Hydrogenation in NaCl
Cyclic Voltammetry