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E.M.F. study of lower oxidation states in molten sodium tetrachloroaluminate

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E.M.F. STUDY OF LOWER OXIDATION
STATES IN MOLTEN SODIUM TETRA-
CHLOROALUMINATE.

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E.M.F. STUDY OF LOWER OXIDATION STATES IN MOLTEN
SODIUM TETRACHLOROALUMINATE

by

Theodore Charles Fegley Munday

A Dissertation Submitted to the
Graduate Faculty in Partial Fulfillment of
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Approved:

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1964

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DEDICATION

To my father and mother

INTRODUCTION

In recent years much has been learned about the solution of metals in their molten salts. Many of the observed phenomena have been successfully correlated and interpreted by the theory which proposes lower oxidation states. This explanation holds that solution takes place by reactions between the metal and its ions in a normal oxidation state in the melt to yield one or more lower oxidation states. Thus, the nature of the lower oxidation state species is and has been of interest.

The lower oxidation state explanation has served especially well for the solution of post-transition metals in their molten halides. For many of the elements, the stability of lower states is large enough under certain conditions to permit isolation of discrete solids. Besides the common mercury(I) and thallium(I) compounds, solid, lower state phases of cadmium [$\text{Cd}_2(\text{AlCl}_4)_2$ (1)], gallium [GaI (2) and GaAlCl_4 (3)], indium [InAlCl_4 (4)], and bismuth [$\text{BiCl}_{1.167}$ (5, 6)] have been isolated. In addition, a substance of composition $\text{Al}_{1.22}\text{I}$ was prepared and interpreted to be a mixture of aluminum and AlI (7).

For cases where such reduced solids have been found,

the existence of the same lower state as a melt species would seem probable. For instance, a wide variety of solution studies point to the existence of Cd_2^{2+} (8) in the Cd-CdCl₂ system where no reduced solid exists. Definitive evidence for melt species related to the stoichiometry of isolated solids is limited to Raman spectra of melts which first, show Cd_2^{2+} in molten $\text{Cd}_2(\text{AlCl}_4)_2$ - $\text{Cd}(\text{AlCl}_4)_2$ (9) and second, eliminate all but Ga^+ in molten "gallium dichloride" (10).

The isolated reduced solid $\text{Al}_{1.22}\text{I}$ (7), gas phase spectra for the Al-AlCl₃ system (11), and calculations on AlI which agree with observed solubilities in the Al-AlI₃ system (12) all attest to the probable existence of Al^+ in melts. Nevertheless, direct experiments on the melts themselves are still lacking. In^+ remains consistent with studies of the In-InCl₃ (13-15), InCl-InCl₃ (4), and InCl-AlCl₃ (4) phase diagrams, but compounds such as In_4Cl_5 , In_2Cl_3 , In_4Cl_7 , In_5Cl_9 are reported as well as InCl, so complex species may also be present in addition to the simple ion, In^+ . Evidence for two reduced states of bismuth in Bi-BiX₃ melts does not include the Bi_9^{5+} unit present in the solid $\text{BiCl}_{1.167}$ (8).

Separation of solid subsalts of the remaining post-transition metals has not been achieved. Studies of the Zn-ZnX₂ systems are scarce and do not give any clear indication of what reduced species is in the melt. Topol (16) attempted e.m.f. measurements on the Zn-ZnCl₂ system, but was not successful because potentials were unsteady. The existence of a lower oxidation state of tin is suggested by its small solubility in molten SnCl₂ and is supported by Russian polarographic (17), chronopotentiometric (18), and electro-deposition (19, 20) observations, but a specific species has not been claimed.

Early e.m.f. work by Karpachev, et al. (21) suggested a Pb⁺ solute in Pb-PbCl₂ at 700^o, but more recent determinations by the same method conclude that Pb₂²⁺ is present in the Pb-PbI₂ system at 585 and 693^o, and is probably present in Pb-PbCl₂ melts (16). Egan (22) also arrived at Pb₂²⁺ by polarographic determination of the concentration of the reduced species in PbCl₂ equilibrated with Pb-Au alloys of known Pb activity. For antimony, e.m.f. studies suggested Sb₂I₄ for solutions of Sb in SbI₃ (23), which agrees with results of vapor pressure measurements (24).

While some of these studies were being carried out, the effects of various solvents on the solubility of metals in their molten salts were receiving attention. An interpreta-

tion in terms of acid-base reactions developed by Corbett, Burkhard, and Druding (1) has proven valuable for understanding post-transition metal solubilities and stimulating further research. This interpretation recognized that for a suggested equilibrium in the cadmium-cadmium(II) chloride system, $\text{Cd}^0 + \text{Cd}^{2+} \rightleftharpoons \text{Cd}_2^{2+}$, a decreased solubility on addition of basic chloride ions in the form of KCl could be due to stabilization of the more polarizing Cd^{2+} ion. Corresponding increased solubilities on addition of acidic substances such as CeCl_3 and AlCl_3 were then attributed to reduction of the effective basicity of chloride ions already in the melt by the more polarizing or complexing Ce^{3+} and Al^{3+} . Such "acid stabilization" has been substantiated by the isolation of solid subsalts such as $\text{Cd}_2(\text{AlCl}_4)_2$ (1), GaAlCl_4 (25), and " BiAlCl_4 " (26).

In this investigation, a combination of acid stabilization with e.m.f. measurements was developed for the further identification of species formed by solution of metals in their molten salts. Previous workers have used e.m.f. determinations to examine the species involved in molten systems (16, 21, 23, 27). In general, this involves plotting e.m.f. versus a logarithmic function of the activities

of the chemical units involved in the electrode reactions, according to the Nernst equation

$$E = E^{\circ} - RT/nF \ln \frac{a_C^c a_D^d}{a_A^a a_B^b}$$

where E represents the e.m.f. for the reaction $aA + bB \rightleftharpoons cC + dD$ (where a, b, c, and d are the number of moles of substances A, B, C, and D), E° is the standard e.m.f. for the reaction, \underline{n} is the number of electrons exchanged in the reaction, R is the gas constant, T the absolute temperature, F the Faraday constant, and a_X the activity of substance X. For constant temperature the slope of such a graph is equal to $-RT/nF$, and since R, T, and F are known, \underline{n} may be determined.

At low concentrations, the activities in the Nernst equation can often be replaced by concentrations without serious effects on the result. For instance, Flengas and Ingraham (28) have shown that the activity coefficient for Ag^+ in NaCl-KCl (1:1) remains constant to at least 6 mole percent, and deviations in e.m.f. studies on cobalt occur only in excess of 4 mole percent.

A review of previous electrochemical studies in molten salts showed that the reference couple $Ag:AgCl$ (~1%) in

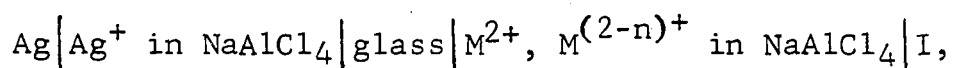
halide melts had been frequently and successfully used. Junctions employed varied from the fine porosity frit used by Hill, et al. (29), to the asbestos fiber sealed through glass used by both Senderoff and Brenner (30) and Flengas and Ingraham (28), to the thin glass bubble developed by many workers and applied specifically to dilute Ag^+ solutions by Bockris, et al. (31).

Laity (32) has discussed the junction potentials associated with glass diaphragms. At the contact between the diaphragm and the melt, very large concentration gradients occur for the conducting species of both the melt and the glass. An accurate description of what actually occurs in such a case would be difficult to achieve. But, if identical melts are placed on both sides of the diaphragm, the gradients at the second glass-melt contact are exactly opposed to those of the first contact, and junction potentials can be expected to cancel. This proposition is supported by measurements on the two cells, $\text{Ag}|\text{AgCl}|\text{glass}|\text{AgCl}|\text{Cl}_2$ and $\text{Ag}|\text{AgCl}|\text{Cl}_2$ (32), which produced the same results. Additional evidence was provided by Kolotii (33), who found no disparity between asbestos and Pyrex or molybdenum glass junctions used in cells containing molten PbCl_2 - NaCl .

For this study NaAlCl_4 was chosen as a solvent which could provide acid stabilization. In order to make substitution of concentrations for activities reasonable and to eliminate junction potentials, elements of interest were to be added to NaAlCl_4 as chlorides or tetrachloroaluminates in amounts of only a few mole percent. The addition of 5 mole percent AlCl_3 was planned to insure the acidity of the melt. Even at the lowest temperature possible for the suggested NaAlCl_4 - AlCl_3 melt (34), its AlCl_3 vapor pressure is of the order of 1 to 8 mm. (35, 36). Therefore, any cell containing the NaAlCl_4 - AlCl_3 melt had to be sealed, or significant losses of AlCl_3 would have resulted in a short period of time.

Due to the low solubilities of some of the metals of interest in their salts and the dilution with 95 or more percent NaAlCl_4 - AlCl_3 , the problem of making proportionate, small changes in concentration of reductant was extreme. Since the addition of metals or salts in small enough amounts would be clearly impractical, some method such as coulometric production was essential.

The cell upon which measurements were made was thus of the following type:



where M is the metal of interest and I is an inert electrode.

Some aspects of the approach outlined above have been successfully used for studies of lower oxidation states in molten halides by Topol and co-workers (16, 27). Their measurements were made in three-compartment cells which contained asbestos fibers or ultrafine frits for junctions. The reference was usually either a .5 mole percent or a saturated solution of the metal of interest in its molten halide. Concentrations were changed coulometrically, and the cells were operated at temperatures between 240 and 700°, generally under a flow of argon.

The first elements chosen for this study were cadmium and lead. Based on past studies of cadmium in the closely related $\text{Cd}(\text{AlCl}_4)_2$ melt (9), it seemed likely that the species formed by interaction of cadmium and cadmium(II) in NaAlCl_4 would also be Cd_2^{2+} . A high solubility (~40 mole percent dissolved metal) of cadmium relative to cadmium(II) was also probable in the NaAlCl_4 solvent. These factors meant that equipment and procedure could be developed with a minimum of problems while the cadmium species was being studied under different solvent conditions. Evidence for a reduced lead species had also been found, but for the less-

closely related pure chloride melt (16, 22). Also, the solubility of lead in its chloride (.006 mole percent at 500° (37)) is much less than that for cadmium in its chloride, so the effectiveness of the combination of acid stabilization and e.m.f. measurements could be further tested.

Subsequent experiments were carried out with tin, nickel, and zinc. Tin was selected because of its group relation to lead and because of a lack of published information about the tin reaction. Nickel was chosen as the first-transition-series element most likely to form measurable amounts of reduced species. This choice was based on the high solubility of nickel in its molten chloride (9.1 mole percent at 978° (38)) and on Born-Haber cycle calculations of the stability of first-transition-series elements in various oxidation states (39). Zinc shows a very low solubility in its chloride (.18 mole percent at 500° (37)), but its group relation to cadmium and mercury is of interest because the latter elements both form the dimerized reduced species, M_2^{2+} .

EXPERIMENTAL DETAILS

General Cell Design

The cell used in this study (Figure 1) consisted of three compartments constructed primarily of Pyrex glass. The indicator electrode compartment was flanked on one side by the reference electrode compartment and on the other side by the working anode electrode compartment. The junction between the reference and indicator compartments was a thin glass diaphragm, and that between the indicator and working anode compartments was a 10 mm. diameter, ultrafine, sintered-glass frit. The coulometric reduction in these experiments was carried out against the working anode. This procedure allowed the reference half-cell to remain undisturbed during concentration changes in the indicator compartment.

Wires leading to the electrodes within the cell were silver. These entered the cell through 1/8 inch Kovar metal-to-glass graded seals soldered around the wire. About 15 cm. of each wire formed a coil inside the cell, and the end of the coil was attached to the electrode. The electrodes nearly touched the bottom of the cell and were between

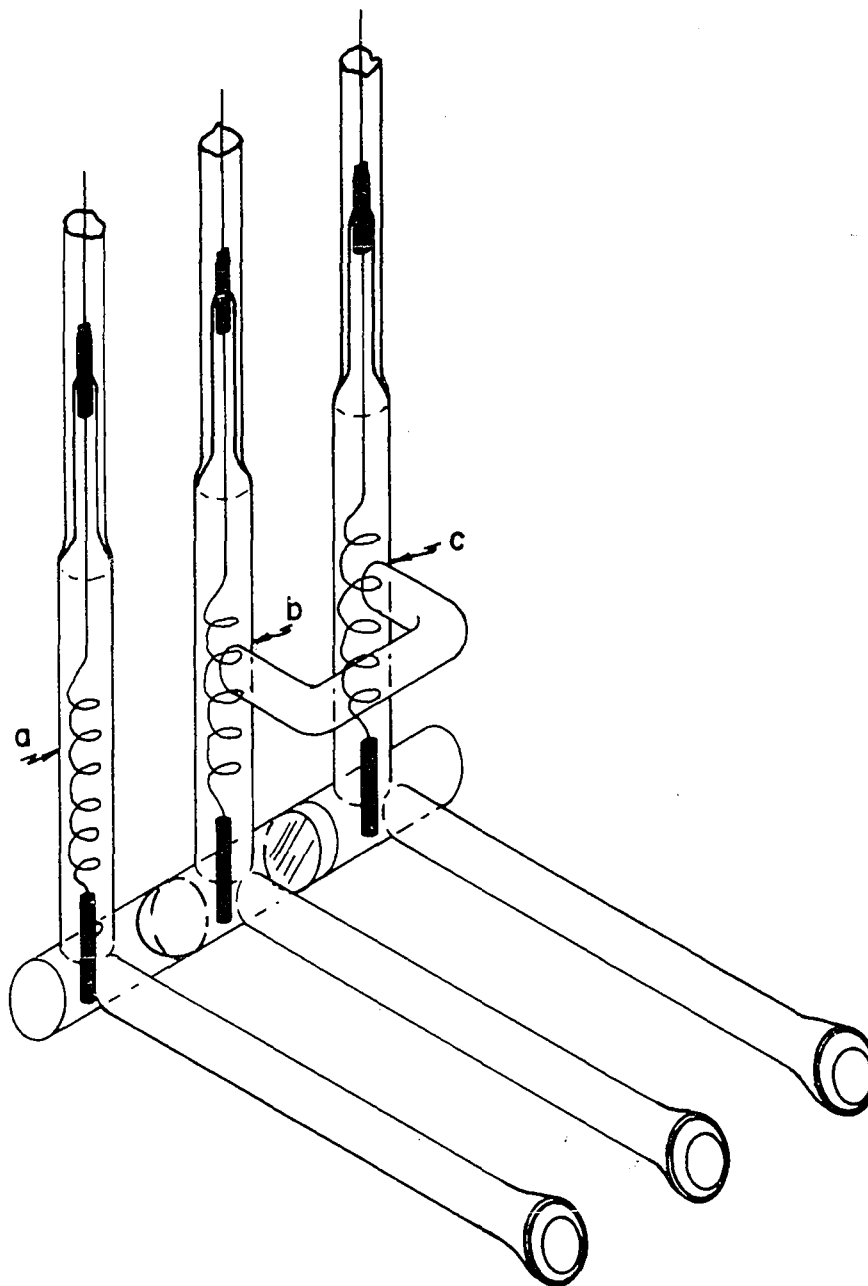


Figure 1. General cell design: a - reference compartment, b - indicator compartment, c - working anode compartment

2 1/2 and 4 cm. long.

A sidearm of 10 mm. glass tubing was connected to each cell compartment at the base of the cell, perpendicular to the plane of the three electrodes. These sidearms served as a place in which to freeze the melts at the completion of the experiment in order to protect the fragile diaphragm. A 4 to 6 mm. glass tubing connected the indicator and working anode compartments 2 1/2 to 4 cm. above the bottom of the cell and served as a pressure equalizing passage between the two compartments.

Ring-sealed to the outside of the cell just below the Kovar metal-to-glass graded seal was a 20 to 24 cm. length of 10 mm. glass tubing which shielded the silver wire from the corrosive, conductive liquid in the thermostat.

Cell Components and Construction

The diaphragms were made by heating the closed end of a 10 mm. diameter tube and sucking on the blow tube to form a thin bubble inside the tube (Figure 2, a). Another tube was later butt-sealed to the end (b). The resistance of each diaphragm was tested in molten NaNO_3 containing several percent AgNO_3 , using silver wires and a vacuum-tube voltmeter.

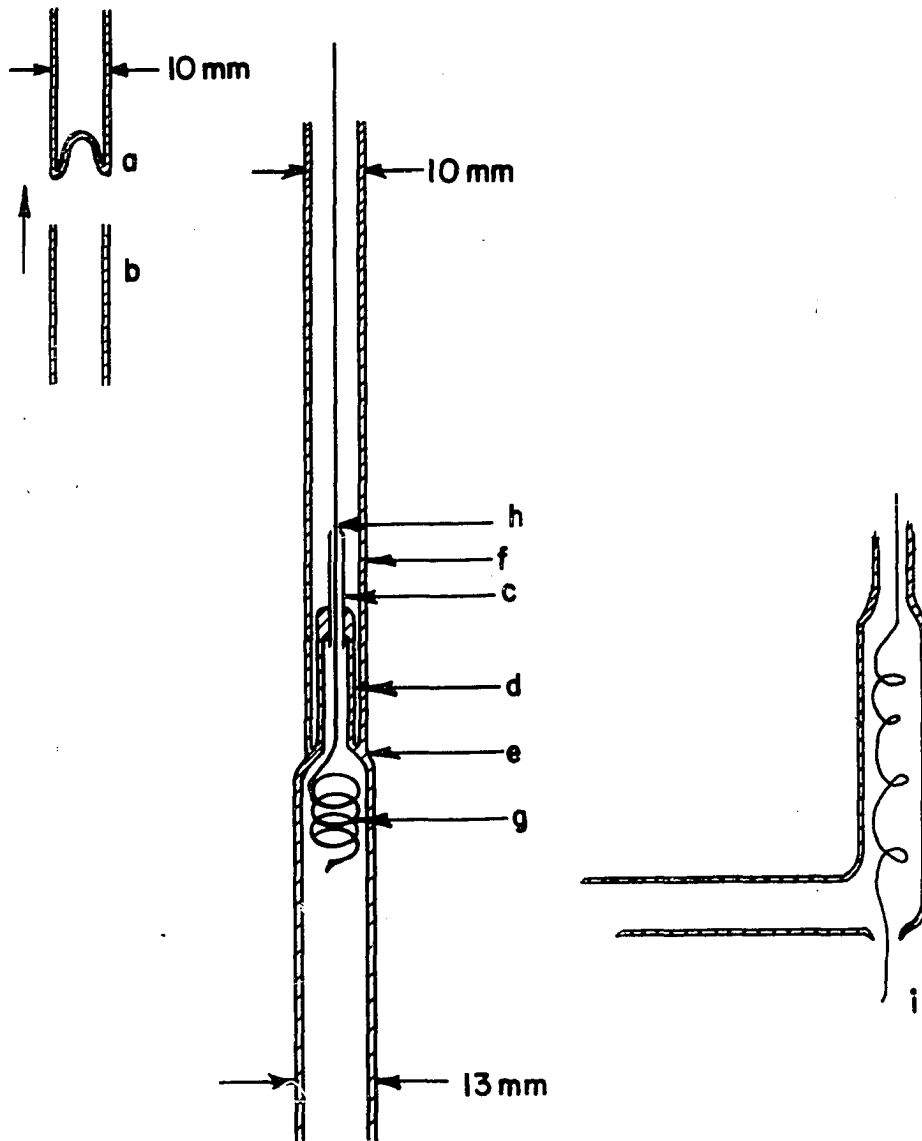


Figure 2. Details of cell construction: a - diaphragm formed in end of glass tube, b - tube butt-sealed near diaphragm, c - Kovar metal, d - graded seal, e - shield tube joint, f - shield tube, g - coil of silver wire, h - vacuum tight soldered seal, i - addition of electrode to cell

For these measurements, special precaution was required to remove air trapped inside the bubble. Also, a pipette was used to fill the inside of the tube so the entire tube did not need to be submerged, which would have allowed conductivity around, rather than through, the diaphragm.

Temperature dependences of a variety of diaphragms were plotted so that the behavior of others could be roughly estimated from a single resistance measurement. Satisfactory diaphragms had no visible imperfections and had resistances of 60 K Ω or less at the temperature at which they were to be used. Such diaphragms allowed cell voltages to be determined accurately to the nearest millivolt or better. The diaphragms were washed extensively with water to prevent a yellow coloration of the glass by silver during later glassblowing.

The soldered seals where silver wires passed through the Kovar metal-to-glass graded seals (Figure 2, c and d) were also pre-tested. The Pyrex end of the graded seal was joined to a glass tube 13 mm. in diameter, and the shield tube, 10 mm. in diameter, was sealed at the same joint (e). The long end of the shield tube was then cracked off at (f) to expose the Kovar metal tube. About 15 cm. of a 45 cm.

long silver wire (99.9% .025 inch diameter, from American Platinum Works) was wound into a coil (g) which would fit inside the 13 mm. tube. Then the wire was threaded through the Kovar tube, the tube pinched against the wire (h) and soldered closed (#655 Ag-Cu-Mn-Ni braze, m.p. 752°, from Handy and Harmon). The lower tube was connected to a vacuum system, and the soldered seal was tested for leaks. If it remained below discharge when held overnight at 300°, it was used in a cell after the end of the shield tube was reconnected at (f).

Next, the parts of the cell other than electrodes were carefully combined while the 15 cm. silver wire remained coiled and thus out of the way of glassblowing. The small tube, which connected the indicator and working anode compartments (Figure 1) was added to the cell to equalize AlCl_3 vapor pressures over the melts in the two compartments. Previously, small inequalities in the percentage of AlCl_3 added to the two compartments had forced the melts through the frit in one direction or the other.

A sample of each electrode material was tested for inertness in the NaAlCl_4 - AlCl_3 - MCl_2 melt, where M represents the metal of interest. Zinc was rejected because it reduced

aluminum from the melt. Other materials showed no weight loss on 24 or more hour contact with the melt at 300°. Materials that form intermetallic compounds or large amounts of solid solution with the metal of interest were not used in the indicator compartment since such interactions would have occurred during coulometric reduction. For situations not covered by Hansen (40), weight loss tests were run in $\text{NaAlCl}_4\text{-AlCl}_3\text{-MCl}_2$ melts at temperatures above the melting point of the metal M.

On these bases, tantalum was used as the indicator electrode for measurements on cadmium, lead, and zinc; tungsten or carbon was used for tin studies. Tantalum is known to form an intermetallic compound with aluminum (40), but no apparent problems related to this compound arose. Also, the tantalum electrodes themselves appeared unaffected by cell operation. If the rate of coulometric reduction during cell operation had been higher, concentration polarization of the reacting ion might have occurred, and the more electropositive aluminum would have been reduced.

The electrode for the working anode compartment was commonly composed of the same metal as that being studied. Early in the work it seemed desirable to use a metal here

which was more active than the metal being studied, as indicated by Delimarskii's electromotive series in NaAlCl_4 (41). Such an anode produced ions incapable of interaction with the reduced species coulometrically produced in the indicator compartment. However, attempts using aluminum and thallium produced unexplained problems, suspected to be due to diffusion of unknown active species through the frit.

In order to eliminate these problems, two changes were made to the working anode compartment. The working anode electrode was thereafter composed of the same metal as that being studied. Secondly, the salt of the metal of interest was placed in the working anode compartment at the same concentration as that placed in the indicator compartment. In order to restrict diffusion further, the pores of the frit were partially heat-collapsed for several cells. The frit resistances produced in this manner showed extreme variations, so subsequently, unaltered frits were again used.

The cadmium and thallium electrodes were 3 mm. in diameter and were cast from 99.999 and 99.9% metal respectively. The tantalum electrodes were made of 1/8 inch diameter tantalum rod, the tungsten electrodes of 1/16 inch diameter Linde Heliarc, pure tungsten electrodes with ground

finish, the silver electrodes of 10 gauge wire, the aluminum electrodes of 99.99%, iron-free, 1/8 inch diameter wire (A. D. Mackay), and the carbon electrodes from spectroscopic grade carbon rod.

Each electrode was joined to a few centimeters of silver wire as follows: the silver, lead and cadmium electrodes were melted at one end, and the wire was pushed into the electrode a short distance; a small groove was filed around the tantalum electrode, and the silver wire was wrapped tightly in the groove and joined to itself by melting; nickel was plated on the end of the tungsten electrode, and the silver wire was joined to the nickel by melting; the wire was pushed into a tightly fitting hole in the end of the carbon electrode.

Finally, a small hole was blown at the bottom of each compartment (Figure 2, i), and the end of the Ag wire coil was pulled out through the hole. The short wire attached to the electrode was joined to the coil wire by melting. Each electrode and wire was pushed back into the cell, collapsing the Ag coil. Electrical continuity between the electrodes and the wires outside the cell was checked. The small holes were then sealed.

Experimental Procedure

The cell was thoroughly washed with dilute acid and water and then quickly dried by evacuation so as to minimize oxidation of the Kovar and other metals involved. Both sides of the diaphragm were evacuated or returned to atmospheric pressure simultaneously, since the diaphragm was often too fragile to survive a large pressure differential.

Chemical materials were loaded into the cell through the sidearms. The transfers were made in an argon-filled dry box fitted with an evacuable entrance lock, a circulating system using a blower and Linde 4A and 13X molecular sieves, and an open flat tray containing P_2O_5 . A Welch triple-beam balance (calibrated to .01 grams) within the dry box was used for all weighings.

Each compartment was loaded with 4 to 6 grams of $NaAlCl_4$ and .2 to .3 grams of $AlCl_3$. On the order of .3 grams of $AgAlCl_4$ were added to the reference. Equal amounts of the chloride or tetrachloroaluminate of the metal being studied were added to the indicator and working anode compartments. The cell was evacuated and subjected to dynamic high vacuum (below discharge) for several hours. Then the sidearms were

sealed about 10 cm. from the electrodes.

The silver wires of the cell were joined (by melting) to the silver wires leading to the potentiometer. To minimize thermal shock, the cell was clamped directly above the thermostat for several minutes, then slowly lowered into the bath. At first the cell was tilted so the melts remained in the sidearms and did not contact the electrodes. If leaks existed where the sidearms had been sealed, bubbling occurred in the melts at this time. Also, the presence or absence of any slowly-dissolving materials was observed. The cell was then tilted so the melts surrounded the electrodes, taking care that the inside of the diaphragm was filled with melt rather than vapor.

At this point the resistances of the diaphragm and frit were measured with a vacuum-tube voltmeter. Because of the potential of the cell itself, only a rough estimate could be obtained by reversing the voltmeter leads and averaging the results. The diaphragm resistance was within 10 K Ω of that measured during cell construction. The resistance across the cell wall to the thermostat melt was two to three times the resistance across the diaphragm. The resistance of the frit was usually of the order of 10 to 100 ohms. For a partially

heat-collapsed frit, the resistance calculated using Ohm's Law and the voltage and current measured during electrolysis was 31 K Ω versus 28 K Ω measured directly during e.m.f. measurements.

Voltages were followed until equilibrium was reached, as indicated by constant voltage. This usually required about 24 hours. Concentrations were then changed coulometrically at a rate of .05 microequivalents per second for .1 to 10 microequivalents. During the measurement period the cell was "rocked" several times an hour to aid in reaching constant voltage.

When the working anode half-cell was altered to reduce suspected diffusion, a saturated electrode of the metal being studied was thereby established in the working anode compartment. If the half-cell voltage of this saturated electrode were not affected during small amounts of coulometric concentration changes, it could also serve as a reference for the indicator half-cell. Therefore, in the remaining experiments, the e.m.f.'s of both the indicator-reference and indicator-working anode couples were monitored.

Materials

All materials were purified in glass using common vacuum line techniques and electric resistance furnaces connected to controllers and/or Powerstats. In order to eliminate impurities, the glass sublimation or distillation tubes were washed and then heated with a torch or baked in a furnace while under a dynamic vacuum which was held below discharge. Materials were stored in the original, evacuated preparation tubes or in argon-filled sample containers. All transfers were made in the dry box.

Aluminum trichloride

Reagent grade AlCl_3 was doubly sublimed under 10 to 15 cm. pressure of helium at approximately 180° . The first sublimate was allowed to form a thick deposit and was then sealed under vacuum in the glass tube. The ampoule thus formed was placed in a second sublimation tube where, upon heating, the thick deposit fractured the ampoule. The temperature of fracture varied widely, occurring at 120 to 155° . Rate of heating was no doubt a factor in this variation, since Foster (42) has reported that AlCl_3 is a poor heat conductor. The residue of the second sublimation was

merely a thin shell of oxide. This procedure produced a white product which contained no traces of yellow impurity.

Sodium tetrachloroaluminate

A weighed amount of reagent grade NaCl was placed in one end of a glass tube which contained a medium-grade frit. The salt was then dried overnight at 480° under dynamic vacuum. A stoichiometric quantity of AlCl_3 was added to the same tube, and the tube was then evacuated and sealed. This mixture was heated above the melting point of AlCl_3 and shaken until the NaCl dissolved. The melt at this point was commonly brownish and could not be cleared by addition of either aluminum or sodium. Therefore, according to a procedure suggested by Morrey (43), the melt was digested at 450° for one or more days and filtered to remove a black solid which agglomerated during digestion. This solid was insoluble in common acids and volatilized without residue upon heating, indicating that it was probably carbon. The NaAlCl_4 product was a white solid which produced a water-white melt.

Cadmium(II) chloride

Reagent grade CdCl_2 was doubly sublimed under vacuum at 500° in an 18 mm. diameter glass tube which was partitioned in two places by small (7 mm. diameter) tubing, so the

residue could be sealed and discarded after each sublimation. A supplementary furnace was used to maintain the empty part of the tube at 300° . This prevented a small amount of cadmium metal, which commonly sublimed at the beginning of the operation, from depositing where CdCl_2 would later deposit.

Cadmium(II) tetrachloroaluminate

A stoichiometric mixture of AlCl_3 and CdCl_2 was sealed in glass, heated above 200° , and rocked until all the CdCl_2 dissolved. This produced $\text{Cd}(\text{AlCl}_4)_2$, previously reported by Corbett, Burkhard, and Druding (1). It was later found desirable to digest and filter the product to remove carbon, but undigested salt was used in this study.

Lead(II) chloride

PbCl_2 , obtained as a Pb-PbCl_2 mixture from Corbett and von Winbush (12), was distilled at 920° under 75 mm. pressure of chlorine. After transfer to a new distillation tube, the product was again distilled under chlorine at 920° . A transparent white solid resulted.

Lead(II) tetrachloroaluminate

Stoichiometric amounts of PbCl_2 and AlCl_3 were heated together. When the AlCl_3 melted at 193° , it reacted to form

a white solid which did not melt though the temperature was raised to 260° . In order to produce a homogeneous melt without encountering the dangerous pressures of AlCl_3 which occur above 250° (35, 36), the tube was pushed gradually into a furnace held at 340° . The product was digested at 450° and filtered through a medium-grade frit to produce a white solid. The melting point was found to be congruent at $275 \pm 2^{\circ}$. The product was also distinguished from PbCl_2 , AlCl_3 , and physical mixtures of PbCl_2 and AlCl_3 by powder patterns. On one occasion a small quantity of an unknown liquid was formed by the procedure outlined here. Digestion of $\text{Cd}(\text{AlCl}_4)_2$ preparations also frequently produced this liquid.* Since the liquid had a high vapor pressure at room temperature and a freezing point considerably below 0° , it was evacuated from the $\text{Pb}(\text{AlCl}_4)_2$.

$\text{Pb}(\text{AlCl}_4)_2$ has been reported previously by Jander and Swart (44), who obtained it as the product of a conductimetric titration in SbCl_3 . Their compound, however, was

*Barnes, R. D., Ames Laboratory, U. S. Atomic Energy Commission, Iowa State University of Science and Technology, Ames, Iowa. Digestion of $\text{Cd}(\text{AlCl}_4)_2$ preparations. Private communication. 1964.

black and thus most likely contaminated.

Tin(II) chloride

SnCl_2 , obtained as a Sn- SnCl_2 mixture from Corbett and von Winbush (12), was distilled at 920° under 75 mm. pressure of chlorine. After transfer to a new distillation tube, the product was distilled a second time under chlorine at 920° . A translucent, colorless solid resulted.

Tin(II) tetrachloroaluminate

Two moles of AlCl_3 and one mole of SnCl_2 were heated together. The SnCl_2 dissolved quickly when the AlCl_3 became molten. Overnight digestion at 390° and filtration through a medium-grade frit produced a slightly greenish-colored melt which froze to an off-white solid. Several preparations produced the same result. The compound melted congruently at $223 \pm 2^\circ$ and was differentiated from SnCl_2 , AlCl_3 , and physical mixtures of SnCl_2 and AlCl_3 by powder patterns.

Zinc(II) chloride

Reagent grade ZnCl_2 was distilled under vacuum at 350° , transferred in the dry box to a new tube, chlorinated overnight under 58 mm. of chlorine at 500° , and distilled again at 420° . The product melt was clear and without solid impurities.

Nickel(II) chloride

NiCl_2 , prepared by F. C. Albers, was sublimed once at 670° in a fused silica tube.

Silver(I) tetrachloroaluminate

Stoichiometric amounts of AlCl_3 and reagent grade AgCl were heated to 210° and rocked to dissolve the AgCl . The product was then digested at 300° for several days and filtered through a medium-grade frit. A clear melt and a white solid resulted. Its melting point was congruent at $170 \pm 2^\circ$. Digestion at temperatures above 300° was avoided because a yellow coloration of the glass container occurred which indicated reaction with the container.

Other Equipment

In order to maintain constant temperature, the cell was immersed in a molten salt bath while measurements were being made. The bath was contained in a common enameled pot and heated by a 1000 watt Edwin Wiegand heater, which was in turn controlled by a Powerstat. The heater and bath were insulated with firebrick, asbestos, and Transite. Bath temperature could be controlled within $\pm 1^\circ$ by the Powerstat and the amount of insulation used on top of the bath.

The bath consisted of a mixture of 73 mole percent NaNO_2 and 27 mole percent KNO_3 . It was stable for over 24 months and suitable for temperatures as low as 195° , where surface freezing began. However, the corrosive, conductive nature of the melt necessitated using shields around wires leading into the cell.

An arrangement of 1/2 inch aluminum rods allowed the cell to be rocked by hand. The cell itself was held by a Castaloy clamp connected to a long rod which pivoted over a third rod as a see-saw.

Voltages were measured with a Leeds and Northrup #7552 Potentiometer in conjunction with a Leeds and Northrup #2430 Galvanometer. These instruments were necessary because of the high resistance of the diaphragm. The power source was a Willard 2 volt lead storage battery; the standard cell was made by Eppley Laboratory. No. 26 copper wires joined the potentiometer and the silver wires leading to the cell. The copper-silver junctions were outside the heated region of the bath, and therefore thermocouple e.m.f.'s were avoided. A reversing switch was placed in the copper section of the wires to facilitate measuring voltages of different polarities. A second switch allowed measurement of either

the indicator-reference or the indicator-working anode voltage. All wires were protected by insulation sleeves.

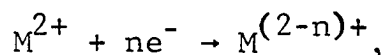
Coulometric reductions were made with a Model IV Sargent Coulometric Current Source capable of delivering as little as .05 (\pm .1%) microequivalents per second for intervals as small as .1 seconds.

RESULTS AND DISCUSSION

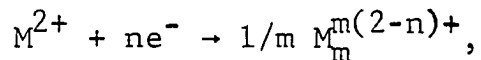
Data Treatment

The data were analyzed by a plot of $\log q_i$ versus E , where E is the voltage of either the indicator-reference couple or the indicator-working anode couple, and q_i is the total amount of reduction carried out in the indicator compartment up to that time. This relation may be derived in the following way.

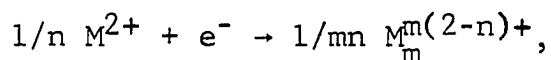
For any reducible, divalent ion present in the indicator compartment, coulometric reduction will produce an undesig-nated, reduced ion according to the reaction



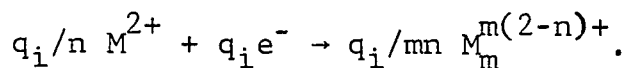
where M represents the metal atom and n the number of elec-trons (e^-) involved in reduction of each M^{2+} . To account for possible catenation of the reduced species, the reduction can be rewritten as



or



where m is the degree of catenation. Thus, for every q_i equivalents of current passed through the cell, q_i/mn equivalents of the reduced species will be formed, as



Therefore, if the original concentration of divalent ion is C_0 , the concentration will be $(C_0 - q_i/n)$ after q_i equivalents of reduction. Similarly, if the original concentration of reduced species is zero, its concentration after q_i equivalents of reduction will be q_i/mn equivalents.

The potential observed for the indicator-reference couple can be written as

$$E = E^\circ - 2.3 RT/nF \log \frac{[a_{M^{2+}}] [a_{Ag^0}]^n}{[a_{M_m^{m(2-n)+}}]^{1/m} [a_{Ag^+}]^n} + E_j$$

for the reaction $1/m M_m^{m(2-n)+} + nAg^+ \rightleftharpoons M^{2+} + nAg^0$. The terms m and n , the junction potential E_j , and the activities associated with the reference are assumed to be constant.

Separating all the constant terms as C gives

$$E = -2.3 RT/nF \log \frac{[a_{M^{2+}}]}{[a_{M_m^{m(2-n)+}}]^{1/m}} + C.$$

Assuming that, as noted in the Introduction, activities may be replaced by concentrations for the low concentrations used, and substituting the terms derived previously for these concentrations, give

$$E = -2.3 \text{ RT/nF} \log \frac{[C_o - q_i/n]}{[q_i/mn]^{1/m}} + C,$$

or $E = 2.3 \text{ RT/mnF} [\log q_i - m \log [C_o - q_i/n] - \log mn] + C.$

Remembering that mn can be treated as a constant,

$$E = 2.3 \text{ RT/mnF} [\log q_i - m \log [C_o - q_i/n]] + C'. \quad (1)$$

The second log term is also constant for values of q_i which are very small compared with C_o , so

$$E = 2.3 \text{ RT/mnF} [\log q_i] + C''. \quad (2)$$

Thus, a graph of $\log q_i$ versus E will yield a slope of 2.3 RT/mnF . All factors of this last expression except m and n are known, so the mn product may be found.

If q_i is not small compared with C_o , a plot of $\log q_i$ versus E will produce a curve, rather than a straight line. Therefore, the data must be plotted according to Equation (1) which takes into account the effect of q_i on C_o . This

procedure, of course, demands an assumption of m and n values. The catenation of the reduced species, \underline{m} , is reasonably limited to small whole number values, while \underline{n} may vary between zero and two. Further, the product mn must be integral. These considerations are necessary for the treatment of the cadmium data.

If the working anode remains continuously saturated and diffusion and solute migration are not important, it has a constant potential analagous to the reference, and a graph of $\log q_i$ versus E for the indicator-working anode couple also yields mn .

Sodium ions were assumed to provide most of the ionic exchange through the frit required to retain charge equality in the indicator and working anode compartments during coulometric reductions. This dilution was considered negligible, since it amounted to only .1 mole percent of the indicator compartment melt for a typical experiment.

In the case that more than one reduced species exists in the melt in the concentration range studied, it is possible that two or three linear portions of the plot might appear, each corresponding to an mn value for a major species at concentrations where it prevailed. If comparable amounts

of two reduced species have been formed, such experiments would not be able to distinguish between them.

Initial Impurities

In every case the first few points showed a negative deviation from the linear portion of the $\log q_i$ versus E plot. It is unlikely that a species in a different, lower oxidation state was the cause of these deviations, since the slope would correspond to a higher mn value and therefore correspond to a more complex species which became simpler at high concentrations. Also, the deviated points formed a curve, rather than a straight line, and the deviations were much the same for all experiments.

Topol (27) was able to polarographically detect a reduced bismuth ion during an e.m.f. study of the Bi-BiCl₃ system that had similar negative deviations. In subsequent e.m.f. studies in which an initial impurity was also apparently present, the amount of this initial "impurity" of the reduced species was calculated from the first datum and a presumed mn data (16). A correction factor was then added which brought the first few points into line with the remainder of the data. In these later experiments, however,

no attempt was made to show that an oxidizable entity was indeed present.

In this study the initial voltage observed upon immersion of each cell in the thermostat drifted in a positive direction. This change is in the same direction as that caused by coulometric production of a reduced species. Equilibration of the melts in the sidearms during this initial period did not significantly affect the amount of the drift, so diffusion through the frit and interactions with the electrode materials could not have been responsible. Thus, it is likely that a reduced species was being produced during the initial decay.

Further experiments would be required to decide whether reducing impurities present in the components or some interactions with the glass container were responsible. In view of difficulties encountered in purification of AlCl_3 and the subsequent appearance of a black solid in all digested tetrachloroaluminates made from AlCl_3 , this material is suspect. It is possible, as well, that the e.m.f. drift and the initial deviations of the plot were unrelated. In this case, perhaps a different electrochemical reaction was responsible for the early deviations but was later largely

drowned out by the reaction of interest.

Corrections for the effects of initial impurities were calculated. The correction factor for this impurity must be added to all q_i values, not just the first. This means that the slope of the uncorrected graph in each case is higher than the correct slope, since the plot involves a log function. The integral mn product obtained from the $\log q_i$ versus E plot was assumed to be correct. Then $(q_i + q_0)$, where q_0 was the initial impurity, was substituted for q_i in Equation (2), and q_0 was calculated using E and q_i values from the first and last points on the graph. For cadmium, Equation (1) was employed in a similar manner.

The calculated initial impurities so deduced were much smaller for the lead and tin experiments than for the cadmium determinations. The average value for cadmium was .02 mole percent of the melt, while that for tin and lead was only .007 mole percent. The latter value is considerably better than the .01 to .02 mole percent found by Topol (16). Considered as a percentage of C_0 , the initial M^{2+} concentration, cadmium impurities averaged 4.6 percent, while those for tin and lead averaged only .14 percent.

Cadmium

Since cadmium has a high solubility in the melt used in this study (43 mole percent dissolved metal, based on Cd(II)), smaller initial concentrations of Cd^{2+} (C_0) were used than in the lead or tin cells. This was an attempt to minimize diffusion through the frit by decreasing the concentration gradients across the frit. Therefore, for all three successful cadmium cells, q_i was not negligible compared with C_0 .

For Run 20, however, q_i was only 4.6 percent of C_0 at the final point, so only small errors were introduced by considering that $[C_0 - q_i/n]^m$ was constant. For the uncorrected indicator-reference data, a plot of $\log q_i$ versus E yields $mn = 2.56$. A correction of $7 \mu \text{ eq.}$ was calculated (see Data Treatment) assuming $mn = 2$ to be the correct value. This is a reasonable choice since mn must be integral, and even the $1.6 \mu \text{ eq.}$ correction calculated using $mn = 3$ results in a corrected mn nearer 2 than 3 (2.42). Further, a correction of $1.6 \mu \text{ eq.}$ does not bring the early deviations into line with the remainder of the data. The corrected data (using $7 \mu \text{ eq.}$) yields $mn = 1.98$.

Further support for $mn = 2$ was obtained by using Equation (1) to analyze the data from Runs 8, 20, and 21. This procedure requires a choice of m and n values, as outlined previously (see Data Treatment). The species Cd^0 , Cd_2^{2+} , Cd_3^{4+} , etc. are all consistent with an mn product of 2. Though the graphs for $m = 1$, $n = 2$ (Cd^0) were slightly curved, rough mn values between ~ 1.5 and ~ 2.5 were calculated from the various slopes possible. For instance, mn is 1.83 for points in the middle of the plot and $mn = 2.35$ for the last few points for the indicator-reference data of Run 21.

The selection of $m = 2$, $n = 1$ (Cd_2^{2+}) produced straight lines which yielded sensible values for the mn product. Figures 3 and 4 show typical graphs of $\log [C_o - q_i]^2/q_i$ versus E for data from both the indicator-reference and indicator-working anode couples. The corrections for q_o have been applied as outlined previously, assuming $m = 2$, $n = 1$. Table 1 gives the results for this choice of m and n .

Table 1 shows the agreement between the corrected mn values for the indicator-reference couples of Runs 8, 20, and 21. The result from Run 8 is somewhat low, but the average deviation is twice that for the indicator-reference results of the other experiments. An average deviation of .002 volts

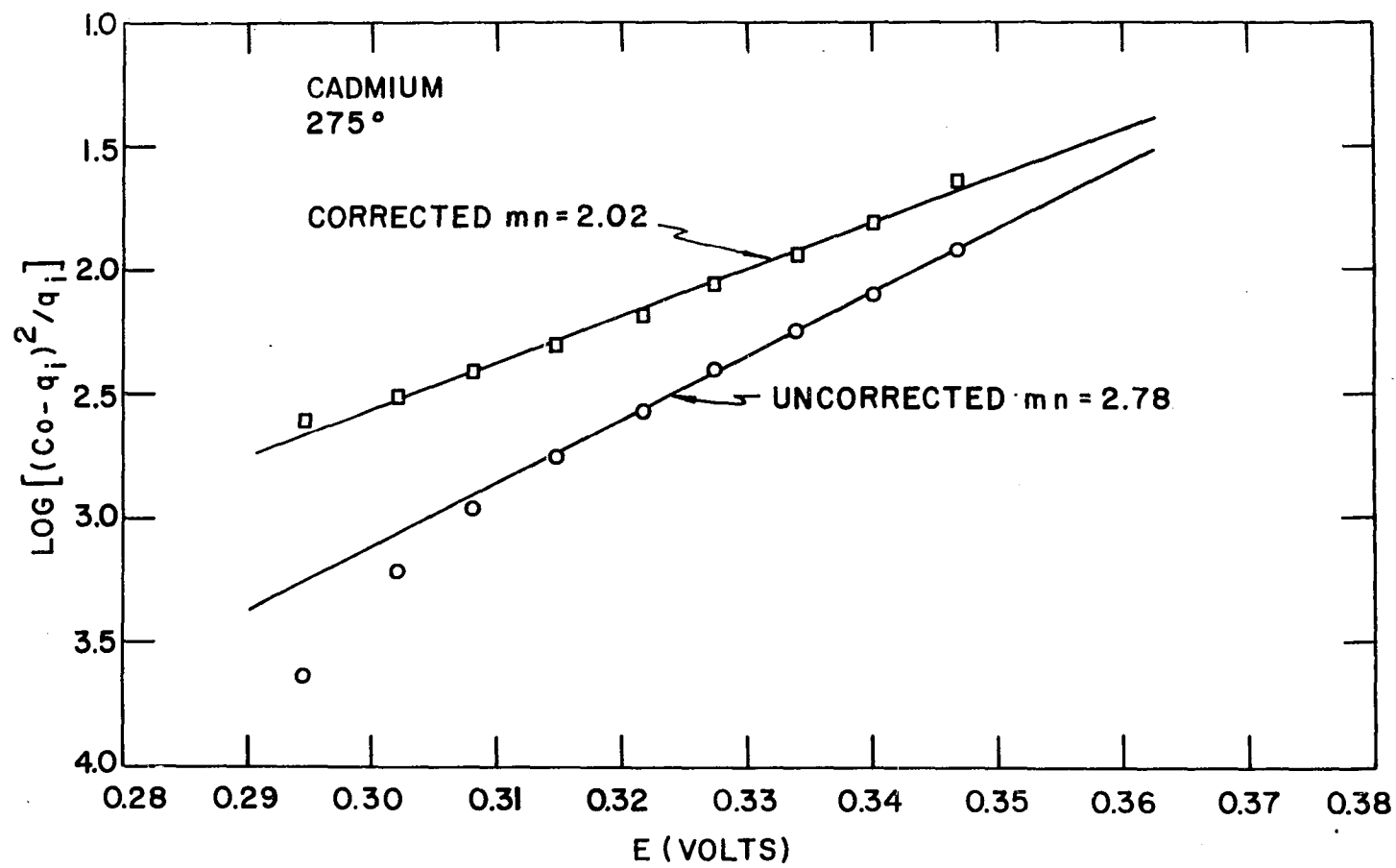


Figure 3. Indicator-reference potentials for cadmium, Run 21

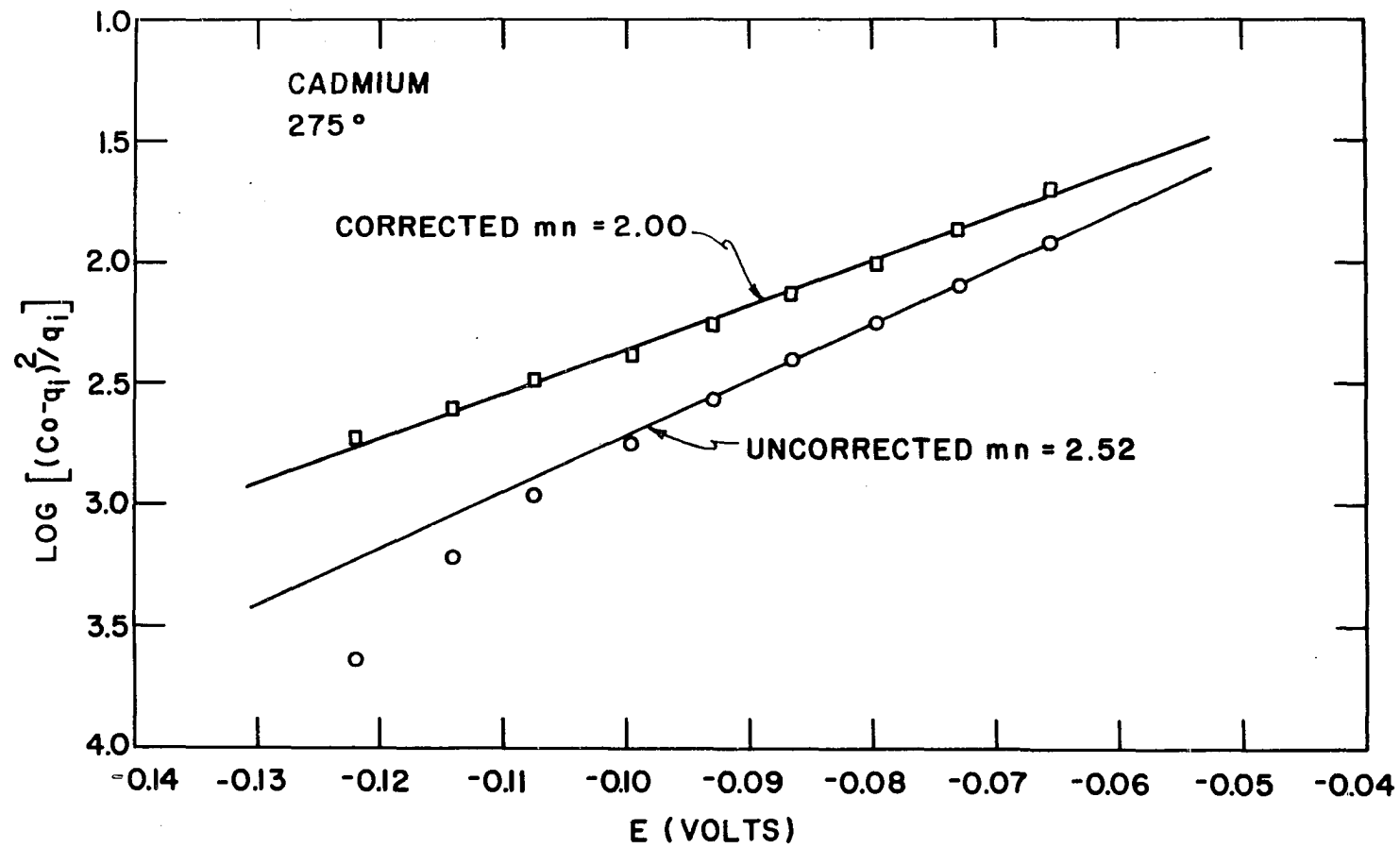


Figure 4. Indicator-working anode potentials for cadmium, Run 21

Table 1. Results for cadmium

	Indicator-reference couple			Indicator-working anode couple	
	Run 8	Run 20	Run 21	Run 20	Run 21
Uncorrected mm	1.93	2.73	2.78	1.50	2.52
Corrected mm	1.84	2.03	2.02	1.44	2.00
Average deviation from corrected plot (volts)	.002	.001	.001	.006	.001
C_0 (initial Cd^{2+} concn.) (μ eq.)	27	890	67	890	67
(mole %)	.1	3.8	.2	3.8	.2
Calculated impurity q_0 (μ eq.)	.7	8	7.5	1.3	5.8
mole % of melt	.0003	.03	.02	.01	.02
% of C_0	2.4	.9	11	.1	8.6
Mole % dissolved Cd for final data point	18.5	2.3	17	2.3	17
Mole % dissolved Cd at saturation, based on Cd(II)				14	40
Temperature	293	276	275	276	275

corresponds to an average deviation in mn of .1, which could account for a large part of the difference between 1.84 and 2.00.

The indicator-working anode result of 1.44 for mn from Run 20 deviates markedly from the other runs, but this result also shows by far the least linearity, as indicated by the large average deviation. Also, the disagreement between the calculated impurities for the two couples of Run 20 contrasts with the agreement for Run 21 and is further evidence for undetermined problems in the use of the working anode as a reference. The working anode compartment of Run 8 contained no Cd^{2+} and an aluminum, rather than cadmium, electrode. No data for the indicator-working anode couple were taken.

A third species which is consistent with an mn product of 2 is Cd_3^{4+} , for which $m = 3$, $n = 2/3$. This choice of m and n led to plots which had larger scatter than $m = 2$, $n = 1$ graphs. The mn product calculated from the rough slope was ~ 4 for Run 21 and ~ 3 for Run 20.

A single plot of $m = 4$, $n = 1/2$, for Run 21 produced $mn = 6.4$. Plots for $m > 4$ are expected to show even greater inconsistencies between the mn corresponding to the slope

of the plot and the $mn = 2$ values upon which the plot is based.

The limit of maximum reduction was not reached for any run. A saturation limit of 50 mole percent dissolved metal would correspond to reduction of all Cd^{2+} to a monovalent state. The saturation limits given in Table 1 were calculated from the value of $\log q_i$ (corrected) which corresponds to 0 volts for the indicator-working anode couple. The Run 21 limit of 40 mole percent dissolved metal (based on $Cd(II)$) is comparable to the $43 \pm 3\%$ determined by the loss in weight of metal buttons equilibrated with the melt. The calculated value for Run 20 is probably low because of the low value for the slope upon which the calculation is based. Thus, the indicator-working anode data are less consistent than the indicator-reference data. However, the excellent agreement between the saturation limit measured by loss in weight and the saturation limit calculated from the indicator-working anode data of Run 21, which also produced an mn value consistent with that from the indicator-reference data, is further confirmation of the conclusions of these experiments.

All three cadmium cells used tantalum indicator electrodes, and cadmium was added to the cells as $Cd(AlCl_4)_2$.

In general, the calculated impurities in the cadmium studies were far greater than those found with lead; results could probably have been improved by the use of digested $\text{Cd}(\text{AlCl}_4)_2$.

Studies in several different melts have now reached the same conclusion regarding a lower oxidation state species of cadmium. Only the Raman study by Corbett (9) has designated Cd_2^{2+} unequivocally from the series Cd^0 , Cd_2^{2+} , Cd_3^{4+} , etc., but data from CdCl_2 (8) and $\text{CdCl}_2\text{-KCl-NaCl}$ (45), as well as $\text{Cd}(\text{AlCl}_4)_2$ (9), are in agreement that a species from this series is formed. Since this study in $\text{Cd}(\text{AlCl}_4)_2\text{-NaAlCl}_4$ (90 mole percent)- AlCl_3 points to the same series and suggests Cd_2^{2+} , it appears likely that Cd_2^{2+} is indeed the species commonly formed when Cd dissolves in melts containing Cd^{2+} .

Lead

The results for two lead cells are shown in Table 2. In both cases q_i is negligible compared with C_o , so the data were analyzed unambiguously by a $\log q_i$ versus E plot according to Equation (2). Typical graphs for the indicator-reference and indicator-working anode couples are shown in

Table 2. Results for lead

	Indicator-reference couple		Indicator-working anode couple	
	Run 14	Run 18	Run 14	Run 18
Uncorrected mn	1.04	1.26	1.24	1.42
Corrected mn	.90	1.00	1.04	1.08
Average deviation from corrected plot (volts)	.003	.002	.003	.003
C_0 (initial Pb^{2+} concn.)				
(μ eq.)	1760	1760	1760	1760
(mole %)	5	5	5	5
Calculated impurity q_0				
(μ eq.)	.7	3.2	.7	6.5
mole % of melt	.002	.009	.002	.02
% of C_0	.04	.2	.04	.4
Mole % dissolved Pb for final data point	.2	.6	.2	.6
Temperature	276	279	276	279

Figures 5 and 6. Impurities were calculated assuming $mn = 1$.

Any possible variations in the reference cell were eliminated by using the same reference for both Run 14 and

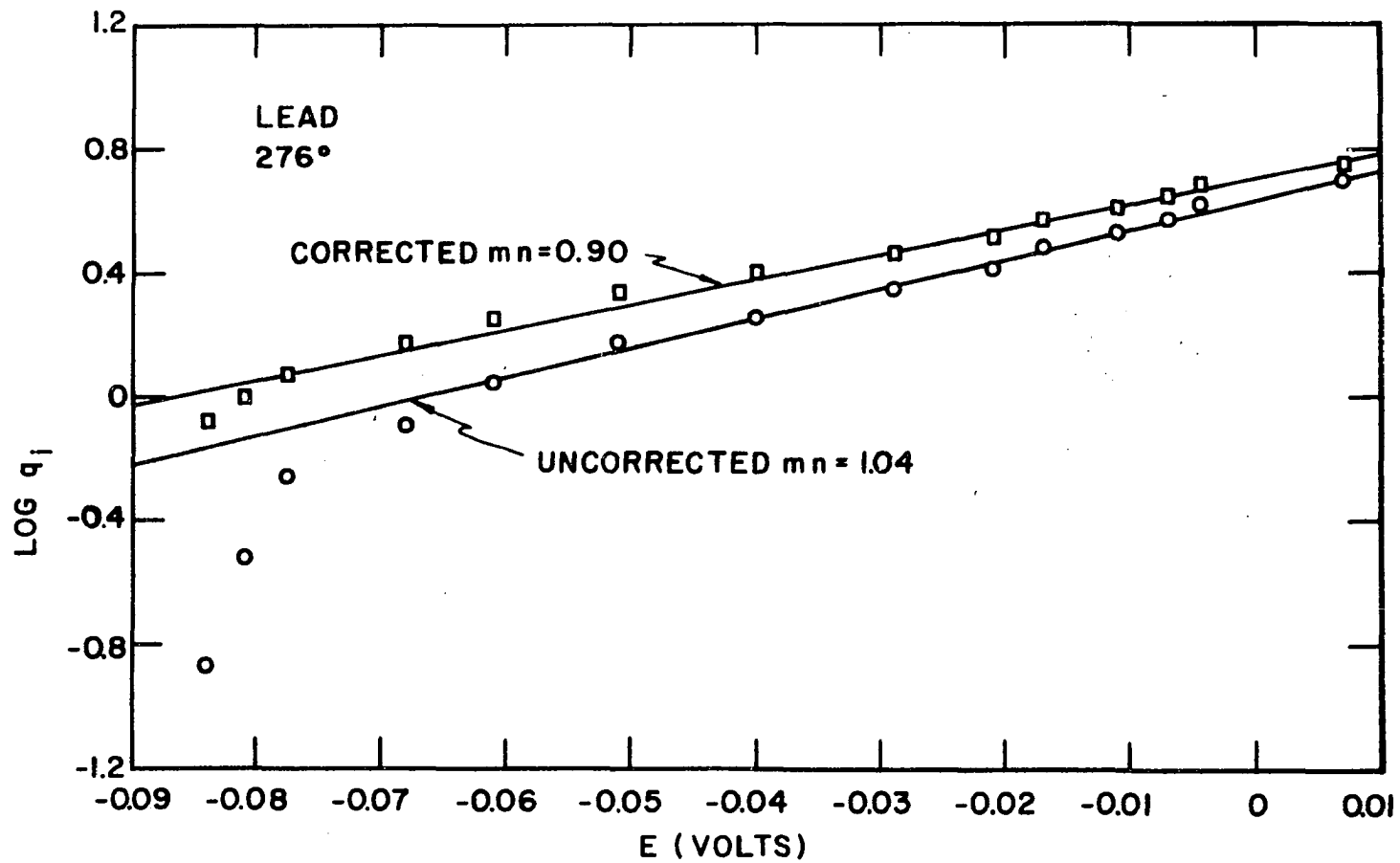


Figure 5. Indicator-reference potentials for lead, Run 14

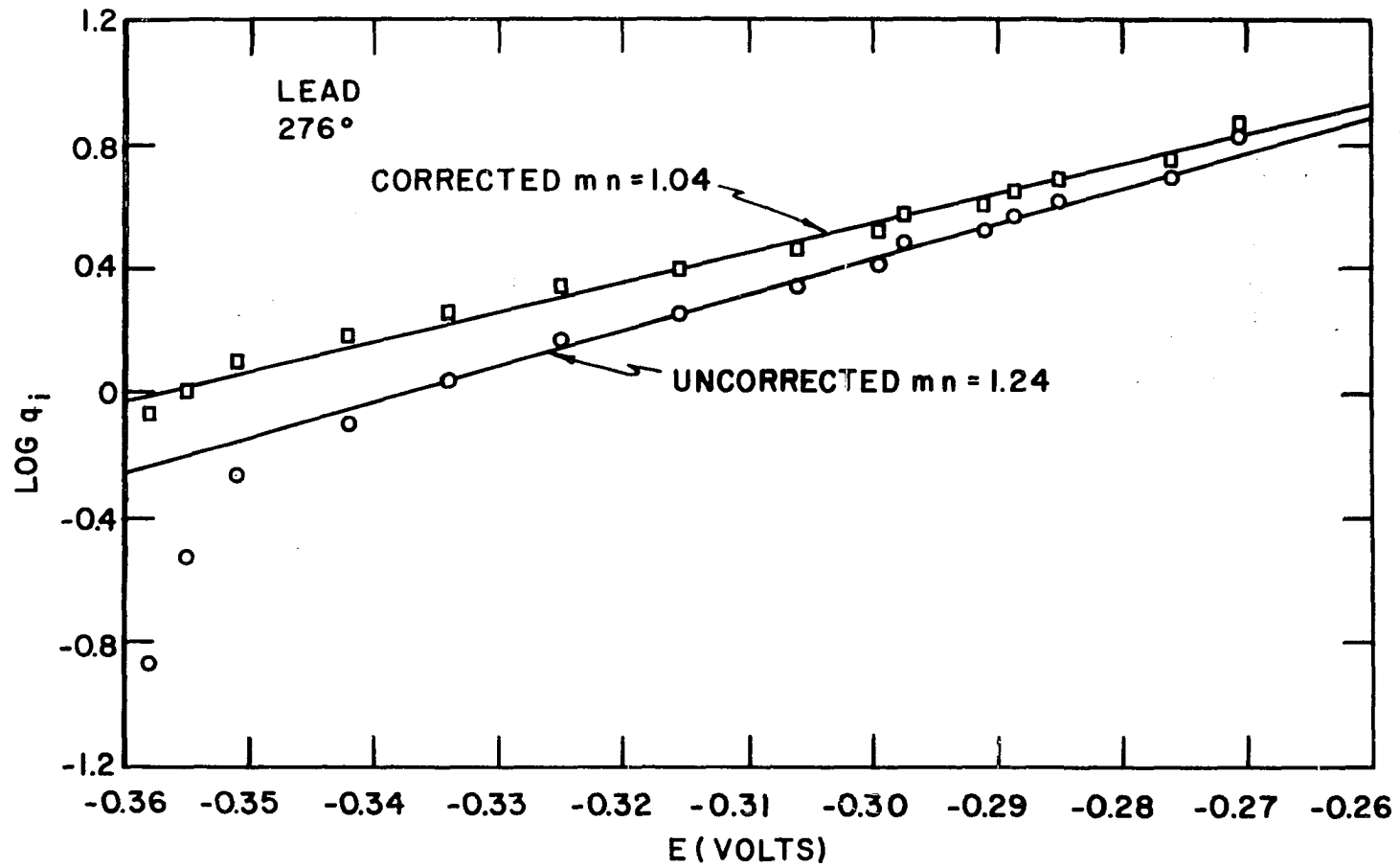


Figure 6. Indicator-working anode potentials for lead, Run 14

Run 18. The indicator electrode in both cases was tantalum. Run 18 contained a new frit and an unused lead working anode. Lead was added to the cells as $\text{Pb}(\text{AlCl}_4)_2$.

Attempted calculations for the limit of reduction yielded meaningless values in excess of the initial amount of Pb^{2+} , but extreme extrapolations of the data were required for these calculations. As for cadmium, the reduction limit was not actually reached during cell operation.

The results clearly indicate that $mn = 1$ for the solution of lead in $\text{Pb}(\text{AlCl}_4)_2\text{-NaAlCl}_4$ (90 mole percent)- AlCl_3 . The species Pb^+ , Pb_2^{3+} , Pb_3^{5+} , etc., are all consistent with an mn product of 1, and no further restriction is possible on the basis of these experiments. The results are surprising because they indicate that a different species is formed in $\text{Pb}(\text{AlCl}_4)_2\text{-NaAlCl}_4\text{-AlCl}_3$ than in PbCl_2 . For the latter, both Topol's e.m.f. study and Egan's polarographic measurements suggest that Pb_2^{2+} (Pb^0 , Pb_3^{4+} , etc.) is formed.

Since all of the species possible for $mn = 1$ would be paramagnetic while Pb_2^{2+} would be diamagnetic, qualitative susceptibility measurements were made. These were carried out on the related $\text{Pb}(\text{AlCl}_4)_2$ melt where the solubility of lead (see Other Experiments) is higher than in the $\text{NaAlCl}_4\text{-}$

diluted melt used for e.m.f. measurements. Unfortunately, no difference could be detected between the saturated and pure melts at 300°. The sensitivity of the equipment was checked with aqueous solutions containing specific concentrations of paramagnetic species, and these measurements showed that the possible concentration of paramagnetic lead species should not be detectable. However, the possibility remains that more accurate susceptibility measurements would provide confirmation for the existence of two different reduced lead species in different melts.

Tin

A modified cell was developed and used for experiments with tin because the data from three earlier cells, Runs 15, 16, and 19, were of dubious significance. The earlier cells contained molten tin anodes and either tungsten or carbon indicator electrodes. The molten tin was contained in a well at the bottom of the working anode compartment. Electrical contact between the silver entrance wire and the tin was established by a tungsten rod shielded from the NaAlCl_4 - AlCl_3 - $\text{Sn}(\text{AlCl}_4)_2$ melt by a glass tube collapsed around the rod.

Graphs of the data from Run 16 were reasonably linear, but m_n for the indicator-reference couple was about 9 while that for the indicator-working anode couple was 5.6. The frit had been partially heat-collapsed to reduce diffusion because results from Run 15 showed the indicator compartment was initially saturated with tin. Consequently, the resistance of the frit used in Run 16 was 28 $K\Omega$, and the potential across the frit during coulometric reduction reached 150 volts compared to the 1 volt normally observed.

An uncollapsed frit was employed for Run 19. The indicator-reference slope could be variously interpreted to give $m_n = 4.5$ to 7. The indicator-working anode plot was curved so no m_n could be determined.

Because of these results, the cell for Run 23 was modified to essentially eliminate diffusion. The frit was offset from the line joining the electrodes by placing it in a U tube extending in the opposite direction from the sidearms (see Figure 1). Qualitative determinations of the density of the melt and the capacity of each cell compartment were made. After loading with amounts of salts calculated to fill the compartments to a designated level, the sidearms were sealed at predetermined points. These adjustments allowed

the melts to be tipped into the sidearms with the electrodes and diaphragm still immersed. In this position the frit was not immersed, so no diffusion occurred during either the initial decay or the necessary equilibrations after coulometric reductions. Pressure equalization could also take place through the frit so the pressure equalizing passage was eliminated from the cell. During the relatively short periods of time required for coulometric reductions, the cell was tilted in the opposite direction to immerse the frit, while the electrodes remained immersed. In both positions the electrodes were immersed to approximately the same level.

Silver was used for the working anode and carbon for the indicator electrode. Tin was added to the cell as SnCl_2 . In order to minimize diffusion, no data were taken for the indicator-working anode couple.

The results of Run 23 are shown in Table 3 and Figure 7. Corrections were calculated as outlined previously, assuming $mn = 3$. This is reasonable since the corrected mn is 3.26 even if $m = 4$ is assumed. The calculated impurity was based on the second data point since the first point was not consistent with the rest of the data and led to a cor-

Table 3. Results for tin, Run 23

Uncorrected mn	3.55	Mole % dissolved Sn for final data point	.45
Corrected mn	2.92	Calculated impurity q_o (μ eq.)	2.8
Average deviation from corrected plot (volts)	.001	mole % of melt	.004
C_o (initial Sn^{2+} concn.) (μ eq.)	3477	% of C_o	.08
(mole %)	5.4	Temperature	277°

rected plot which was not linear. This first point was probably not significant because of the extremely low amount of reduction (.25 μ eq.).

While not conclusive, the results for Run 23 suggest that the lower oxidation state species of tin formed by dissolving tin in $Sn(AlCl_4)_2-NaAlCl_4$ (90 mole percent)- $AlCl_3$ is one of the series Sn_2^+ , Sn_3^{3+} , Sn_4^{5+} , etc. This is the first evidence for a specific reduced tin species in a melt, so no direct comparisons can be made with other work. Four previous references (17 - 20) have postulated the existence of a lower oxidation state of tin in melts in order to account for various electrochemical observations. These

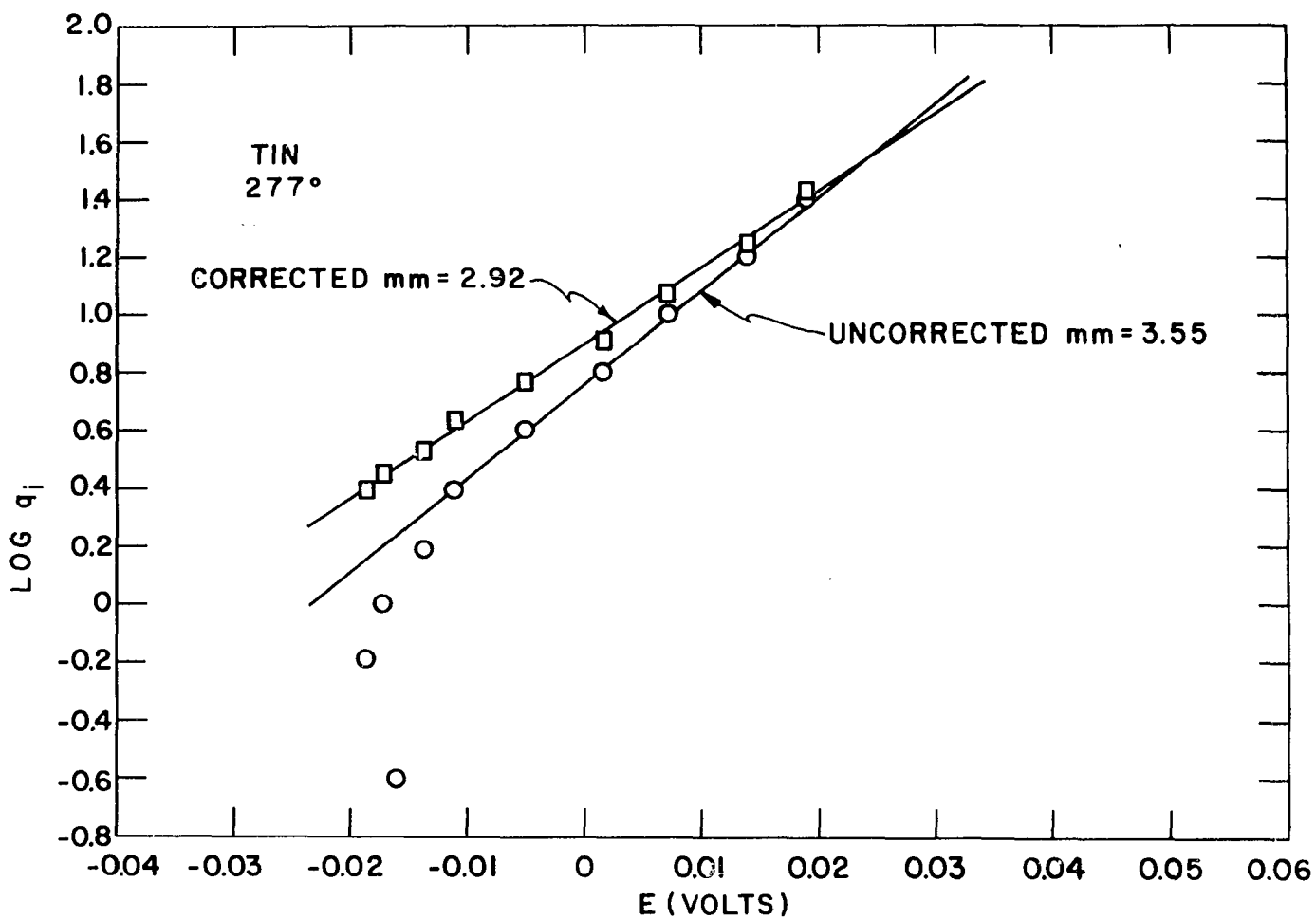


Figure 7. Indicator-reference potentials for tin, Run 23

include otherwise unexplained breaks in polarograms of molten SnCl_2 (17) and chronopotentiometric studies in the same melt (18).

As with lead, the e.m.f. measurements suggest species which are paramagnetic. However, qualitative susceptibility determinations similar to those carried out with lead were also unsuccessful for pure and saturated $\text{Sn}(\text{AlCl}_4)_2$. Further studies with more accurate equipment are in order.

This investigation has demonstrated the feasibility of electrochemical measurements on reduced tin species, particularly in the presence of added AlCl_3 , which significantly increases the concentration of the reduced species (see Other Experiments). However, other such studies are still required to confirm the somewhat unusual results found here.

Zinc

E.M.F. measurements were made on only one cell containing divalent zinc. A lead working anode was used because zinc reduced aluminum from NaAlCl_4 . Zinc was introduced as ZnCl_2 . No meaningful results were obtained because the cell potentials drifted continuously. The direction of the drift was consistent with diffusion of the reduced zinc species

through the frit.

In separated experiments ZnCl_2 was found to be slowly soluble in 93 mole percent NaAlCl_4 -7 mole percent AlCl_3 . The limit of solubility was 4.2 mole percent at 300° and was very temperature dependent.

Other Experiments

Attempts to study nickel failed because suitable concentrations of Ni^{2+} in NaAlCl_4 - AlCl_3 melts could not be achieved. NiCl_2 did not dissolve in AlCl_3 to any appreciable extent at 160° , 225° , or 240° when heated for three weeks. Heating AlCl_3 at 240° in one end of a tube and NiCl_2 at 500° in the other end also failed to produce significant reaction. Two NiCl_2 - AlCl_3 (1:2 mole ratio) mixtures were heated in sealed tubes with 25 and 83 mole percentages NaAlCl_4 , respectively. One end of each sealed tube was heated at 370° and the other at 270° . This produced transparent yellow hexagonal crystals, which powder patterns indicated were merely recrystallized NiCl_2 . In many cases, a rose-to-salmon coloration of the melt was produced, but the solubility of NiCl_2 remained very small. This is somewhat surprising since the preparation and structure of $\text{Co}(\text{AlCl}_4)_2$ has been reported

(46). The solubility of NiCl_2 in a melt composed of 93 mole percent NaAlCl_4 -7 mole percent AlCl_3 was estimated at < 0.1 percent at 300° , in agreement with the report of Delimarskii for pure NaAlCl_4 (47).

In the course of this work, solubilities of the respective metals in the pure tetrachloroaluminates and in 90 mole percent NaAlCl_4 -5 mole percent AlCl_3 -5 mole percent tetrachloroaluminate were determined. The results, together with other values from the literature, are contained in Table 4. All tetrachloroaluminates prepared were found to be miscible with NaAlCl_4 .

The table shows that for tin and lead, as well as cadmium, the solubility is increased by adding AlCl_3 to the metal chloride. This is further substantiation for the concept of acid stabilization developed by Corbett, Burkhard, and Druding (1).

If the same reduced species is formed in the pure tetrachloroaluminates as in the 90 mole percent NaAlCl_4 melts, the data indicate that percent reduction of the divalent cations is increased upon dilution with NaAlCl_4 for tin and lead, but not for cadmium. If the cadmium dissolves according to the reaction $\text{Cd}^0 + \text{Cd}^{2+} \rightleftharpoons \text{Cd}_2^{2+}$, the equilibrium constant

Table 4. Solubilities in different solvents (mole percent dissolved metal)

M	MCl ₂ (Ref.)	M(AlCl ₄) ₂ (Ref.)	90 mole % NaAlCl ₄ 5 mole % AlCl ₃ 5 mole % M(AlCl ₄) ₂
Cd	15 @600° (1)	40 @335° (1)	3.8 ^a ± .3 or 43 ± 3 ^b @300°
Pb	.006 @500° (12)	.2 @305°	.16 ^a or 2.4 ^b @300°
Sn	.003 @500° (12)	.1 @290°	.06 ^a or 1.1 ^b @305°

^aBased on total melt.

^bBased on moles of M(II) only.

$K = \frac{[Cd_2^{2+}]}{[Cd^{2+}]}$ is (as observed) not affected by dilution.

However, the simplest proposed species for lead and tin correspond to the equilibrium constants $K = \frac{[Pb^+]^2}{[Pb^{2+}]}$ and

$K = \frac{[Sn_2^+]^2}{[Sn^{2+}]}$, for which the mole percent dissolved metal

based on M(II) must increase (as observed) with dilution if the K is to remain constant. The measured solubilities are thus in accord with the designation of $mn = 2$ for cadmium and $mn = 1$ and $mn = 3$ for lead and tin, respectively. Calculations show that the increased solubility caused by dilution

would be .9 mole percent dissolved metal (based on M(II)) in the 90 percent NaAlCl_4 melt for lead and .48 mole percent for tin for the two proposed equilibria. Since the measured solubilities are better than twice these amounts, other factors involving the altered ionic environment of lead and tin ions in the 90 percent NaAlCl_4 melt compared with the undiluted tetrachloroaluminates must also have an effect. In the pure tetrachloroaluminates there are effectively two AlCl_3 molecules competing with each M^{2+} for basic Cl^- ions, while in the 90 percent NaAlCl_4 melt there are three AlCl_3 molecules per M^{2+} due to the addition of 5 mole percent AlCl_3 . This increase in acidity might reasonably have little effect on the cadmium equilibrium which is already shifted far toward Cd_2^{2+} , but yet account for the increased solubility of lead and tin.

Proposed Research

Further e.m.f. studies with several of the post-transition metals would be of interest. In particular, complex, reduced species of indium and bismuth should be detectable. Since phase studies involving In(I) in chloride melts show four compounds other than InCl , it seems likely

that ions related to these compounds occur in the melts. Bismuth systems have already been extensively investigated, but ions such as Bi_3^{+*} and Bi_9^{5+} are interesting possibilities for e.m.f. determination. For gallium, there is no reason to expect other than the simple Ga^+ ion, but its confirmation would be relatively easy. These elements are most likely susceptible to e.m.f. studies with approximately the same equipment and techniques developed in this work. The modified cell used for tin should also eliminate or pinpoint the problems encountered with zinc.

For the remaining elements, direct measurements of the solubility of metals in their salts should be made prior to more e.m.f. studies. Measurements in this study show that the concentration of dissolved lead and tin in their chlorides can be increased significantly by the addition of AlCl_3 or NaAlCl_4 plus AlCl_3 . Therefore, the effect of added AlCl_3 or NaAlCl_4 on metal solubilities in such halides as MnCl_2 , CrCl_2 , CoCl_2 , AgCl , ZnCl_2 , Hg_2Cl_2 , and TlCl should be

*Corbett, J. D., Ames Laboratory, U. S. Atomic Energy Commission, Iowa State University of Science and Technology, Ames, Iowa. The reduction of $\text{Bi}(\text{AlCl}_4)_3$ with excess bismuth metal. Private communication. 1964.

determined. In this connection, zinc must be measured by some method other than weight loss, since zinc metal reduces aluminum from AlCl_4^- melts. Germanium halides are probably too molecular and Ge(II) too weak an oxidizing agent to show reduction by germanium metal, but addition of AlCl_3 or NaAlCl_4 might be tried. In any case, reduction limits for most post-transition elements are known to increase from chlorides to iodides, so the effects of addition of AlI_3 and NaAlI_4 to the iodides might be interesting. The effects of mixing halides are also as yet unknown. The substitution of other acids for AlCl_3 has been explored to some extent (8), but various silicate melts remain as possibilities.

Additional e.m.f. studies might be more successful than otherwise if several factors are considered. With the present cell, some balance exists between eliminating junction potentials and increasing the concentration of the oxidized ion to allow higher absolute quantities of reduced species. For systems which have even lower solubilities than those already studied, the amount of oxidized ion can perhaps be increased above 5 mole percent without introducing errors. Within limits of salt preparation and thermostat size, the amount of melt used in a cell may also be increased.

In this connection, e.m.f. measurements might detect a reduced aluminum species, if it could be formed in suitable quantities. The calculated solubility of Al in AlCl_3 ($\sim 10^{-7}$ mole percent at 230° (11)) is extremely low. Also, aluminum has been used previously as an electrode material in NaCl-KCl-AlCl_3 melts by Verdieck and Yntema, who did not note any special problems (48). However, in the present work, surfaces of aluminum anodes disintegrated in NaAlCl_4 . On one particular occasion with a cell for measurements on lead, aluminum crystals were formed on the working anode side of the frit, and lead crystals on the indicator side. This occurred before coulometric reductions were begun. Both of these observations suggested that a reduced aluminum species was formed in the working anode compartment. Studies would no doubt be more successful if iodides could be used, because the solubility of Al in AlI_3 is .02% at 230° (37).

The designation of a reduced nickel species may also be possible, since Verdieck and Yntema (48) reported 1 mole percent solubility in a 66 mole percent AlCl_3 -20 mole percent NaCl -14 mole percent KCl melt at only 156° . Substitution of NaCl-KCl-AlCl_3 for NaCl-AlCl_3 would not require any radical cell changes.

The $\text{Ag}:\text{Ag}^+$ half-cell has been shown in this work to provide a more consistent reference than the saturated working anode compartments. However, the anode compartment can profitably be used as a reference for preliminary measurements in systems where solubilities are as large as those found for lead. This will allow simpler cells to be used for part of the work.

Higher purity materials are still desirable. The unknown liquid which was present at room temperature in one $\text{Pb}(\text{AlCl}_4)_2$ preparation and the initial "impurities" consistently observed both indicate that purification of materials should continue to be an important part of further e.m.f. work.

A continuously reading or recording electrometer would greatly facilitate making measurements but probably cannot be justified because of expense.

Certainly the possible tetrachloroaluminate compounds have yet to be exhausted. Known phase diagrams for metal halide-metal tetrachloroaluminate or metal halide-aluminum chloride systems are sparse, and though many such diagrams are no doubt simple, others might be interesting.

Further confirmation of the results of this work can be

obtained by polarographic measurements using approximately the same cell. There is some evidence that decomposition potentials can be determined through a glass diaphragm if the melt contains sodium ions (49). Otherwise, an asbestos fiber sealed through glass, such as that used by Topol and Osteryoung (50), can be substituted for the diaphragm. In addition to the large electrode used for coulometric reductions, a solid microelectrode would have to be added to the indicator compartment.

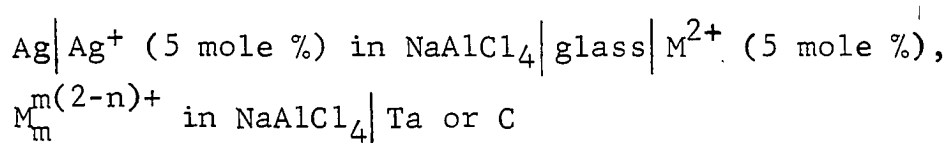
Vapor pressures, freezing points, or other properties of the solvent for even the undiluted tetrachloroaluminates would not be affected enough to infer particular reduced lead or tin species.

Since this study indicates that paramagnetic species are present in the solutions of lead or tin in their tetrachloroaluminates plus NaAlCl_4 , careful susceptibility measurements with good equipment could provide interesting results.

SUMMARY

E.M.F. measurements were used to designate the lower oxidation state species formed when cadmium, lead, and tin dissolve in NaAlCl_4 melts containing divalent tetrachloroaluminates of those metals. The effectiveness of the addition of the acid AlCl_3 to increase the solubility of metals in their molten chlorides was further substantiated. Similarly, the usefulness of acid stabilization to increase the concentration of lower oxidation states for electrochemical measurements was demonstrated.

Sealed cells of the type



were employed for $\text{M} =$ cadmium, lead, tin, and zinc at 275 to 305°. The acidic solvent NaAlCl_4 was chosen to stabilize the lower state species, $\text{M}_m^{m(2-n)+}$. The concentration of this reduced species was increased coulometrically against a third half-cell connected to the cell by an ultrafine frit. Thin glass bubbles were used for the reference junctions.

The data were analyzed by the use of a $\log q_i$ versus e.m.f. plot, where q_i is the equivalents of current passed for the production of the lower oxidation state. Initial

negative deviations from the linear portion of the plot were assumed to be due to the presence of some of the reduced species before its coulometric production began. The amount of this initial "impurity" was calculated and corrections were applied to the data.

The corrected values of the mn products are $2.0 \pm .1$ for cadmium, $1.0 \pm .1$ for lead, and ~ 3 for tin. The cadmium result concurs with previous studies which suggest that Cd_2^{2+} is the reduced species of cadmium formed in various melts. However, $mn = 1$ for lead indicates that an ion of the type Pb^+ , Pb_2^{3+} , Pb_3^{5+} , etc. is formed in $Pb(AlCl_4)_2$ - $NaAlCl_4$ (90 mole percent)- $AlCl_3$, while other workers have concluded that Pb_2^{2+} is formed in molten $PbCl_2$. The mn product for tin suggests one of the species Sn_2^+ , Sn_3^{3+} , Sn_4^{5+} , etc., which is the first determination of a specific reduced species for tin. Drifting potentials prevented the designation of a value for zinc. The study of nickel was not successful because $NiCl_2$ is insoluble in $NaAlCl_4$.

$Pb(AlCl_4)_2$ and $Sn(AlCl_4)_2$ were synthesized. Procedures were developed for preparing highly pure $AlCl_3$, $NaAlCl_4$, $Pb(AlCl_4)_2$, and $Sn(AlCl_4)_2$. Solubilities were determined for lead and tin in their tetrachloroaluminates and for cadmium,

lead, and tin in their tetrachloroaluminates (5 mole %) in NaAlCl_4 (90 mole %)- AlCl_3 (5 mole %). The changes in these solubilities caused by addition of NaAlCl_4 - AlCl_3 to the pure cadmium, lead, or tin tetrachloroaluminates are semi-quantitatively consistent with the above formulations of lower oxidation state species.

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APPENDIX

Table 5. X-ray powder diffraction data for $\text{Pb}(\text{AlCl}_4)_2$

$d(\text{\AA})$	Relative intensity	$d(\text{\AA})$	Relative intensity
7.02	100	3.13	40
6.32	10	3.06	10
6.15	40	2.97	30
5.03	5	2.69	20
4.82	20	2.26	10
4.55	70	2.24	10
3.62	20	1.69	5
3.28	20		

Table 6. X-ray powder diffraction data for SnCl₂

$d(\text{\AA})$	Relative intensity	$d(\text{\AA})$	Relative intensity
4.57	20	2.20	20
3.95	30	2.17	10
3.54	100	2.11	50
2.95	10	1.92	5
2.92	5	1.77	5
2.78	30	1.70	5
2.52	40	1.58	5
2.29	5	1.42	5
2.25	10		

Table 7. X-ray powder diffraction data for $\text{Sn}(\text{AlCl}_4)_2$

$d(\text{\AA})$	Relative intensity	$d(\text{\AA})$	Relative intensity
7.37	20	2.93	10
6.19	100	2.87	10
5.15	40	2.82	5
4.62	10	2.75	10
3.88	40	2.60	50
3.62	5	2.57	10
3.53	10	2.52	60
3.40	20	2.46	10
3.20	10	2.37	10
3.10	30	2.19	5
2.99	10	2.15	5