

REDUCTION MECHANISMS
IN
FUSED SALT-ALLOY SYSTEMS

by

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B.A.Sc., University of British Columbia, 1962

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We accept this thesis as conforming to the
required standard

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Department of Metallurgy

The University of British Columbia,
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The University of British Columbia

FACULTY OF GRADUATE STUDIES

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REDUCTION MECHANISMS IN FUSED SALT-ALLOY SYSTEMS

ABSTRACT

Reactions between ions in LiCl-KCl eutectic melt and lead alloys have been studied kinetically between 370 and 450°C.

Diffusion of the reducing ionic species across the salt-phase boundary layer was shown to be the rate controlling step for the reductions of Pb^{++} , Cd^{++} , Ag^+ and In^{+++} by lithium and of Cr^{+++} by lead. Values of the salt-phase boundary layer thickness were estimated.

Limited solubility of the reduced metal in the molten alloy resulted in metal deposition at the phase boundary during the reductions of Co^{++} , Cr^{+++} and Ti^{+++} by lithium.

An apparent homogeneous reaction in the salt occurred during the reductions of Ni^{++} and Pt^{++} by lithium. The mechanisms have not been established but may involve solubility of either lithium or a Li-Pb intermetallic compound in the salt.

The interfacial reactions were primarily electrochemical in nature, and never rate-controlling.

The diffusion coefficients of a number of ions in LiCl-KCl at 400 C were determined. The values showed that ionic diffusion in this eutectic was influenced primarily by the ionic charge of the diffusing species.

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INTRODUCTION

General

In metal reduction processes at furnace temperatures, the chemical reactions of primary interest are those occurring between a slag and a metal phase. The physical chemistry of these systems is defined for practical purposes by the thermodynamic properties of the slag and metal phases, and by the thermochemistry of the component reactions taking place. The rate of approach to equilibrium of such reactions is generally considered to be governed by mass transfer processes. The chemical reactions not involving mass transfer have usually been considered virtually instantaneous.

This situation may be contrasted to the physical chemistry of aqueous metal producing processes. Here the thermodynamics are almost completely understood (up to the boiling point) and mass transfer steps that might be slow can be accelerated by suitable agitation, but many chemical reactions are astonishingly slow. The most interesting portions of the physical chemistry of these processes are therefore the kinetics and mechanisms of the slow homogeneous and heterogeneous chemical reactions themselves.

The difference between furnace reductions and aqueous processes is essentially one of temperature. Fused salt processes lie in an intermediate temperature range, but seem to resemble the high temperature furnace systems more than the hydrometallurgical processes.

A fundamental study of the mechanisms occurring in metal reductions by alloys from fused salts at the minimum practical temperatures thus seemed worthwhile for purposes of completely defining the physical chemistry of such reaction systems.

Previous Work

The rate processes leading to high temperature equilibria are not nearly as well understood as their thermodynamics and have attracted the attention of investigators only recently, with the result that the body of literature on metallurgical kinetics is small.

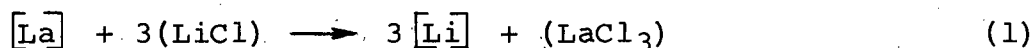
Slag-metal reactions have generally received the most attention, since they are fundamental to the processing of steel, lead, nickel, copper and other metals. Reactions between iron alloys and slags, such as the desulphurization of iron^{1,2} and silica reduction by carbon-saturated iron³⁻⁶, have been examined in some detail.

Reactions between metallic phases and fused salts, which are similar to slag-metal reactions, have risen in importance with the increased production of reactive metals such as titanium, zirconium, uranium, thorium, tantalum, niobium, etc. These metals are usually obtained by sodium, magnesium or calcium reduction of their chlorides or fluorides.

Henrie and Baker⁷ have studied the mechanism of sodium reduction of titanium chlorides in fused salts. The process involves an initial reaction between sodium and titanium chloride vapours producing titanium subchlorides, which form a condensed phase with sodium chloride. Final reaction takes place electrochemically between two salt phases, one containing free sodium in sodium chloride and the other, titanium subchlorides in sodium chloride.

Fused salt-metal reactions also have application in alloy production. Cadmium-lead bearing alloys have been made commercially by the reaction of a sodium-lead alloy with either pure CdCl_2 or a mixture of CdCl_2 with other inert chlorides. Applications of such systems to metal purification include the removal of Pb from tin by SnCl_2 ⁸ and the removal of In and Zn from lead with PbCl_2 ⁹. The pyrometallurgy of halides has been reviewed by Kroll¹⁰.

Recent developments in nuclear fuel processing have led to the use of fused salt-metal reactions for the removal of fission products from molten uranium and plutonium. Motta¹¹ has shown that the removal of Pu from liquid uranium fuel by contact with UF_3 (usually in a solution with BaF_2) is about 90% complete. The same process removes most of the reactive fission products, e.g., 99.9% removal of Cs, Sr and Ce. Bareis et al¹² have examined the removal of La from bismuth-uranium fuel via the reaction,



The process involves a continuous removal of reactive fission products from the fuel at 450°C using LiCl-KCl or NaCl-KCl-MgCl₂ eutectics.

Martin and Miles¹³ pointed out the possibility of first oxidizing fission products to the salt, then contacting the salt with liquid lead to reduce these impurities. The lead alloy can then be conveniently stored.

Kinetics of Heterogeneous Processes

The kinetics of heterogeneous processes have been reviewed by Wagner¹⁴ and by Darken¹⁵. These processes involve three general steps:

- (1) Transport of reactants from the bulk phases to the reaction interface.
- (2) Reaction at the phase boundary.
- (3) Transport of reaction products from the interface to the bulk phases.

Ideally two limiting cases are possible:

- (1) Equilibrium is virtually established at the interface, and the reaction rate is controlled by the mass transport of one or more of the species involved in the reaction.
- (2) The phase boundary reaction is much slower than any of the transport processes, and so controls the overall rate.

Transport Control

Transport in liquids involves both diffusion and convection. The flux of a material in a direction x perpendicular to the interface is given by

$$j_x = -D \frac{\partial C}{\partial x} + C U_x \quad (2)$$

where j_x = flux ($\text{mole cm}^{-2} \text{ sec}^{-1}$)

D = diffusion coefficient ($\text{cm}^2 \text{ sec}^{-1}$)

C = concentration (mole cm^{-3})

U_x = flow velocity (cm sec^{-1})

The concept that significant concentration differences are confined to the vicinity of the interface, i.e., to a "boundary layer", has been shown to be valid in many instances, especially in situations where forced convection (e.g. stirring) is present.

Considering Figure 1, an "effective" boundary layer is defined by the thickness δ .

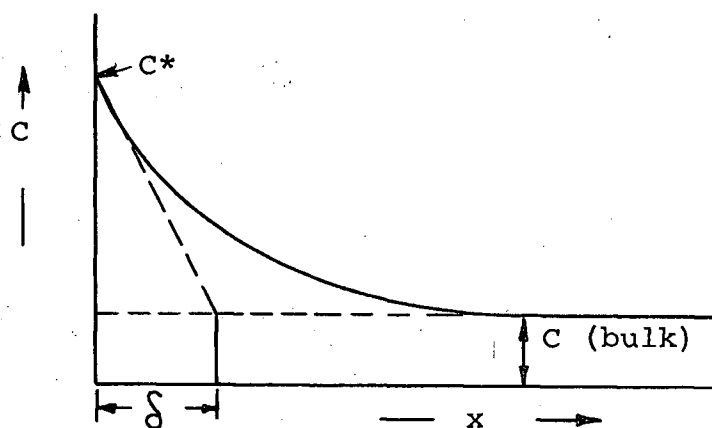


Figure 1: Concentration Profile of the Boundary Layer

$$\delta = \frac{C - C^*}{(\partial C / \partial x)_{x=0}} \quad (3)$$

At $x = 0$, $U_x = 0$ (assuming streamline or viscous flow)

$$j_x = -D (\partial C / \partial x)_{x=0} \quad (4)$$

$$= D \frac{(C^* - C)}{\delta} \quad (5)$$

Since $(\partial C / \partial x)_{x=0}$ is proportional to $(C^* - C)$, δ is independent of the values of C^* and C .

The rate of a transport process, $\dot{n}$, in moles sec^{-1} , is given by

$$\dot{n} = Aj = \frac{DA}{\delta} (C^* - C) \quad (6)$$

where A is the phase boundary area.

In terms of moles $\text{cm}^{-3} \text{sec}^{-1}$,

$$\frac{dc}{dt} = \frac{DA}{\delta V} (C^* - C) \quad (7)$$

where V is the phase volume.

A transport rate constant is then defined

$$k = \frac{DA}{\delta V} \quad (8)$$

Note that the equations of the virtual maximum rate concept (see reference 14) are derived from flux relationships such as equation (5); these maximum rate equations can be used

(in most cases) to calculate transport rates essentially identical to those predicted by the flux equations.

The nature of the boundary layer thickness, δ , can be qualitatively discussed. The value of δ for any particular system will be a function of the geometry and flow conditions in the bulk liquid. Since two phase metallurgical reactions generally involve complex flow conditions it has so far been impossible to characterize these flow conditions by dimensionless groups. Qualitatively δ should be smaller for higher flow velocities and low viscosities. Bircumshaw and Riddiford¹⁶, in a detailed review of heterogeneous processes in aqueous systems, reported that the effect of stirring on δ for many of these systems can be expressed by the simple power relation,

$$k \propto (\text{rpm})^a \quad (9)$$

where $a \leq 1$.

Several aqueous investigations have revealed that

$$k \propto D^b \quad (10)$$

with typical values of b from 0.65 - 0.75. In terms of the dependence of δ on the diffusion coefficient D ,

$$\delta \propto D^{(1-b)} \quad (11)$$

Transport controlled reactions should show a dependence of the rate on convective conditions; this effect may not be

significant if natural convective conditions are sufficiently effective. Generally experimental activation energies for reactions of this type are found to be in the same range as those for diffusion processes, i.e., below 10 k cal mole⁻¹ for fused salts and alloys.

Darken¹⁷ used a value of $\delta = 0.003$ cm for molten steel in a calculation of the rate of carbon drop during the boil. The calculation predicted a rate of 0.11% per hour, in reasonably good agreement with observed rates of 0.12 to 0.18% per hour. Darken pointed out that this value of δ should actually be multiplied by the ratio of actual slag-metal interface area to the nominal area, in view of the violent disturbances of the interface caused by emerging CO bubbles. A value of δ for the slag phase of 0.012 cm was estimated for the same process.

Slag boundary layer thicknesses during the steel refining period have been calculated from the results of Fornander and Nilsson¹⁸. With no induction stirring $\delta = 0.015$ cm; this value decreased to 0.006 cm upon the application of induction stirring.*

* The accurate description of a boundary layer thickness should be in terms of the Reynolds number. In the cases discussed here, values of δ are not quoted in these terms, and should be considered at best as crude approximations. However their use in calculations of reaction rates often yield surprisingly good results.

Morkel¹⁹ has made an examination of the factors affecting mass transport in exchange reactions between molten salts and alloys. The parameters studied included the effect of fluid flow conditions (stirring rate and geometry), temperature, and fluid properties (diffusion coefficient, viscosity, interfacial tension). The following reactions were studied:

- (1) the reduction of BiCl_3 at high concentration in ZnCl_2 - KCl salt by Sn , Pb , Cd and Zn at low concentration in liquid bismuth.
- (2) the reduction of BiCl_3 at low concentration in ZnCl_2 - KCl by pure molten tin.
- (3) the reduction of AgCl at high concentration in BaCl_2 by Cd and Sn in molten silver.

Reactions of class (1) were controlled by mass transport of solutes in the metal; those of class (2), by diffusion of a proposed bismuth complex in the salt. The rates in class (3) were partly determined by evaporation of one of the reaction products from the salt. Tests involving the simultaneous transfer of two solutes indicated that each transferred as if the other were not present.

Values of the exponent of equation 9 were determined for various stirrers, and are outlined in Table I.

TABLE I
VALUES OF STIRRING EXPONENT FROM REFERENCE 19

Stirrer	Baffles	a
Paddle	No	0.3
	Yes	0.3
Propeller (3-blade, one in each phase)	No	0.3
	Yes	1.0
Graphite Rod	No	0.6

Values of δ from 1 to 5×10^{-3} cm were calculated for the Pb and Sn reductions of BiCl_3 , both controlled by diffusion of the solutes in molten bismuth. Measured DA/δ values for salt transport control were in the range 4 to $30 \text{ cm}^3 \text{ min}^{-1}$, consistent with boundary thicknesses ranging from 5×10^{-4} to 1×10^{-2} cm, depending on the value of D assumed for the bismuth complex in $\text{ZnCl}_2\text{-KCl}$.

Activation energies for transport controlled reactions in the alloy phase were in the range 4 to 14 k cal mole⁻¹.

Phase Boundary Reactions

In view of the acknowledged ionic nature of slags and salts, phase boundary reactions undoubtedly involve the charge and discharge of ions at varying anodic and cathodic sites at the two-phase interface.

Experimental evidence for electrochemical mechanisms in slag-metal systems has recently been published. Grimble et al³, in a study of silica reduction by carbon-saturated iron, noted:

- (1) in a graphite crucible with a silica sleeve situated in such a way that the metal phase contacted the graphite but the slag did not, a current flow was observed in an external circuit joining the two phases.
- (2) reduction rates were approximately twice as fast in a pure graphite crucible as in a sleeved crucible, indicating that local cell action occurred at the graphite-slag and graphite-alloy interfaces. In view of the respective areas, the authors concluded that at least 50% of the reaction was electrochemical.
- (3) experiments were conducted in which liquid copper formed the metal phase; connection was made externally via a carbon electrode in the slag and a tungsten wire in the alloy. The current flow was measured, and the amount of silica reduction predicted from Faraday's laws. The predicted Si concentrations in the alloy agreed reasonably well with the chemical analyses, although large errors were present in both current measurement and analysis.

Rawling and Elliott⁴ also studied silica reduction, and showed that their results from concentration cell experiments could be successfully explained in terms of consecutive electrochemical processes at the slag-metal interfaces.

The nature of possible rate controlling phase boundary reactions is open to speculation. An activation-type polarization could result from some sort of homogeneous reaction occurring before the deposition step. For example, silicon deposition from slags may involve the dissociation of silica complexes. Similarly, fused salt reductions could involve the dissociation and reduction of complex ions. Bloom and Bockris²⁰ have discussed evidence for complex ions in both slags and salts.

In general, most high-temperature processes are likely to be transport controlled. Chemical reactions, with their higher activation energies, are expected to be much faster than diffusive processes. Indeed a fairly large volume of data indicates that activation overpotentials for metal reductions in fused salts are relatively insignificant (e.g., see Liu, Johnson and Laitinen²¹).

Chronopotentiometry

From the preceding discussion it is evident that a knowledge of diffusion coefficients in the various phases involved

in reactions of metallurgical interest is essential. Previous work has been largely concentrated on liquid metal diffusion, and a significant volume of data has been published²². However diffusion data for solutes in fused salts are very limited.

In view of the ionic nature of fused salts, the electrochemical technique of chronopotentiometry can be conveniently applied to the determination of diffusion coefficients of metal solutes at low concentrations in fused salts. The technique involves the measurement of the potential of a polarizable electrode as a function of time during a constant current electrolysis of an unstirred solution containing a reducible species and a supporting electrolyte. Mass transfer of the reducing species to the electrode surface is assumed to be limited only by semi-infinite linear diffusion from a uniform bulk solution.

The early derivations of the fundamental equations are due to Sand²³, with more recent theoretical analyses presented by Delahay²⁴. The theory and derivation of the appropriate relations are outlined in Appendix A.

Chronopotentiometry can be used to:

- (1) measure diffusion coefficients by studying the variation of $\tau^{1/2}$ (transition time, defined in Appendix A) with current density at various concentrations;

- (2) examine the reversibility of metal reduction reactions, through an examination of the slope of an appropriate potential-time function plot; and
- (3) elucidate the steps involved in the reduction of ions with two or more stable valence states in the solvent.

Comprehensive reviews of the application of chronopotentiometry to fused salts have been presented by Liu et al²¹ and by Laitinen and Osteryoung²⁵.

Purpose and Scope of the Present Investigation

A study of the kinetics of reactions between LiCl-KCl eutectic based fused salts and lead alloys was undertaken. This system was chosen for the low melting temperature of the salt eutectic (352°C). The purposes of the study were:

- (1) to measure the rates of some fused salt-metal reactions and to determine their rate controlling steps.
- (2) to correlate these measured rates with diffusion coefficients where applicable.
- (3) to elucidate mechanisms where the simple mass transfer model appeared invalid.

Chronopotentiometric measurements were made for the following purposes:

- (1) to determine the reversibility of metal reduction processes in LiCl-KCl eutectic salts;
- (2) to determine diffusion coefficients where they did not exist or where they were ambiguous.

EXPERIMENTAL

Salts

Dry Bag

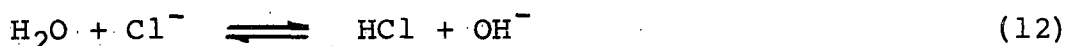
Since many of the salts used in this study are hygroscopic, a dry atmosphere was required for all handling procedures.

A simple dry bag was constructed from a 0.003" thick polyethylene bag, 38" wide by 62" long, containing two glove holes and a 3" diameter port. Nitrogen (Canadian Liquid Air), dried by passage through silica gel and Linde molecular sieve columns, was used to inflate the bag. A small flow of nitrogen was bled in continuously, thus maintaining a positive pressure which prevented the inward diffusion of moisture. The gas was also constantly recycled through the drying columns by means of a small circulation pump.

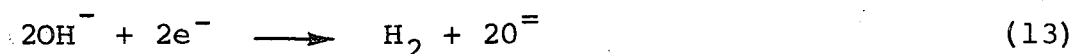
Solvent Salt Preparation

Baker and Adamson reagent grade LiCl and KCl were used for the preparation of the eutectic mixture of **59** mole % (**45** w/o) LiCl and **41** mole % (**55** w/o) KCl.

LiCl-KCl mixtures normally require some degree of purification, principally to remove moisture. These salts undergo hydrolysis, i.e.,



when melted if water is present. These impurities (H_2O , OH^-) may cause difficulties particularly during electrochemical experiments. Selis and McGinnis²⁶ have shown that the proton of the hydroxide ion is cathodically reducible according to the reaction



which occurs in the potential region of -1.6 to -1.7 volts (against 1M Pt(II)-Pt(0)) and could interfere with any measurements in this area. In addition, the presence of moisture and its hydrolysis products may contaminate electrodes and affect the stability of certain solutions.

Other impurities present in solutions of fused salts may include organic matter (from LiCl) and heavy metal ions (from impure salt reagents).

Salt purification procedures are well documented; procedures similar to that of Laitinen et al²⁷ are the most commonly employed. The salt mixture is subjected to vacuum and heat to remove most of the moisture. Final traces are eliminated while keeping the melt saturated with HCl, thus maintaining the equilibrium of reaction (12) to the left.

Heavy metal ions can be removed by precipitation with a reactive metal such as Li, Na or Mg. A final filtration step successfully eliminates organic and other insoluble material.

Two different salt preparation procedures were used in this study. For preliminary reduction experiments, the weighed salts were placed in a flask and subjected to a prolonged vacuum treatment accompanied by slow application of heat. This treatment consisted of 24 hours at room temperature, 24 hours at 110°C and 24 hours at 200°C, all under a vacuum of < 1 mm of Hg supplied by a Duoseal vacuum pump. The salt mixture was then transferred to the dry bag, melted in a pyrex beaker on a hotplate, and the required amount of solute added. The molten mixture was then drawn up through a glass wool plug and frozen in 5mm pyrex tubing. This same procedure was also employed to prepare salt mixtures for several of the main reduction runs.

A more comprehensive purification scheme was used to prepare solvent for the remainder of the reduction runs, and for the chronopotentiometric experiments. Figure 2 is a schematic diagram of the drying apparatus. One hundred and fifty grams of salt mixture were charged to a 48 mm diameter pyrex tube, closed at one end, flared at the other, and fitted with a No. 10 rubber bung which supported a gas inlet tube (extended to the cell

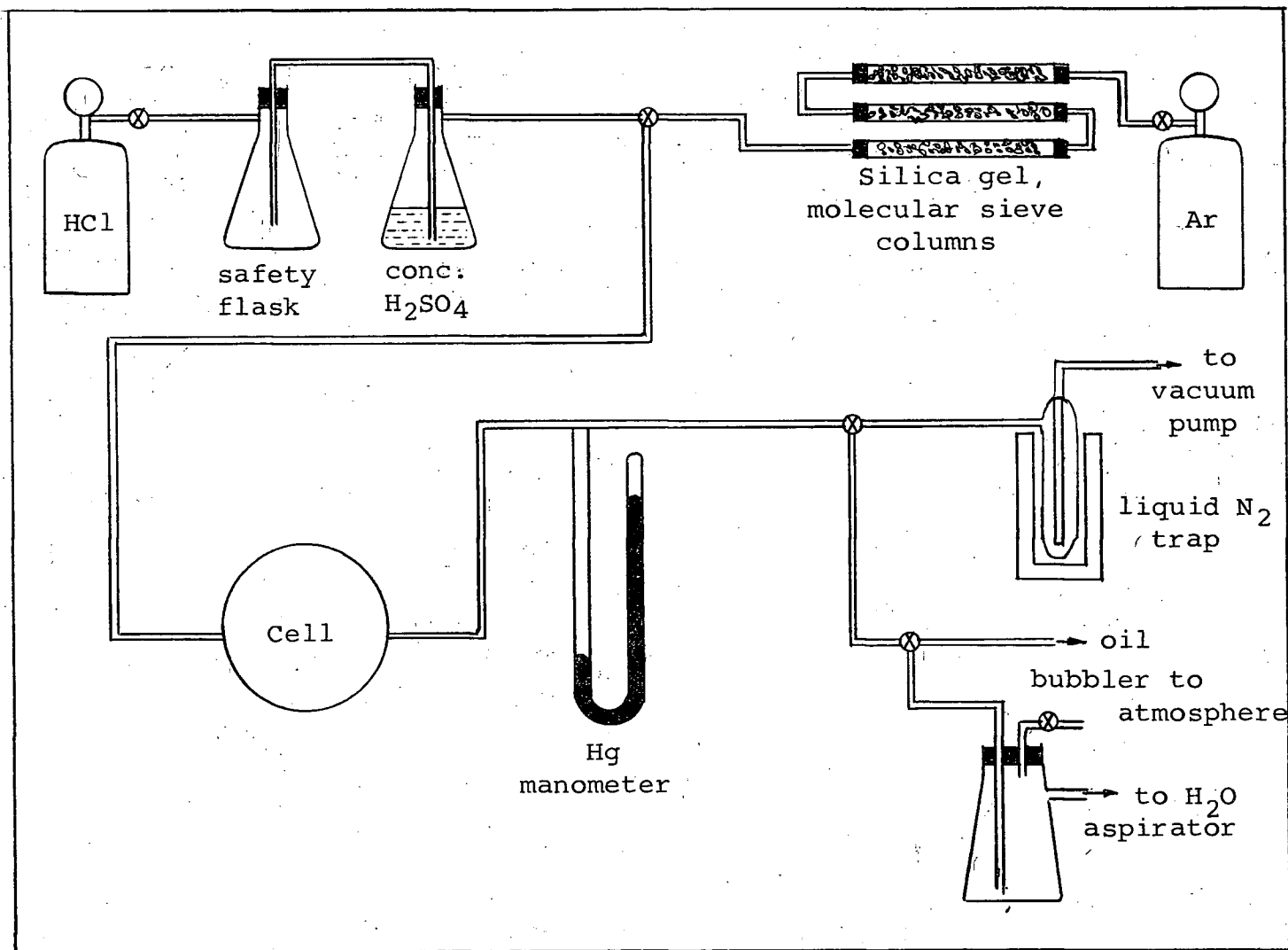


Figure 2: Schematic Diagram of Salt Purification Apparatus.

bottom) and a short gas outlet tube. The salt was heated at 120°C under vacuum for 24 hours. The temperature was then slowly raised to 300°C over a four hour period, still under vacuum. At this time HCl gas (Matheson), dried by bubbling through concentrated H_2SO_4 , was bled into the cell and then flushed through at atmospheric pressure. The temperature was increased in 50° steps, with one half hour at each setting, to 500°C . The HCl flow was maintained for one hour at 500°C , then discontinued, and the salt was aspirated (~ 2 mm Hg) for about one half hour, with one or two argon flushes during the aspiration. A final vacuum treatment of two to three hours duration removed the last traces of HCl.

Salt purity was estimated in two ways. The absence of etching of the pyrex containers after several days at 400°C in contact with the molten salt indicated that most of the moisture had been successfully eliminated. Chronopotentiograms for the solvent alone gave a semi-quantitative estimate of the salt purity; these will be discussed later.

Solutes

Baker and Adamson reagent grade PbCl_2 , CdCl_2 and AgCl were oven-dried at 150°C .

Anhydrous TiCl_3 , MoCl_5 , InCl_3 and PtCl_2 , obtained from A. D. MacKay Co., were used without further treatment.

Anhydrous FeCl_3 , CrCl_3 , CoCl_2 and NiCl_2 were obtained by treatment of the hydrated salts (Baker and Adamson, reagent grade) with thionyl chloride (Baker and Adamson).



Solutes were dropped into the purified molten eutectic in small pyrex tubes. In most cases the salts used for chronopotentiometry were brought to the desired concentrations, frozen, and used for the reduction runs.

Solutions of divalent Cr and Fe were prepared by anodization of Cr and Fe, respectively, against a compartmented Pt electrode.

Alloys

Metals were obtained from the following sources:

Li: Foote Mineral Co., 99.9% guaranteed purity

Na: Foote Mineral Co., 99.9% guaranteed purity

Pb: Consolidated Mining and Smelting Co., 99.99% guaranteed purity.

Lithium and sodium alloys were prepared by similar procedures. The metal was cut and cleaned of oxide under kerosene.

Lead was cleaned in a 50-50 mixture of glacial acetic acid and hydrogen peroxide, rinsed in distilled water, then alcohol, and dried in a blast of air.

Lithium (or sodium) was placed in an iron crucible under petroleum ether, and lead added to hold the reactive metal under the ether. The crucible and contents were located on a pedestal enclosed by a vycor tube, closed at either end by pressure rubber seals. The petroleum ether was drawn off through a liquid nitrogen trap with a Duoseal vacuum pump, argon was bled into the chamber, and the metals were melted using a Philips induction unit. The molten alloy was then either drawn up into 5 mm quartz tubing, allowed to cool in place, or removed and cast into 0.5" diameter iron molds.

Preliminary Experiments

Furnace

The furnace shown in schematic detail in Figure 3 was used for a series of unstirred preliminary reduction experiments. The main furnace body was a 14" diameter, 18" long cylinder filled with insulating brick and vermiculite surrounding a chromel-wound mullite tube. The working chamber was a 60 mm outside diameter vycor tube. Seals were provided by end plates with rubber rings, pressed against the tube at either end and tightened with wing nuts to bolts on the furnace body. As

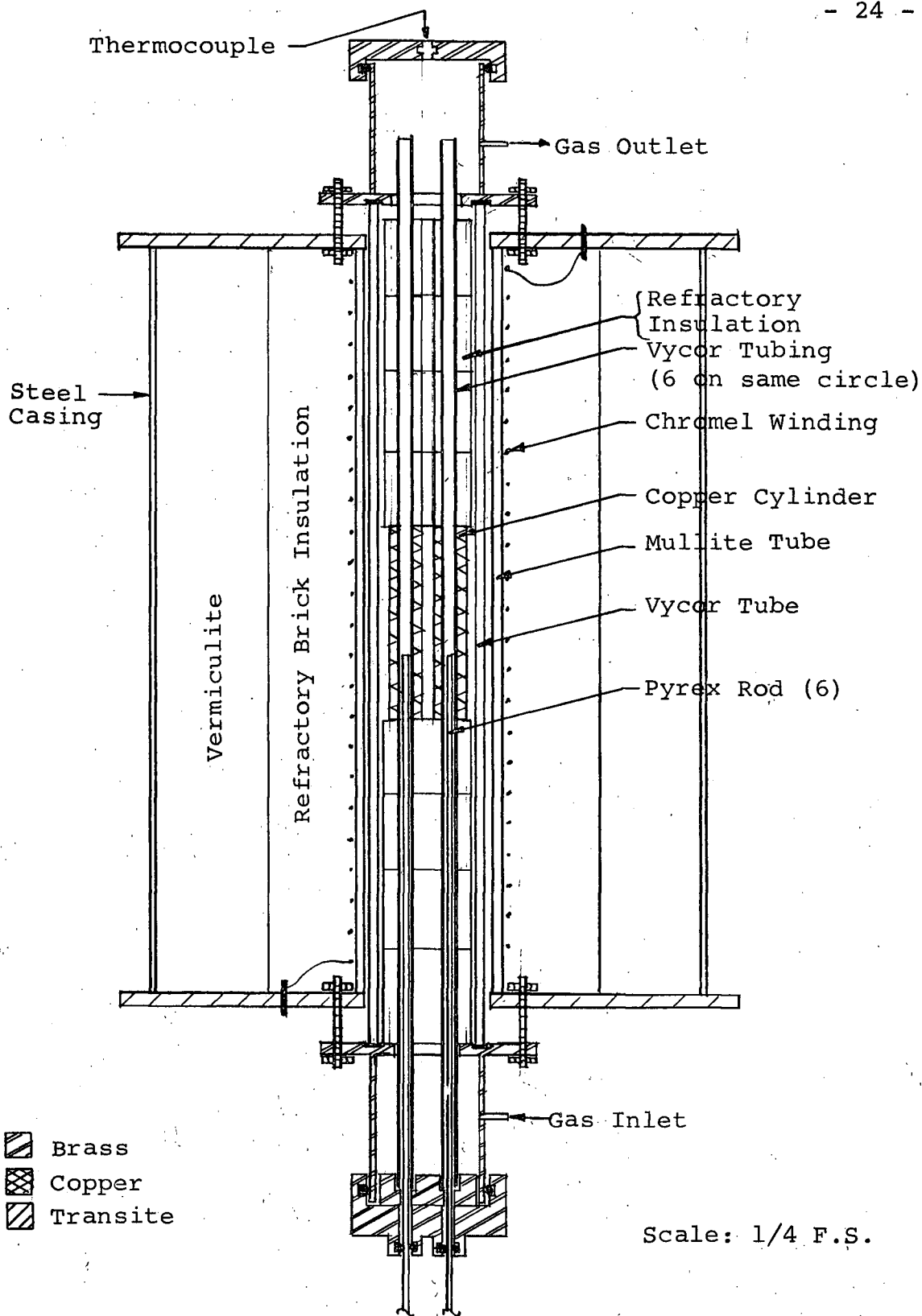


Figure 3: Preliminary Reduction Furnace

shown in Figure 3, the inside of the chamber contained a Cu cylinder in its center, with insulation brick cylinders filling the chamber above and below the copper. Six holes, situated equidistant from one another on a common circle, contained vycor tubes which passed the full length of the furnace. These six tubes enclosed solid pyrex rods which passed through O-ring seals in the bottom furnace head, and which served as supports and lowering mechanisms for the crucibles. A seventh hole down the center contained a thermocouple protection tube.

The furnace temperature was maintained with a Wheelco Model 402 controller and a chromel-alumel thermocouple situated close to the windings. Power was supplied through a 220 volt variac connected with the controller. The temperature at the center of the copper cylinder could be controlled to approximately $\pm 1^{\circ}\text{C}$, and the working zone was 3" long, $\pm 1^{\circ}\text{C}$.

Argon, purified by passage through silica gel and molecular sieve columns, followed by passage over copper turnings at 500°C , provided an inert furnace atmosphere.

Crucibles

Two inch long crucibles were constructed from 3 mm or 5 mm inside diameter quartz (vitreosil) tubing, closed at one end. Before use they were cleaned in chromate-sulphuric acid

solution, rinsed with distilled water and oven dried at 200°C for at least 24 hours. Six crucibles were used for each run, one in each of the six vycor furnace tubes.

Procedure

Identical weights of cleaned alloy were placed in each of six crucibles, along with weighed portions of vacuum dried salt. These tubes were placed in the furnace on the support rods which were situated near the furnace top. Runs were started by quickly lowering the rods until the crucibles were positioned in the center of the Cu cylinder. As samples were required, tubes were lifted to the furnace top. When all crucibles had been raised, they were transferred to the dry bag and broken open. The two phases were analyzed for the appropriate elements.

Zero reaction time was estimated from the curves of concentration versus time by extrapolating the curves back to the known starting concentrations. This time was also checked by a blank run in which the crucibles were raised in one minute intervals after all six had been lowered. An examination of the contents indicated when the phases had both become molten. The time corrections were usually about two to three minutes.

Reduction Experiments

Furnace

The greater portion of the reduction experiments were performed using the furnace set-up shown in Figure 4. It consisted of a chromel wound mullite tube situated in the centre of an 18" diameter, 25" long steel drum. The space surrounding the winding was filled with a castable refractory material. This set-up used the same power source and control circuit as was used for the preliminary reductions. Temperatures were controlled to $\pm 2^{\circ}\text{C}$, and an even thermal zone of $\pm 1^{\circ}\text{C}$ over a 3" length was attained.

The working tube was mullite, fitted with water-cooled brass heads with O-ring seals. The crucible support arrangement could be rotated, using a chain and sprocket drive powered by a 115 watt, 1550 rpm motor (Universal Electric Co.). Different stirring speeds in the range 0-250 rpm were obtained by the use of a variety of sprockets and reduction gears.

Crucibles

Three types of crucibles were used in these experiments.

- (1) Quartz, 1" diameter (inside), 2 1/2" deep, which were constructed by closing standard quartz tubing.

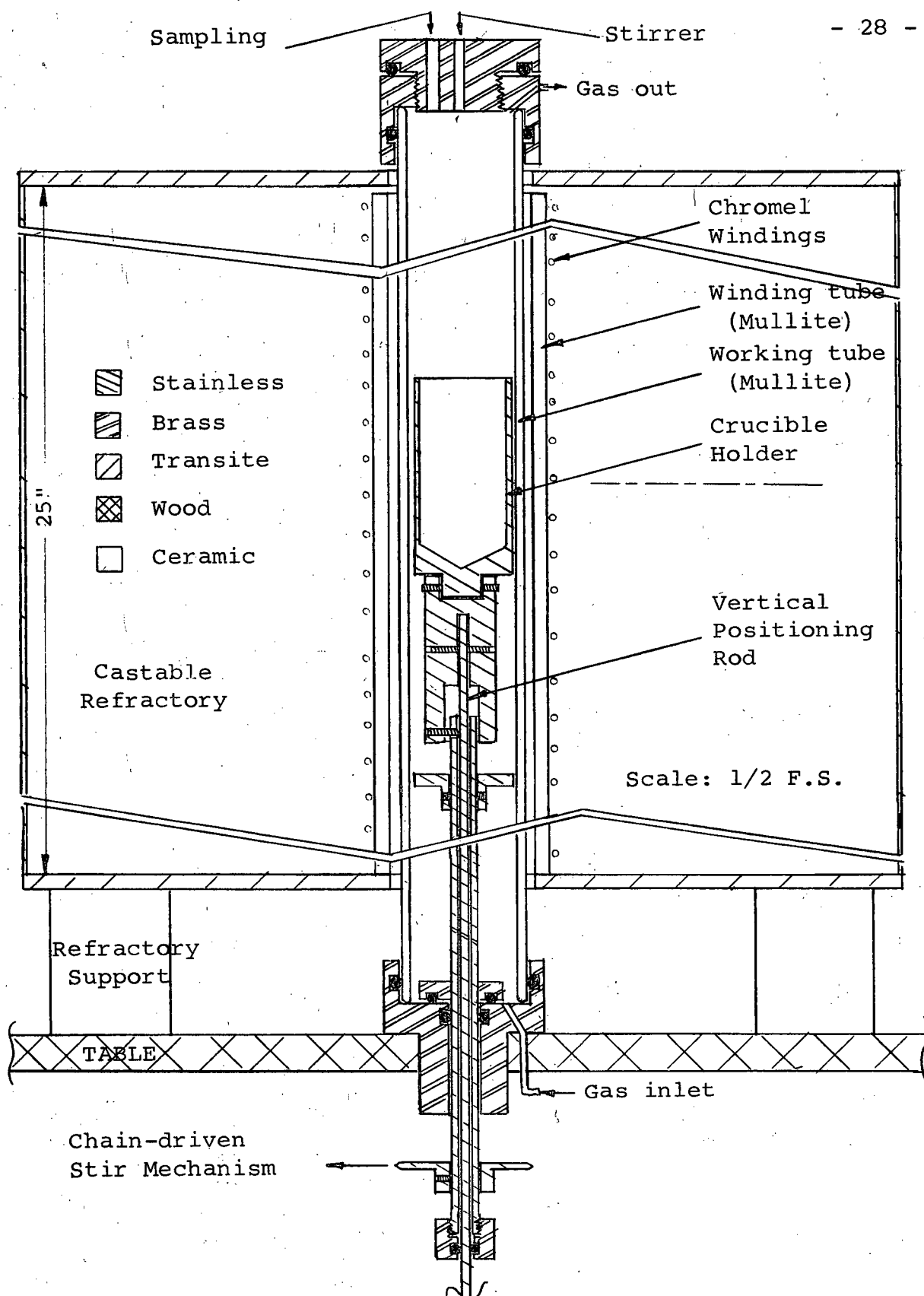


Figure 4: Details of Reduction Run Furnace

- (2) Stainless steel, 1" inside diameter, consisting of 316 stainless steel tubing with welded bottoms.
- (3) Stainless steel crucibles fitted with silica sleeves of the same diameter as the silica crucibles, shown in Figure 5.

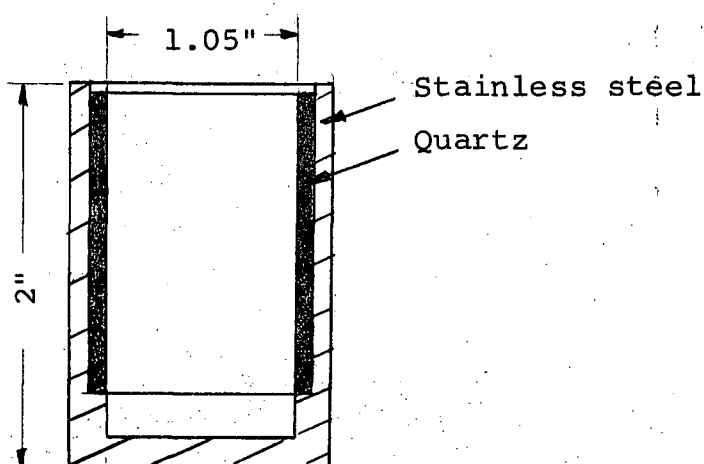


Figure 5: Quartz Sleeved Stainless Steel Crucible

Stirrers

Two types of stirrers were used.

- (1) Two-blade glass stirrers were formed from 3 mm outside diameter pyrex tubing. The blade diameters were about 0.5", and the depth and thickness of the blades were $\sim 3/16$ " and $\sim 1/16$ " respectively.

- (2) A stainless steel paddle was constructed from 1/8" diameter tubing and 0.02" sheet. The paddle had four vertical blades, each 1/4" long, and 3/16" deep.

Temperature Measurement

Temperatures were measured with a chromel-alumel thermocouple situated in the stirrer.

Procedure

All glassware was cleaned in chromate-sulphuric acid solution and oven dried at 200°C. Stainless steel parts were cleaned with emery paper and rinsed in alcohol.

The crucibles were placed in the crucible holder at the top of the furnace about one hour prior to a run. The required weight of cleaned alloy was placed in the crucible, which was then lowered to the thermal centre of the furnace. An hour was allowed for the alloy to melt and reach the preset temperature.

A weighed amount of purified salt, contained in a 22mm diameter pyrex tube which had been necked down at one end and blown to a thin bulb of glass, was melted over a bunsen flame and raised to a temperature at least 50°C higher than the run temperature. The tube containing the salt was then placed in

the furnace, supported in the top head with a rubber bung bored to fit the tube, and situated so that the salt was positioned just above the crucible containing the molten alloy. The salt temperature was then allowed to cool to that for the run. The experiment was started by punching a small hole in the salt tube with a sharpened stainless steel or pyrex rod. Time was allowed for the salt to drain into the crucible (< 5 sec.), and the empty tube was quickly withdrawn and replaced with the brass head containing the stirrer. At the same time the stirrer motor was started.

Periodic samples were taken using 3 mm diameter pyrex tubing and a small rubber bulb. Samples were limited to a maximum of 150 to 200 mgm, 8-10 per run. The salt samples were broken out of the tubing and placed in weighed glass vials which were stoppered and reweighed. The salts were then dissolved in an appropriate manner and analyzed.

Chronopotentiometry

Furnace

Chronopotentiometric tests were conducted in a chromel wound (700 watts, 110 volts) furnace of brick construction, with a 12" deep by 2 1/2" diameter cavity closed at the bottom. A steel pipe with a welded bottom, situated in the cavity,

protected the windings from salt attack in the event of working tube breakage. This steel liner also reduced thermal gradients in the furnace cavity. The furnace temperature was regulated with a Wheelco Model 402 controller, connected through an external relay and a 110 volt variac. The control thermocouple was chromel-alumel. Temperatures were controlled to approximately $\pm 2^{\circ}\text{C}$, as measured in the molten salt.

Cell

The chronopotentiometric cell was a 48 mm outer diameter by 500 mm long pyrex tube. This tube, filled with the solvent to a depth of 55 mm, was mounted vertically, with 200mm of the lower end inside the furnace. A number 10 rubber bung containing three 5 mm holes, two 6 mm holes and two 10 mm holes (drilled using regular twist drills after freezing the stopper in liquid nitrogen) closed the top of the container, and supported within the tube a thermocouple sheath, gas inlet and outlet tubes and various electrodes. The holes were stoppered with glass plugs when not in use.

Constant Current Source

Constant currents were supplied through the circuit shown in Figure 6. The circuit consisted of a Heathkit Variable Voltage Regulated Power Supply, Model PS-2, and several

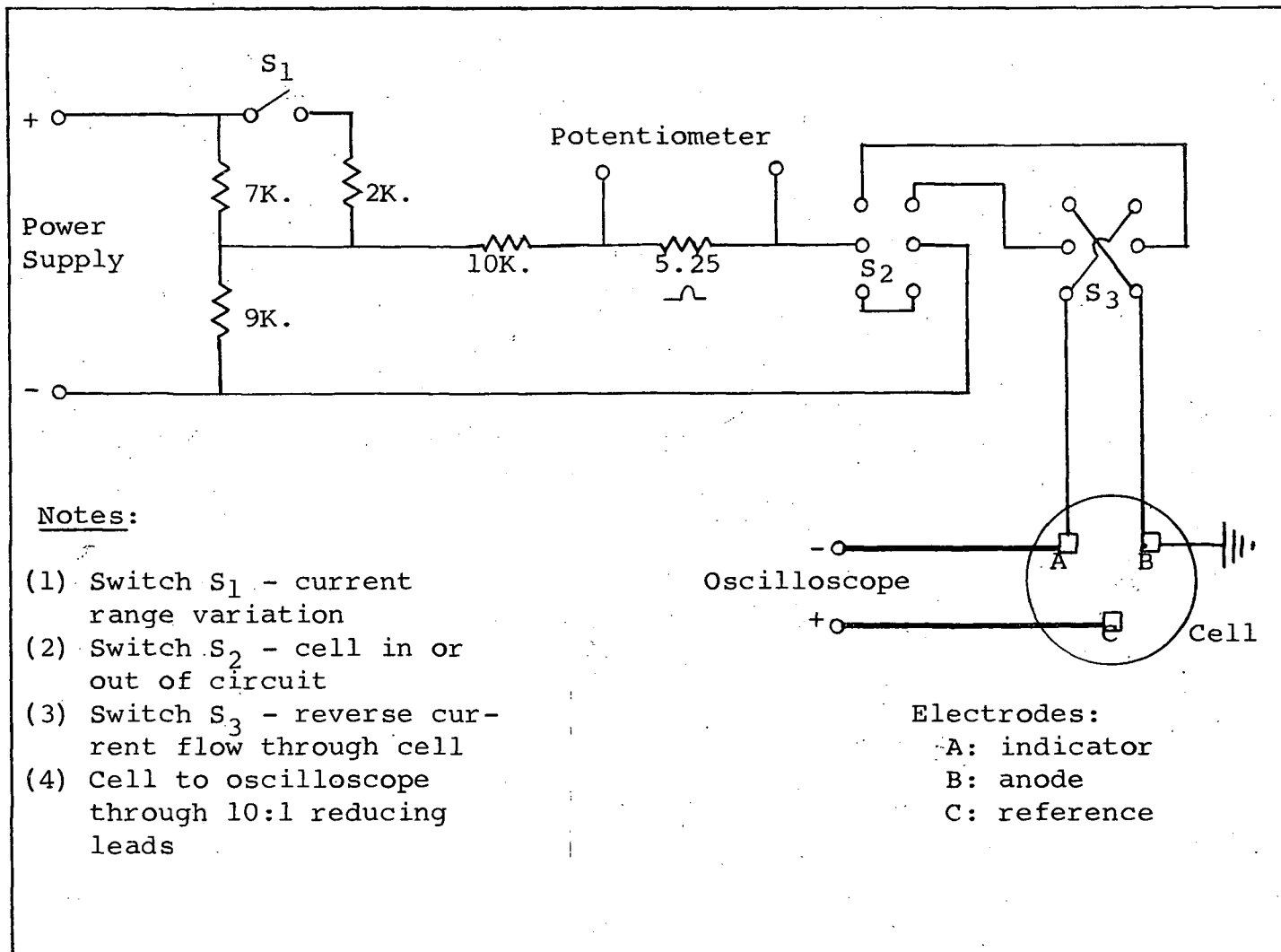


Figure 6: Schematic Diagram of Chronopotentiometric Circuit.

resistors. The current was varied within a certain range (10-25 ma) using the power supply controls. A lower current range (4-10 ma) could be obtained by closing switch S_1 . Current was run continuously through the circuit. Current determination involved the measurement of the potential drop across a precision 5.25 ohm resistor with a Pye potentiometer. Switch S_3 could be set to apply current through the cell in either direction (i.e., plating or stripping of indicator electrode). Currents were accurate and constant to within 2%.

Measurements

Curves of the potential of the indicator electrode against time (chronopotentiograms) were displayed on a Tektronix Type 564 storage oscilloscope (Type 3A3 Dual Trace Differential Amplifier, Type 2B67 Time Base). The measurement circuit is shown in Figure 6. Chronopotentiograms were recorded on 35 mm film, and the actual measurements made from photographic enlargements. A discussion of the measurement of transition times from these curves appears in Appendix B.

Electrodes

Anode

The anode (working electrode) in most tests was a 0.002" Pt sheet spot-welded to 0.01" or 0.02" Pt wire sealed in pyrex. The anode area was usually 100 to 200 mm².

A gold anode similar to the Pt electrodes was used for the MoCl_5 tests.

Indicator Electrodes

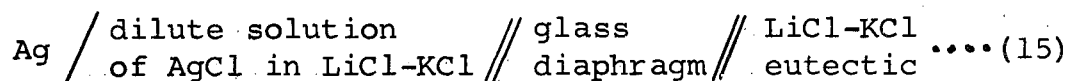
Three types of indicator electrodes were used in this study.

- (a) Platinum: Pt indicator electrodes were fabricated from 0.002" sheet, spot-welded to 0.01" wires sealed in pyrex. Areas were accurately determined with a travelling microscope, and varied between 10 and 100mm².
- (b) Tungsten: W electrodes were made from 0.035" or 0.050" diameter rods. Pyrex-nonex graded seals were used; the rods either projected below the seal, or were flush-ground.
- (c) Gold: Au electrodes were fabricated from .003" sheet spot-welded to 0.006" Au wire, sealed in pyrex.

Reference Electrodes

Three types of reference electrodes were used in this study.

- (a) Silver: Silver reference electrodes similar to those developed by Bockris et al²⁸ were used. These were of the type:



and were constructed from pyrex tubing, with a thin glass bulb blown on the end. The cells were dried at 200°C, and filled with a stock solution of AgCl in LiCl-KCl (concentrations: 0.3 to 0.6 M). Both Bockris et al and Yang and Hudson²⁹ have studied this half cell and found that:

- (1) the membrane thickness does not seem to affect the potential. Bockris et al quote a value of 2000-5000 ohms for the bulb resistance; those used in the present study were probably somewhat higher.
- (2) Li^+ ions are the predominant current carrier through the membrane.
- (3) the electrode is reversible and obeys Nernst's equation from 0.2 M up to AgCl saturation (~2M).

Contact to the electrode melt was made with 0.02" diameter fine Ag wire. The electrodes were expendable and a new one was prepared for each test series.

- (b) Platinum: The platinum reference electrodes were similar to the silver; a stock solution of PtCl_2 ,

0.03M in LiCl-KCl, was used to fill the cells. Contact was made with 0.02" diameter Pt wire. Laitinen et al³⁰ have demonstrated the stability and reversibility of such electrodes.

A Pt sheet in direct contact with the melt was used as a reference electrode for the chronopotentiometry of Pt(II).

- (c) Gold: A gold reference electrode was prepared by anodizing a gold foil at a constant current in a fritted compartment of melt to generate Au(I) coulometrically. The Au(I) concentration was about 0.03M.

Pt in direct contact with the melt was cleaned by flaming to a red heat. Tungsten was electropolished in NaOH solution to a smooth mirror surface.

Temperature Measurement

Melt temperatures were determined with a chromel-alumel thermocouple and a Pye potentiometer. The thermocouple was located in a pyrex sheath near the indicator electrode.

Procedure

The cell was loaded with 150 grams of LiCl-KCl eutectic mixture, and the salt was purified. The electrodes were

placed in position, and the desired quantity of solute was added. After allowing time for dissolution of the solute (aided by continuous Ar bubbling), chronopotentiograms were recorded at a series of current densities. Generally the cathodes were stripped of plated metal after every second test to prevent excessive deposits, which could form dendrites and so alter the electrode area. Ar was bubbled through the melt between each test; this bubbling was stopped 30 seconds before the next test to allow the melt to become still.

A similar procedure was followed at each concentration. Samples for analysis were taken at each concentration for the more volatile solutes, and also in some cases where dissolution was slow.

Analysis

Salts

Lead, cadmium and indium were determined polarographically with a Sargent Model XII Polarograph.

Other metals were determined colourimetrically using a Beckman Model B spectrophotometer. The reagents used for developing the colour and the wavelengths at which the absorbance was measured are listed in Table II.

TABLE II

COLOURIMETRIC ANALYSIS DATA

Element	Colour Developing Agent	Wavelength mu
Cobalt	nitroso-R salt	570
Chromium	diphenylcarbazide	540
Nickel	dimethylglyoxime	465
Iron	1-10 O-phenanthroline	510
Platinum	stannous chloride	406
Titanium	hydrogen peroxide	410
Molybdenum	sodium 2,3-dihydroxy- naphthalene-6-sulphonate	420

Alloys

Alloys were dissolved in 1:4 HNO_3 , and analyzed for Li and Na by flame photometry with an EEL Flame Photometer.

RESULTS

The experiments conducted in this work are summarized below, and their results will be presented in the same order.

- (1) Preliminary metal ion reduction experiments were performed on the two reactions:

- (a) reduction of Li^+ from the LiCl-KCl eutectic salt with Na in a Na-Pb alloy.
- (b) reduction of Pb^{++} from the same salt with Li in a Li-Pb alloy.

- (2) Detailed studies were made of the rates and mechanisms of the following reactions:

- (a) reduction of Pb^{++} from LiCl-KCl with Li in a Li-Pb alloy. Tests showing the electrochemical nature of this reaction were also performed.
- (b) reduction of Li^+ from LiCl-KCl with Na in a Na-Pb alloy.
- (c) reduction of a number of metal ions from LiCl-KCl with either Li in a Li-Pb alloy or pure Pb.

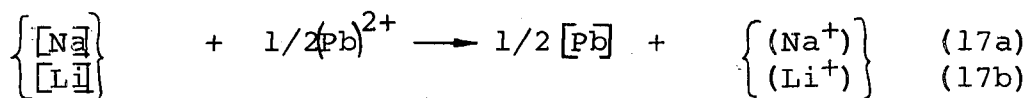
- (3) Chronopotentiometric tests were carried out to measure ionic diffusion coefficients in LiCl-KCl, and to examine the reversibility of the ionic reductions.

Preliminary Reduction Experiments

All preliminary reductions were conducted in 5 mm inside diameter quartz capsules, unless otherwise noted.

Reduction of Li^+ with Na

Initial experiments with Na-Pb alloys and PbCl_2 -KCl-LiCl salts indicated that the mole ratio of oxidized sodium to reduced lead decreased from a value much greater than two to approximately two during the course of the reaction. Alloy analysis for Li showed that two reactions were occurring:



The results of a reaction between a Na-Pb alloy and pure LiCl-KCl are shown in Table III and Figure 7a. The reaction is fast compared with Pb^{++} reduction (to be discussed), and the conclusion can be made that reaction (17b) above is the major source of Pb^{++} reduction. A plot of $\log \left\{ \frac{[\text{Na}]^0 - [\text{Na}]^e}{[\text{Na}] - [\text{Na}]^e} \right\}$ versus t , Figure 7b, gave a first order rate constant $k = 0.15 \pm .025 \text{ min}^{-1}$.

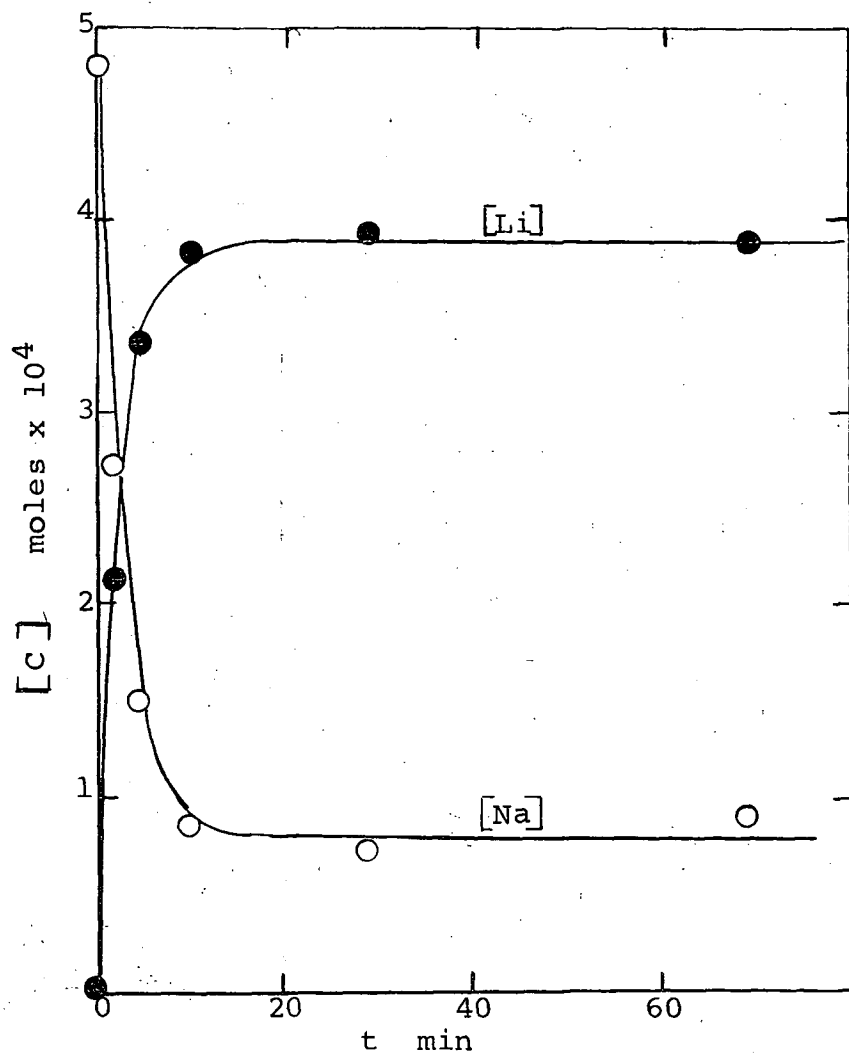


Figure 7a: Experimental Concentration Curves.

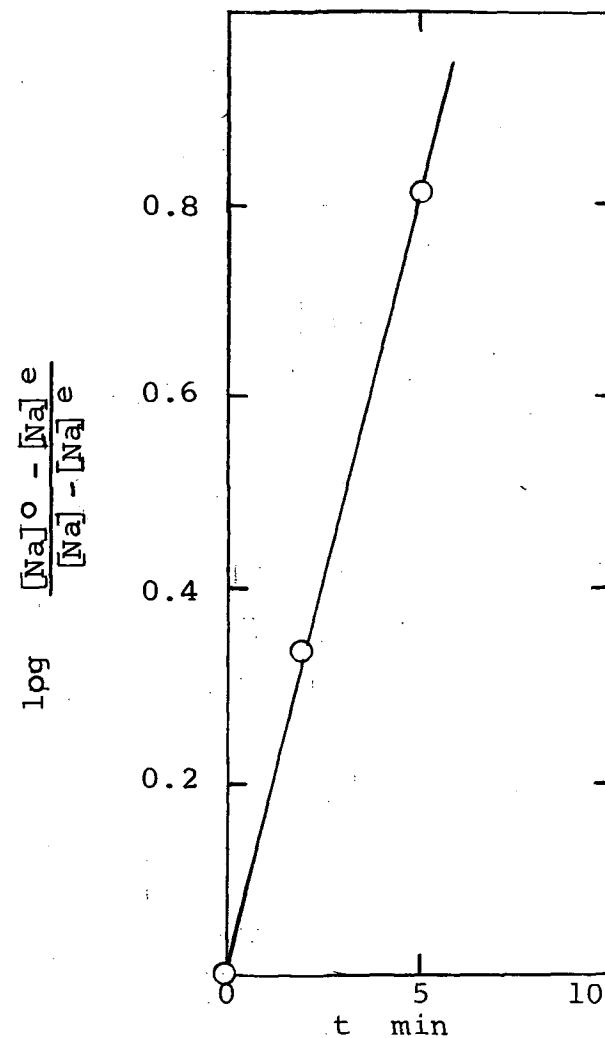


Figure 7b: First Order Plot.

Figure 7: Na Reduction of LiCl (Run 13, 390°C, 1 gm alloy, 0.61 gm salt, 5mm crucibles).

TABLE III
SODIUM REDUCTION OF Li(I)

Conditions: Run 13
 $T = 390^{\circ}\text{C}$
 1.25 gm alloy, 0.90 w/o Na
 0.61 gm salt

t min	$\overline{\text{Na}}$ w/o	$\overline{\text{Li}}$ w/o	moles Na $\times 10^4$	moles Li $\times 10^4$	$\frac{\overline{\text{Na}}^0 - \overline{\text{Na}}}{\overline{\text{Li}}^0 - \overline{\text{Li}}}$ molar ratio
0	0.90	0	4.80	0	
2	0.51	0.12	2.72	2.12	0.98
5	0.28	0.19	1.50	3.36	0.98
10	0.16	0.22	0.86	3.84	1.03
29	0.13	0.22	0.70	3.94	1.04
69	0.17	0.22	0.91	3.86	1.01

A value of K, the equilibrium constant, was calculated, assuming that:

- (1) the activity coefficients of Na and Li in Pb are equal. This assumption is probably fairly accurate in view of the similarity of the Na-Pb and Li-Pb phase diagrams; no thermodynamic data is available on the Li-Pb system.
- (2) the activity coefficients of Na^+ and Li^+ in the salt are equal. Bloom and Bockris²⁰ stated that the three binary systems KCl-LiCl, KCl-NaCl and LiCl-NaCl all have relatively small deviations from ideality.

$$K = \frac{(\text{Na}^+) [\text{Li}]}{[\text{Na}] (\text{Li}^+)} \quad (18)$$

$$= 0.276 \text{ at } 390^\circ\text{C}$$

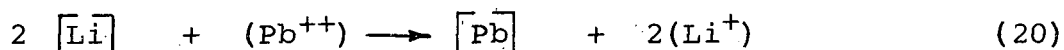
$$\begin{aligned} \Delta E^\circ &= E^\circ_{\text{Na}} - E^\circ_{\text{Li}} = -\frac{RT}{F} \ln K \\ &= 0.073 \text{ v.} \end{aligned} \quad (19)$$

This value of 0.073 v. can be compared with the value for ΔE° of 0.02 v quoted by Delimarskii and Markov³¹ for the pure chlorides at 700°C.

Reduction of Pb^{++} with Li

Stoichiometry

An examination was made of the stoichiometry of the reaction



The mole ratio of oxidized Li to reduced Pb was determined for several runs; the results are shown in Table IV. These ratios were measured from plots of oxidized Li versus reduced Pb; each is then an average of six samples.

Analytical accuracy is such that the ratio cannot be determined to better than ± 0.1 . Run 18, in which LiCl-KCl

eutectic was contacted with Li-Pb alloy, showed no evidence of Li oxidation over one hour. The stoichiometry is therefore as written in equation 20.

TABLE IV

STOICHIOMETRY CHECK

Run	Li/Pb
16	2.01
19	2.12
20	1.99
21	2.20
22	2.10
28	2.18

Possible sources of extra lithium loss are:

- (1) reaction of Li with KCl. Measurement of the potassium content of alloys showed a maximum of 0.025 w/o, or 6.6×10^{-6} moles. An error of +0.1 in the molar stoichiometric ratio would mean a Li loss of 3×10^{-5} moles.
- (2) reaction of Li with moisture or OH^- in the salt. The impurity content of melted, untreated LiCl-KCl has been estimated as 3×10^{-6} moles cm^{-3} , equivalent to $\sim 2 \times 10^{-6}$ moles of Li if all the impurities react.
- (3) solubility of Li in LiCl-KCl. Very little data is available; Dworkin et al.³² measured the solubility of

pure Li in LiCl at 640°C as 0.5 mole%, or $\sim 1 \times 10^{-4}$ moles Li. However the solubility of Li (from Li-Pb) in LiCl-KCl at 400°C is expected to be much lower. A combination of these factors could account for a slightly high mole ratio.

Reaction Variables

Several runs which illustrate the effect of the variables are listed in Table V, with the pertinent conditions. First order rate constants have been determined from $\log (Pb)^0 / (Pb)$ - time plots.

Interface Area

Runs 44 ($A = .07 \text{ cm}^2$) and 45 ($A = 0.2 \text{ cm}^2$) have essentially identical rate constants. This would be expected if $k = DA/\delta V = D/\delta h$, since the salt heights are equal for the two runs.

Alloy Depth

Runs 31, 41 and 49 at one $(Pb)^0$ and Runs 45 and 47 at another show that alloy depth had no significant effect on the reaction rate.

TABLE V

SUMMARY OF SELECTED PRELIMINARY
REDUCTION EXPERIMENTS

Run	T°C	Ma gm	[Li] ^o w/o	Ms gm	(Pb) ^o w/o	D mm	A cm ²	k min ⁻¹
31	392	0.54	0.78	0.60	8.6	5	0.2	0.019
41	388	0.53	0.78	0.60	8.6	5	0.2	0.015
49	389	1.59	0.78	0.60	8.6	5	0.2	0.014
45	388	0.52	0.78	0.60	4.9	5	0.2	0.012
47	388	0.94	0.78	0.60	4.9	5	0.2	0.011
55	390	0.53	0.78	0.30	4.7	5	0.2	0.017
56	390	0.65	0.78	0.90	4.7	5	0.2	0.008
44	389	0.53	0.78	0.22	4.9	3	0.07	0.011
46	384	0.50	0.78	0.60	12.3	5	0.2	0.015
59	388	0.65	0.78	0.60	4.6*	5	0.2	0.015
13	390	1.23	0.90**	0.61	0	5	0.2	0.15

* Cd

** Na

Salt Height

Runs 47, 55 and 56 show a tendency for decreasing rate with increasing salt height (h), as shown in Figure 8. The dependence is roughly $k \propto 1/h$, which supports rate control by Pb^{++} diffusion in the salt.

Initial Lead Content (Pb)^o

Runs 41, 45 and 46, for 4.9 w/o < (Pb)^o < 12.3 w/o, indicate that k is independent of (Pb)^o, consistent with the transport of Pb^{++} as the rate-controlling step.

Temperature

Several runs, not reported here, were conducted in an attempt to determine the temperature effect. The points on a $\log k - 1/T$ plot showed considerable scatter, but an experimental activation energy of 12-18 k cal mole⁻¹ was estimated.

Run 59 was conducted with $CdCl_2$ in place of $PbCl_2$; the rate constant k was 0.015 min⁻¹, similar to those measured for the $PbCl_2$ reductions.

Two points with respect to these experiments should be made. First, the precise determination of zero reaction time was impossible. The assumption was made that a negligible amount of reaction occurred until the crucibles and contents

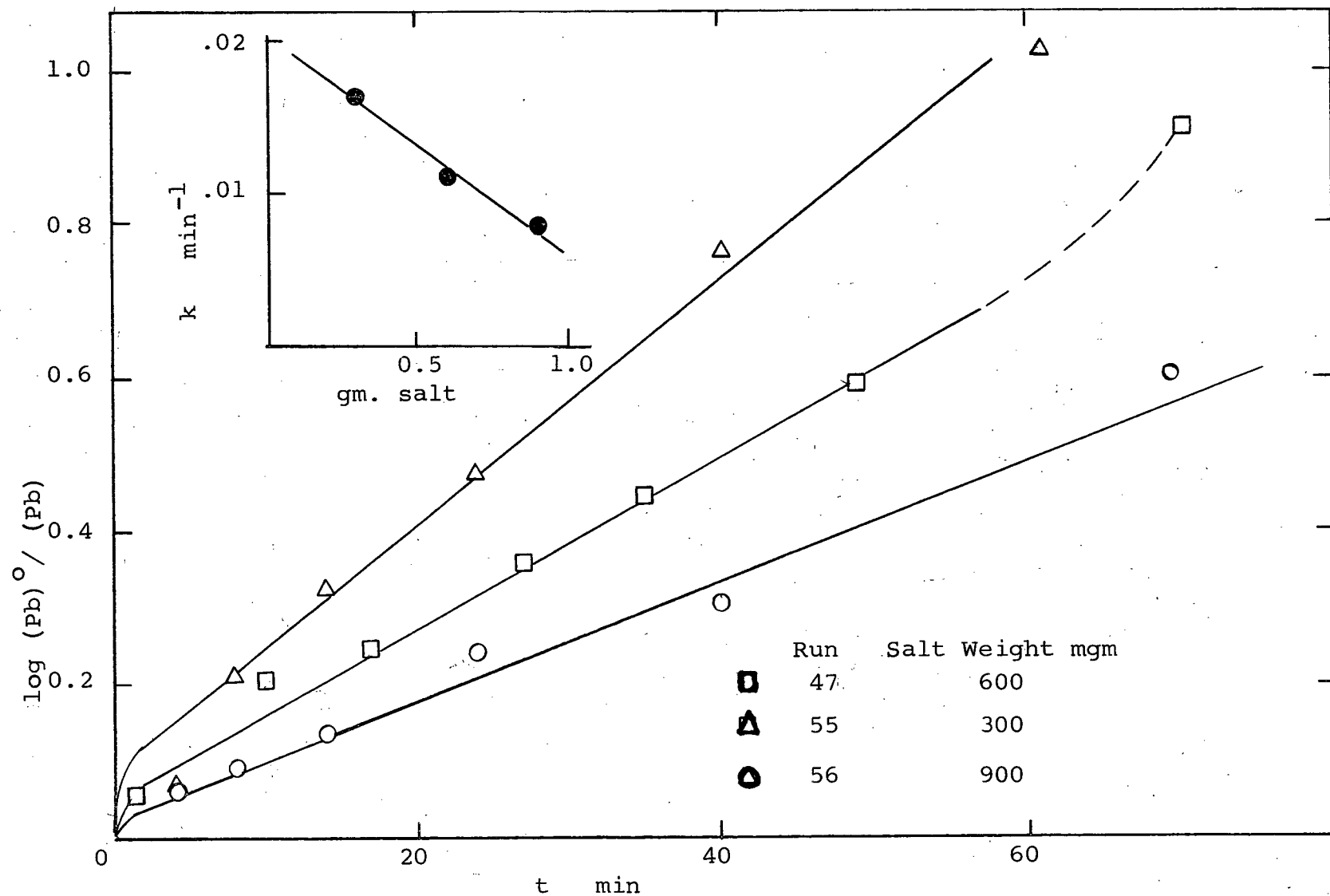


Figure 8: First Order Rate Plots - Salt Mass Dependence Series
(388°C, 4.8 w/o, Pb salt, 0.6 gm, 0.8 w/o, Li alloy).

were at the reaction temperature. This assumption is probably in error, although first order rate plots are surprisingly good. Secondly, convective conditions were largely unknown and undoubtedly varied from one run to the next. In view of this, the reproducibility is thought to be quite acceptable.

Salt Boundary Layer Thicknesses

Boundary layer thicknesses (δ_s) have been calculated from the relation

$$k = \frac{D}{\delta_s h} \quad (21)$$

and are shown in Table VI.

TABLE VI

TYPICAL VALUES OF δ_s FOR PRELIMINARY
Pb⁺⁺ REDUCTION EXPERIMENTS

Run	T°C	h cm	k min ⁻¹	δ_s cm
47	388	1.83	0.011	0.030
49	389	1.83	0.014	0.024
41	388	1.83	0.015	0.022
55	390	0.92	0.017	0.026
56	390	2.75	0.008	0.036
59(Cd)	388	1.83	0.015	0.021

Values of D used were, in most cases, measured in this study.

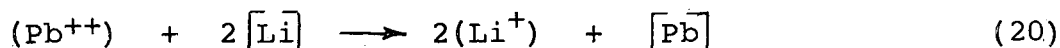
Main Reduction Experiments

The majority of reduction experiments in this work were conducted in 1.050 $\pm$ 0.02" internal diameter crucibles; the reactions were followed by sampling the salt phase.

In stirred runs, the stirrer was situated approximately 8-10 mm above the interface.

Reduction of Pb⁺⁺ with Li

The reaction



which was studied during the preliminary tests, was extensively re-examined, with the results summarized in Appendix F, Tables F-I and F-II.

Reaction Variables

Initial Lead Concentration (Pb)⁰

Plots of $\log (\text{Pb})^0 / (\text{Pb})$ versus time were linear, indicating that the reaction is first order. Typical first order curves are shown in Figure 9. The effect of (Pb)⁰ is examined in Tables VIIa and VIIb for quartz sleeved and stainless steel crucibles respectively. The results show no trend to dependence of the first order rate constant on initial lead concentration, as was also shown by the preliminary tests.

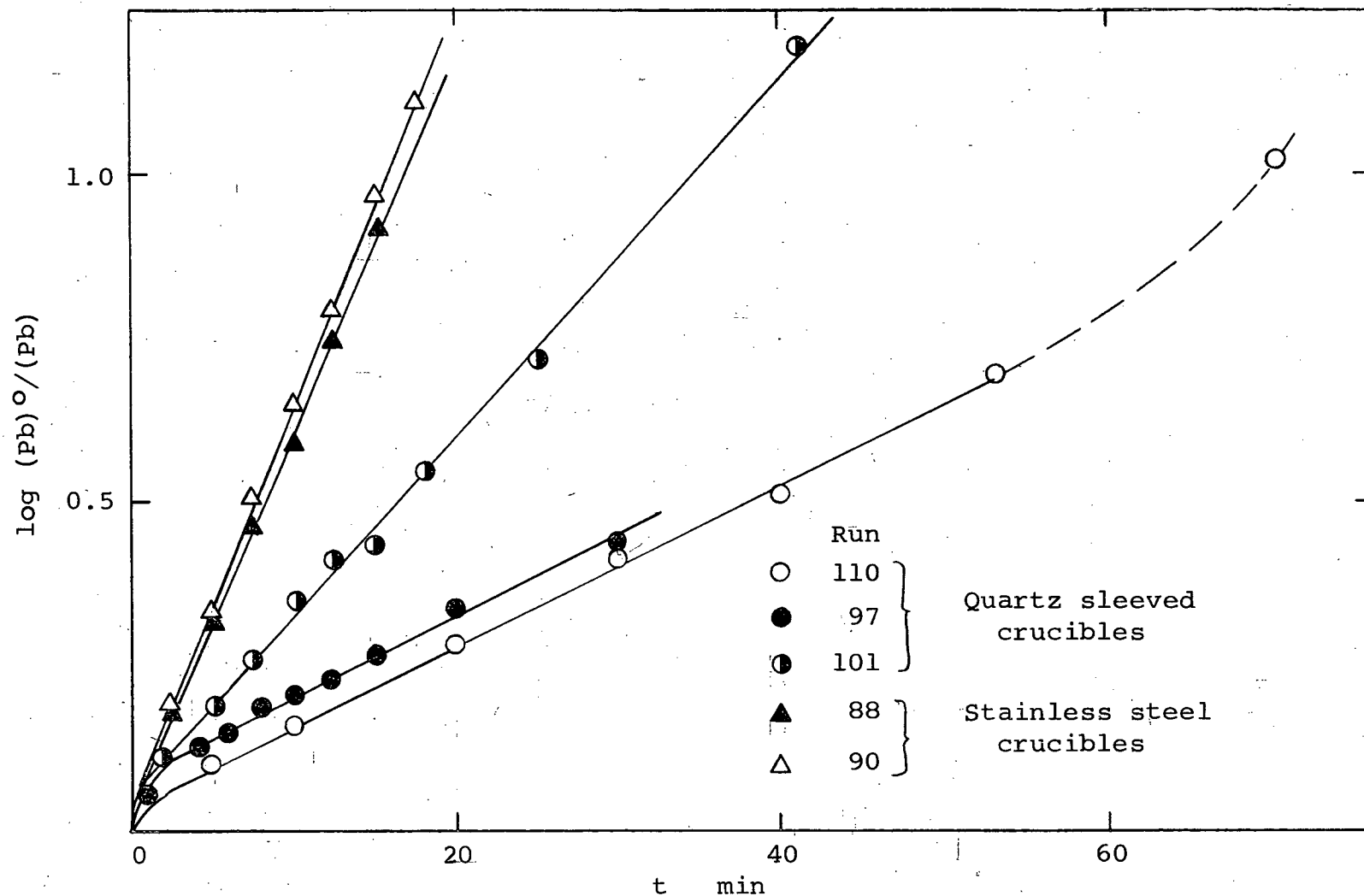


Figure 9: Typical First Order Plots for Pb(II) Reduction in Different Crucibles.

TABLE VII
EFFECT OF $(\text{Pb})^{\circ}$ ON RATE

Conditions: Quartz sleeved crucibles
stirred, 112 rpm, with
stainless steel paddle
 $T = 375 \pm 2^{\circ}\text{C}$
 $[\text{Li}]^{\circ} = 0.18 \pm .02$ w/o

Run	$(\text{Pb})^{\circ}$ w/o	k min^{-1}
112	4.63	0.020
113	4.33	0.022
137	4.75	0.020
138	1.57	0.029
139	2.95	0.029
140	6.80	0.023

Conditions: Stainless steel crucibles
unstirred
 $T = 375 \pm 3^{\circ}\text{C}$
 $[\text{Li}]^{\circ} = 0.25 \pm 0.05$ w/o

Run	$(\text{Pb})^{\circ}$ w/o	k min^{-1}
88	3.8	0.061
90	6.2	0.068
94	7.7	0.073
95	1.22	0.093
98	3.75	0.066

A statistical analysis indicates that both sets of results (i.e., Table VII) have a root mean square error of approximately 16%.

Initial Alloy Lithium Concentration $[Li]^o$

Results in the two types of crucibles are compared in Tables VIIIA and VIIIB

TABLE VIII

EFFECT OF $[Li]^o$ ON RATE OF Pb^{++} REDUCTION

Table VIIIA
Quartz Sleeved Crucibles
Conditions:
Stirred, 112 rpm,
Stainless steel paddle
 $T = 380^{\circ}C$
 $(Pb)^o = 4.75$ w/o

Run	$[Li]^o$ w/o	k min^{-1}
137	0.24	0.020
141	0.08	0.023

Table VIIIB
Stainless Steel Crucibles
Conditions:
Unstirred
 $T = 378^{\circ}C$
 $(Pb)^o = 6.2$ w/o

Run	$[Li]^o$ w/o	k min^{-1}
90	0.21	0.068
91	0.27	0.072
92	0.57	0.068

It is concluded from these results that the rate constant k is independent of the initial lithium concentration of the alloy.

Alloy Depth d

Results are shown in Tables IXa and IXb.

TABLE IX

ALLOY DEPTH PARAMETER

Table IXa

Quartz Sleeved Crucibles

Conditions: Unstirred
 $T = 378 \pm 3^{\circ}\text{C}$

Run	Alloy Mass gm	d cm	k min ⁻¹
110	50	0.95	0.012
108	100	1.90	0.014
99	100	1.90	0.014*

* (quartz crucible)

Table IXb

Stainless Steel Crucibles

Conditions: Unstirred
 $T = 376 \pm 2^{\circ}\text{C}$

Run	Alloy Mass gm	d cm	k min ⁻¹
88	100	1.90	0.061
90	50	0.95	0.068
91	60	1.13	0.072
93	80	1.50	0.058
98	100	1.90	0.066

The alloy depth does not appear to influence the rate constant k , indicating that little or no contribution to rate control arises from diffusion in the alloy phase.

Salt Height h

The effect of the salt height on k is illustrated in Table X.

TABLE X

EFFECT OF SALT HEIGHT ON k

Conditions: Quartz sleeved crucibles
Stirred, 112 rpm, S.S. paddle
 $T = 375^{\circ}\text{C}$

Run	Mass Salt gm	h cm	k min^{-1}
137	20	2.28	0.020
142	30	3.42	0.015
141	20	2.28	0.023
140	20	2.28	0.023

The results indicate that k is inversely dependent on the salt height.

Agitation

The results of a variation of agitation conditions on k are shown in Table XI.

TABLE XI

EFFECT OF STIRRER SPEED

Conditions: Quartz-sleeved crucibles
 $T = 375^{\circ}\text{C}$
 Stainless steel paddle
 (104 used glass stirrer)

Run	rpm	k min ⁻¹
108	0	0.014
110	0	0.012
104	64	0.010
112	112	0.020
113	112	0.022
114	224	0.053

A plot of $\log k$ versus $\log (\text{rpm})$ for $64 \leq \text{rpm} \leq 224$ is a straight line with the slope $a = 0.9 \pm 0.1$.

Temperature

The temperature series data are listed in Table XII; the reduction curves are shown in Figure 10, and the Arrhenius plot in Figure 11. The apparent activation energy measured from the Arrhenius plot is $8.4 \pm 2.0 \text{ k cal mole}^{-1}$.

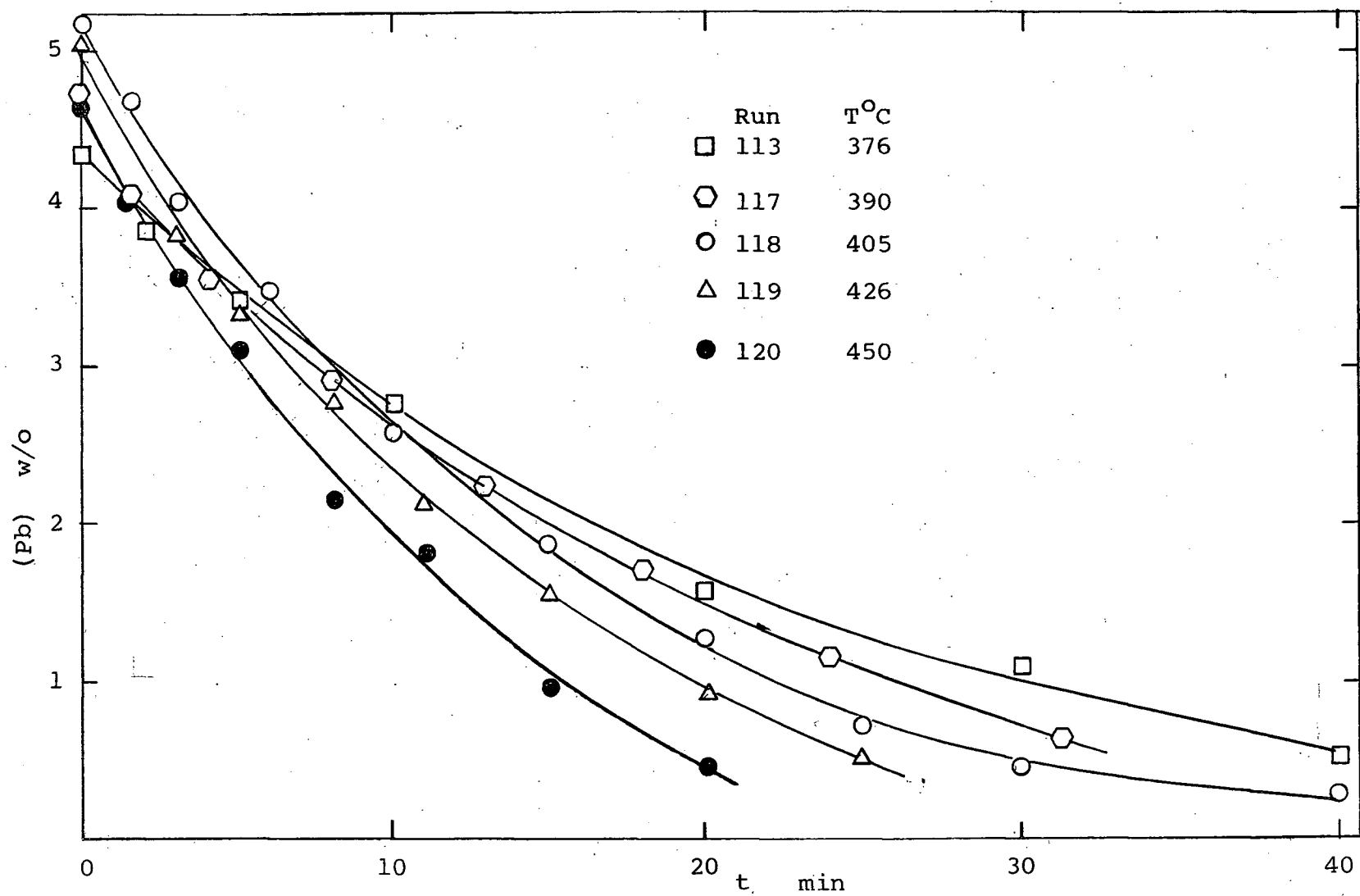


Figure 10: Experimental Curves for Li Reduction of Pb(II) - Temperature Series (Stirred at 112 rpm, 100 gm 0.25 w/o, Li alloy, 20 gm, 5 w/o Pb salt).

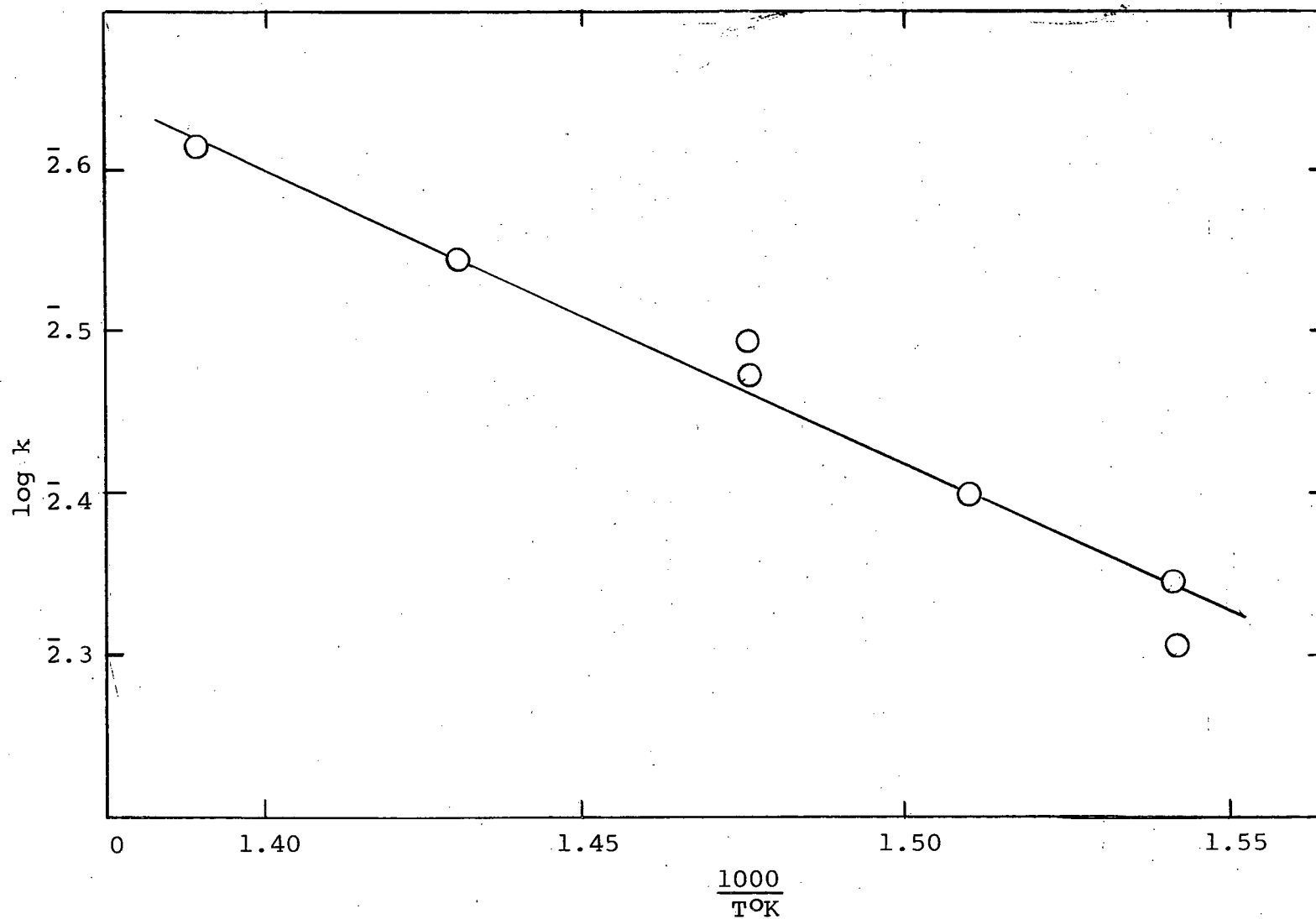


Figure 11: Arrhenius Plot for Li Reduction of Pb(II)

TABLE XII

TEMPERATURE SERIES

Conditions: Quartz sleeved crucible
 Stirred, 112 rpm
 Stainless steel paddle

Run	T°C	k min ⁻¹
112	376	0.020
113	376	0.022
117	390	0.025
118	405	0.031
119	426	0.035
120	450	0.041

The results for Pb⁺⁺ reduction with Li can be summarized as follows:

- (a) First order rate plots are linear.
- (b) The first order rate constant k is independent of alloy depth and initial alloy lithium content.
- (c) First order rate constants are independent of the initial Pb⁺⁺ concentration of the salt.
- (d) k is inversely dependent on h , the salt height, at constant interfacial area.
- (e) k increases with increasing agitation of the salt phase.
- (f) The apparent activation energy of the reduction is $8.4 \pm 2 \text{ k cal mole}^{-1}$, compared to $7.9 \text{ k cal mole}^{-1}$ for Pb⁺⁺ diffusion.

These results are consistent with rate control by transport of Pb^{++} in the salt phase.

Calculation of Salt Phase Boundary Layer Thicknesses δ_s .

Since the Li reduction of $PbCl_2$ is controlled by diffusion of Pb^{++} across an apparent boundary layer, the thickness of this layer may be calculated from the relation

$$k = \frac{D}{\delta_s h} \quad (8)$$

Typical values of δ_s calculated in this manner are listed in Table XIII.

TABLE XIII

SALT PHASE BOUNDARY LAYER THICKNESSES FOR
 Pb^{++} REDUCTION WITH Li

Run	T°C	rpm	k min ⁻¹	δ_s cm
114	376	224	0.053	0.0046
113	376	112	0.022	0.0112
110	376	0	0.012	0.0202
99	376	0	0.014	0.0175
117	390	112	0.025	0.0107
118	405	112	0.032	0.0100

Electrochemical Nature of the Pb^{++} Reduction

Three types of experiments indicated the electrochemical nature of the reaction of Pb^{++} with Li.

Effect of Crucible

The type of crucible used in these experiments was observed to affect the reduction rate. Runs 97, 98 and 99 were all conducted under similar conditions. Run 97, in a quartz sleeved crucible, and Run 99, in a quartz crucible, had essentially identical rate constants. Run 98, in a stainless steel crucible, had a much higher rate. Figure 12 illustrates first order plots for these three tests.

The salt-metal interfacial area in each test was 5.3 cm^2 , and the salt height was 2.3 cm. Run 98 was unusual in that the area of contact between molten salt and electronically conducting material was a factor of 4.5 times higher than in the other two runs (area of salt-metal interface, 5.3 cm^2 , plus the area of salt-crucible contact, 18.8 cm^2). The ratio of rates is, using an average k of 0.0145 min^{-1} for Runs 97 and 99,

$$\frac{k_{98}}{k_{97, 99}} = \frac{0.066}{0.0145} = 4.55$$

This agreement is unlikely to be strictly fortuitous but rather presents good evidence that the reduction of Pb^{++} occurs predominantly by an electrochemical mechanism.

Checks were made to ensure that the runs in stainless steel were valid. Run 66 was performed in which a LiCl-KCl-PbCl_2

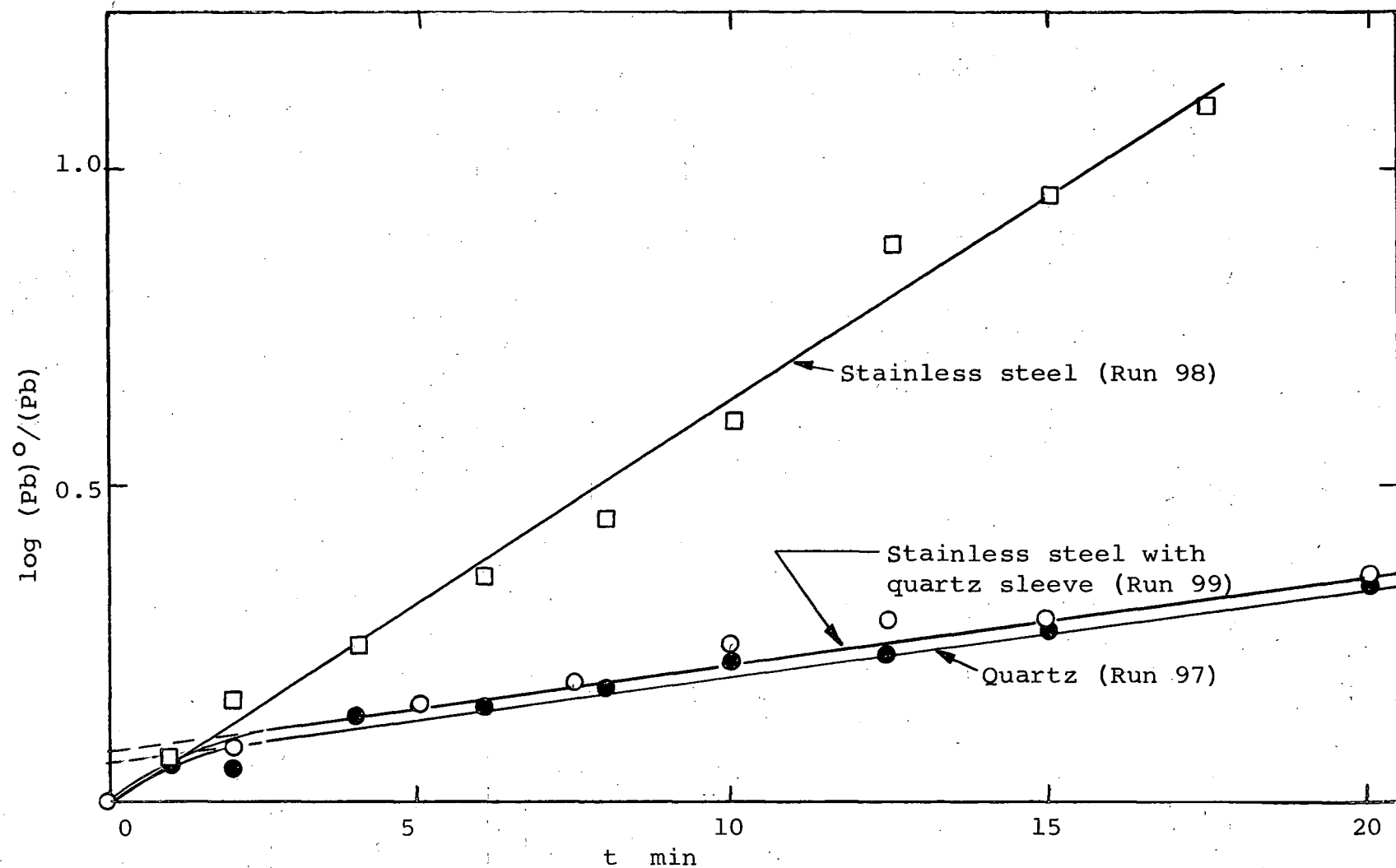


Figure 12: Effect of Crucible on Reduction Rates (unstirred, 374°C , 20 gm., 3.7 w/o Pb salt, 100 gm 0.3 w/o Li alloy).

melt was contacted with pure lead. The salt was periodically analyzed for Pb^{++} content, and no Pb^{++} reduction was observed up to 110 minutes. The salt from Run 81 was tested for iron by addition of potassium thiocyanate to an aqueous solution of the salt. No iron was detected.

Tests with Stainless Steel Strips

Several runs were conducted in which stainless steel strips (316, cleaned with emery paper, washed in acetone and dried) were inserted into both phases; these strips extended the cathodic salt-metal interface.

The data is summarized in Figure 13, which shows k plotted against the salt-stainless steel contact area. The runs were conducted in quartz sleeved crucibles. Points for Runs 97 and 99 (no strips) and Run 98 (stainless steel crucible) are also shown in Figure 13.

A linear relation exists between strip area and k , the strips giving increased reduction rates. The rate increase is smaller than the anticipated effect shown by the dotted line joining points 97 and 99 to 98. The difference appeared to result from incomplete wetting of the stainless steel strips by the molten salt, which means that the contact area is not the geometrical area.

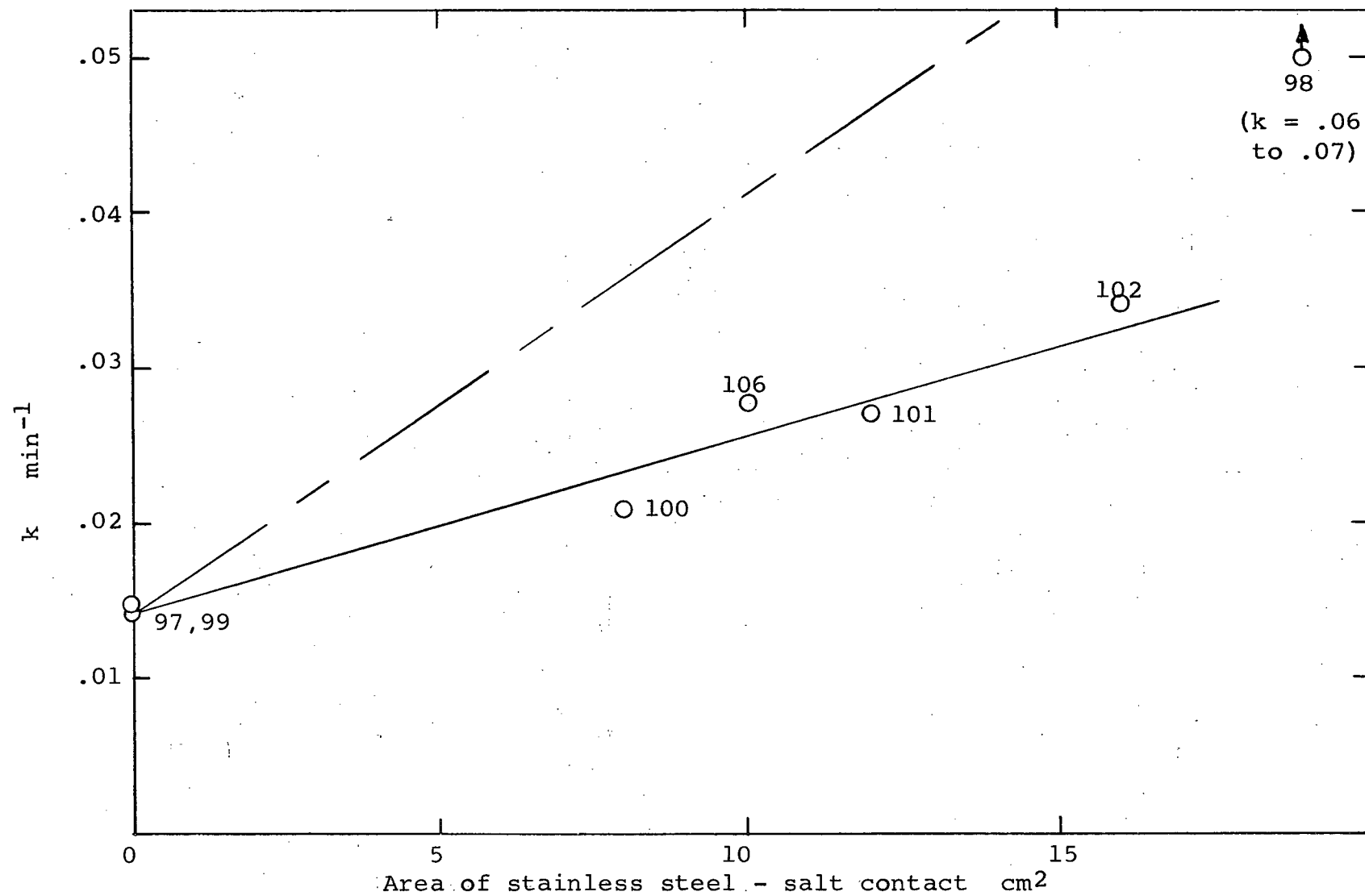


Figure 13: Stainless Steel Strip Immersion Tests - First Order k vs. A (377°C , 20 gm, 4 w/o Pb salt; 100 gm, 0.78 w/o Li alloy).

These results also indicate electrochemical reduction of Pb^{++} .

Current Measurement

Current flow in an external circuit was detected in the following way. A Cu wire was silver-soldered to a quartz sleeved crucible to provide electrical contact with the alloy. A run (109) was performed in the usual manner, except that a stainless steel strip was immersed into the salt phase, and connected through an ammeter to the Cu wire. The current flow was recorded and the melt was sampled at intervals throughout the test.

Figure 14 shows experimentally measured curves of Pb^{++} concentration and current versus time. A sketch of the circuit, with the observed polarity, is shown in Figure 15.

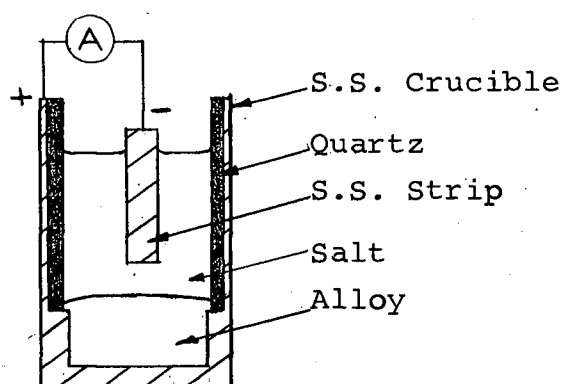


Figure 15: Current Measurement Crucible.

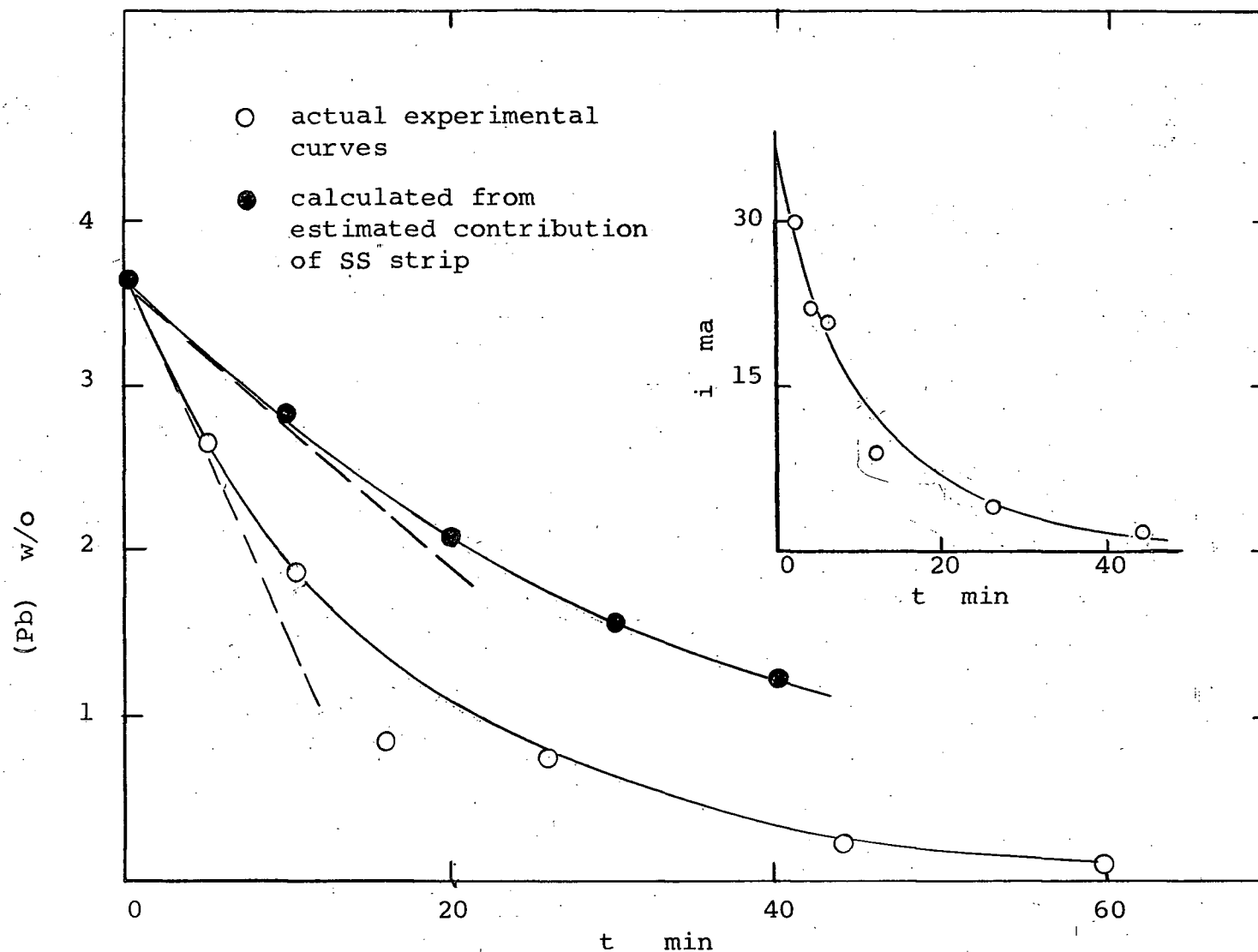


Figure 14: Experimental Curves - Detection of Current Flow (Run 109, 370°C, 20 gm 3.60 w/o Pb salt, 85 gm 0.25 w/o Li alloy unstirred).

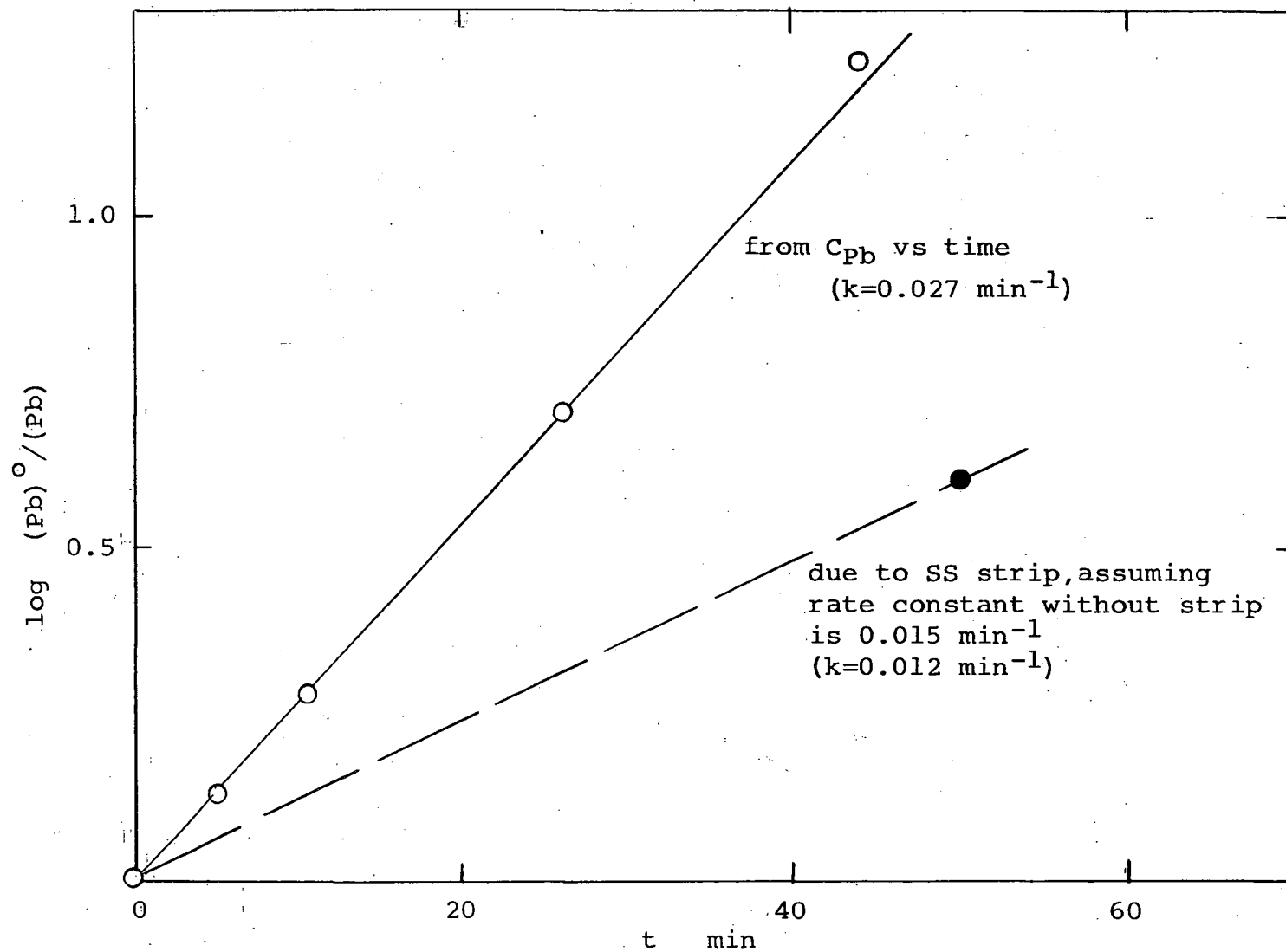


Figure 16: First Order Plots for Run 109.

Figure 16 is a first order rate plot of the data, with $k = 0.027 \text{ min}^{-1}$. The results can be compared to those of Run 97 (quartz sleeved crucible), $k = 0.015 \text{ min}^{-1}$. The rate due to the stainless steel strip is thus 0.012 min^{-1} . In Figure 16, a rate plot is constructed with this slope, and a curve of concentration versus time due to the stainless steel strip was calculated. This curve is shown in Figure 14. Rates measured from the concentration-time curve, and those calculated from the measured currents using Faraday's law are compared in Table XIV.

TABLE XIV
COMPARISON OF CALCULATED AND
MEASURED RATES (RUN 109)

t min	Concentration Rate gm/min	i ma	Faraday Rate gm/min	Difference from average %
0	0.00168	36	0.00232	+38
5		21	0.00135	-20

This agreement provides further evidence that Pb^{++} reduces electrochemically.

The results on Pb^{++} reduction with Li can be summarized as follows:

- (1) Examination of the reaction variables shows that the rate of this reduction is controlled by diffusion of Pb^{++} across a boundary layer of thickness δ_s in the salt phase.
- (2) The reaction is electrochemical in nature.

Reduction of Li^+ with Na in a Na-Pb Alloy

This exchange reaction was re-examined in 25 mm crucibles, with stirring, at 400°C . Runs were conducted at two different initial alloy sodium concentrations. The results of these runs are shown in Table XV and Figure 17.

TABLE XV

REDUCTION OF Li^+ WITH Na

Conditions: 20 gm. salt
 100 gm. Na-Pb alloy
 $T = 400^\circ\text{C}$
 Stirred at 112 rpm, glass stirrer

Run	$\frac{[\text{Na}]}{w/o}$	k min^{-1}
148	$1.02 \pm .05$	0.134
149	$0.49 \pm .05$	0.049

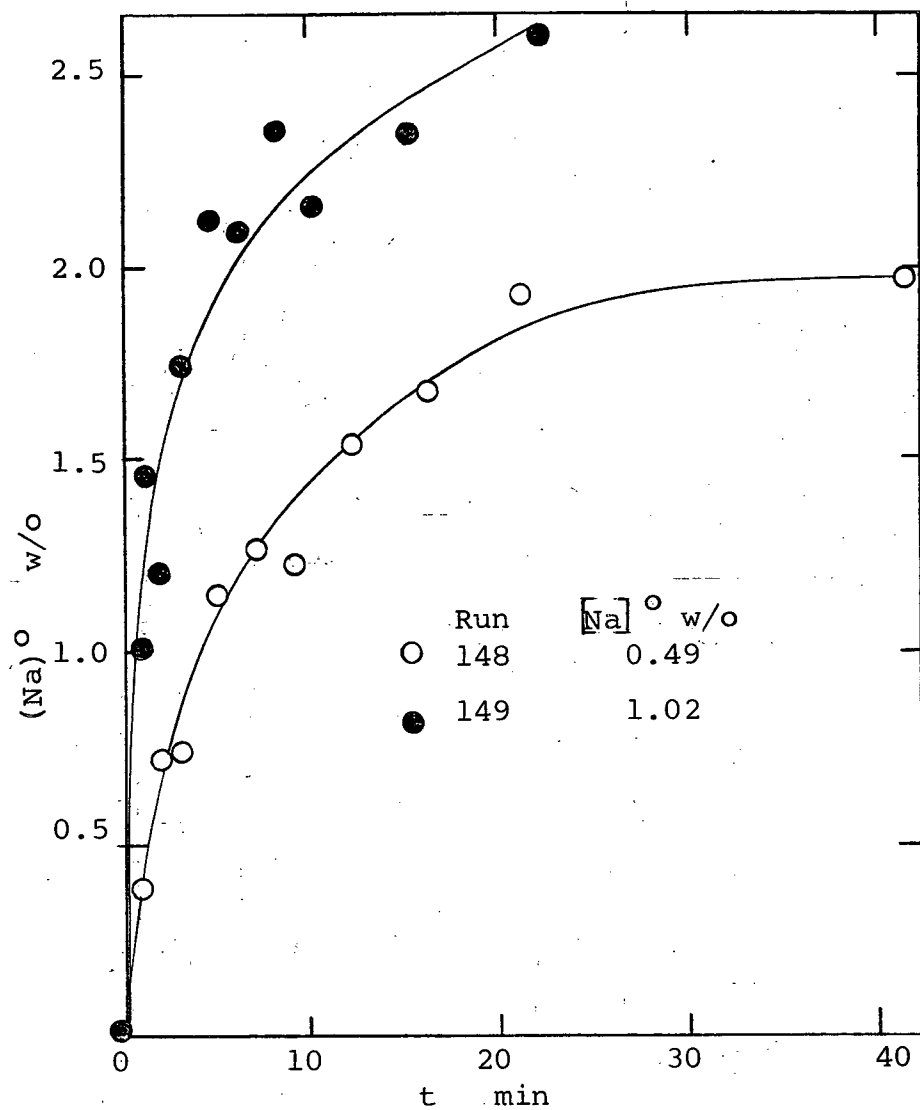


Figure 17a: Na Oxidation Curves

Figure 17: Na - LiCl Exchange (Runs 148,149, 400°C, 112 rpm, 20 gm salt, 100 gm alloy)

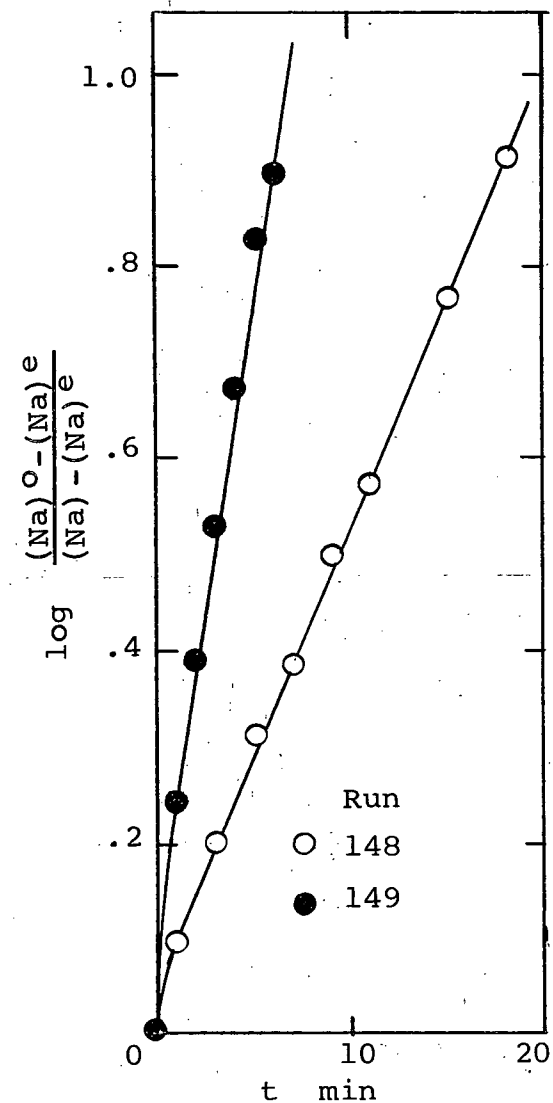


Figure 17b: First Order Plots

These results are consistent with a reaction rate that is controlled by diffusion of Na in the alloy. By comparison, the rate determined in the preliminary reductions is $k_{390} = 0.15 \pm .03 \text{ min}^{-1}$. Since Run 149 had obviously reached equilibrium, the final alloy was analyzed for Li and Na, and the equilibrium constant was calculated. The value determined was $K_{400}^0 = 0.38$. This constant was used to calculate $\Delta E^0 = 0.056 \text{ v}$. These values of K and ΔE^0 can be compared with those previously determined in the preliminary tests, $K_{390}^0 = 0.28$ and $\Delta E^0 = 0.073 \text{ v}$.

The mole ratio of oxidized sodium to reduced lithium for Run 149 was, from analysis, about 1.1. The difference of 10% can easily be accounted for by the variation in $[\text{Na}]^0$ analysis.

These results show that the reduction rate of Li^+ with Na under the present conditions is about five to ten times faster than the reduction rate of Pb^{++} with Li, and the reaction appears to be controlled by the diffusion of Na in the alloy phase.

Reduction of Other Metal Ions

The results for a number of metal reductions examined are listed in Table XVI. These runs were conducted under similar conditions of agitation (112 rpm, glass stirrer) and temperature (400°C), in quartz sleeved crucibles.

First order rate plots for these runs are shown in Figures 18 and 19.

Cadmium, Silver and Indium Ion Reductions

The reductions of Cd^{++} , Ag^+ and In^{+++} with Li, and the reduction of Cr^{+++} to Cr^{++} with Pb (followed by lead analysis of salt) appeared to proceed in a manner analogous to the Pb^{++} reductions. Salt samples were clean and homogeneous, as were the solidified salt masses at the end of the runs. Table XVII lists boundary layer thicknesses calculated for the four reductions, and for a comparable Pb^{++} reduction (Run 118). These results fit the relation $\delta \propto D^{0.28}$ (with the exception of Cr(III)), in the same range observed in aqueous solutions, i.e., $\delta \propto D^{0.25-0.35}$ (reference 16).

TABLE XVI

METAL REDUCTION RESULTS

All Experiments: 400°C
 112 rpm, glass stirrer
 100 gm alloy
 20 gm salt (30 gm, Run 126)

Solute	Run	(M^{n+}) ^o w/o	M cm ⁻³ * x10 ⁴	[Li] ^o w/o	k min ⁻¹	Metal Obsvd.
Ag(I)	144	1.50	2.31	0.30	0.063	No
Pb(II)	118	5.18	4.15	0.25	0.032	No
Cd(II)	125	1.85	2.73	0.30	0.030	No
Cd(II)	126	1.25	1.84	0.31	0.022	No
In(III)	128	1.90	2.75	0.25	0.017	No
Cr(III)	150	1.00	3.19	0	0.011	No
Cr(III)	131	0.79	2.52	0.25	0.04	Yes
Co(II)	121	1.03	2.90	0.26	0.093	Yes
Co(II)	122	1.03	2.90	0.31	0.105	Yes
Co(II)	124	1.03	2.90	0.37	0.118	Yes
Ni(II)	130	0.86	2.44	0.23	0.143	Yes
Ni(II)	146	0.86	2.44	0	0.057	Yes
Ni(II)	147	0.70	1.99	0	0.052	Yes
Ti(III)	145	0.43	1.49	0.24	0.050	Yes
Pt(II)	143	1.20	1.02	0.23	0.22	Yes

$$* \text{ M cm}^{-3} = \frac{\text{w/o}}{100} \times \frac{\rho}{M}$$

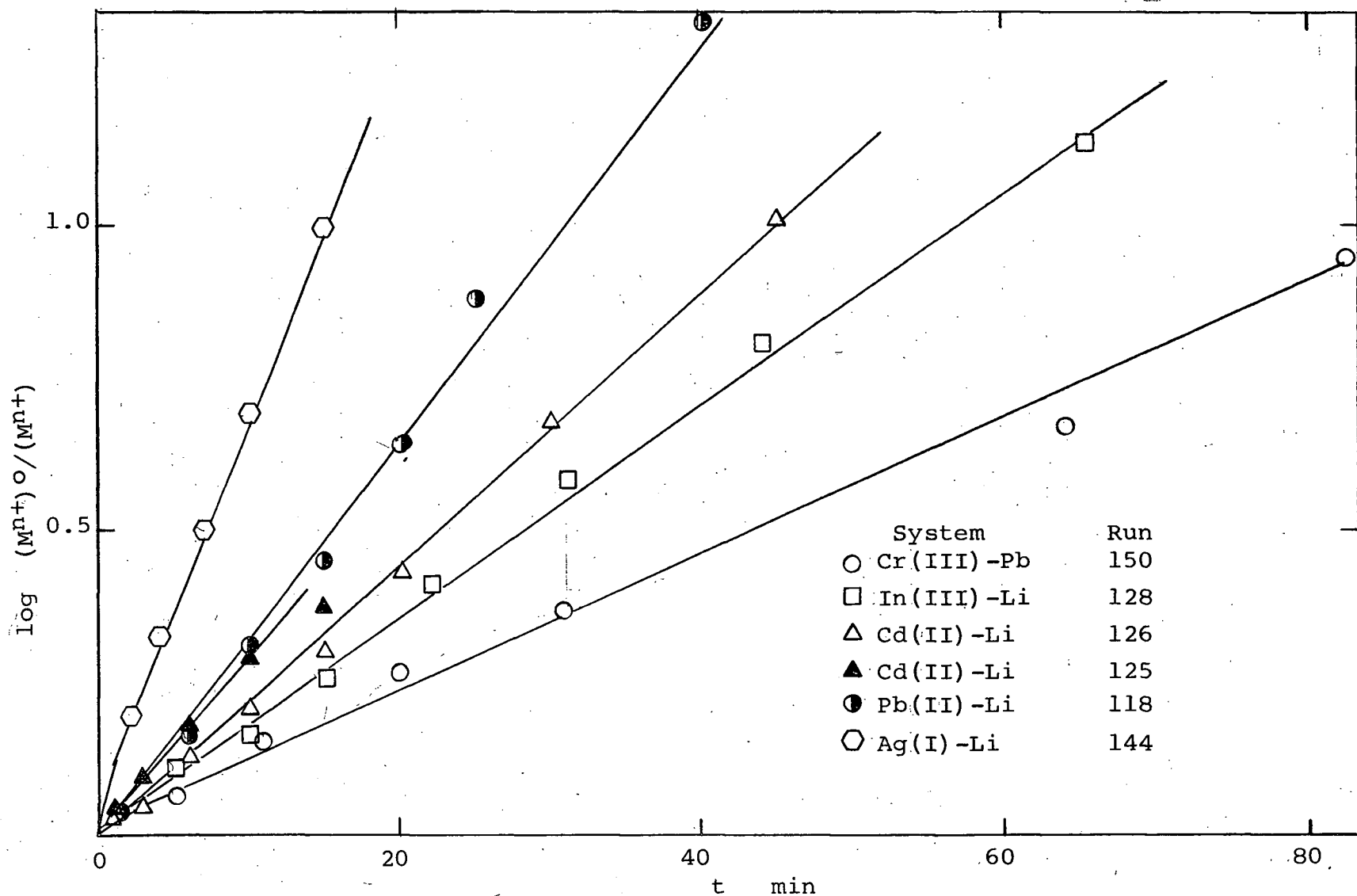


Figure 18: First Order Rate Plots for Several Metal Ion Reductions
Group 1 (400°C, 112 rpm, 100 gm alloy, 20 gm salt)

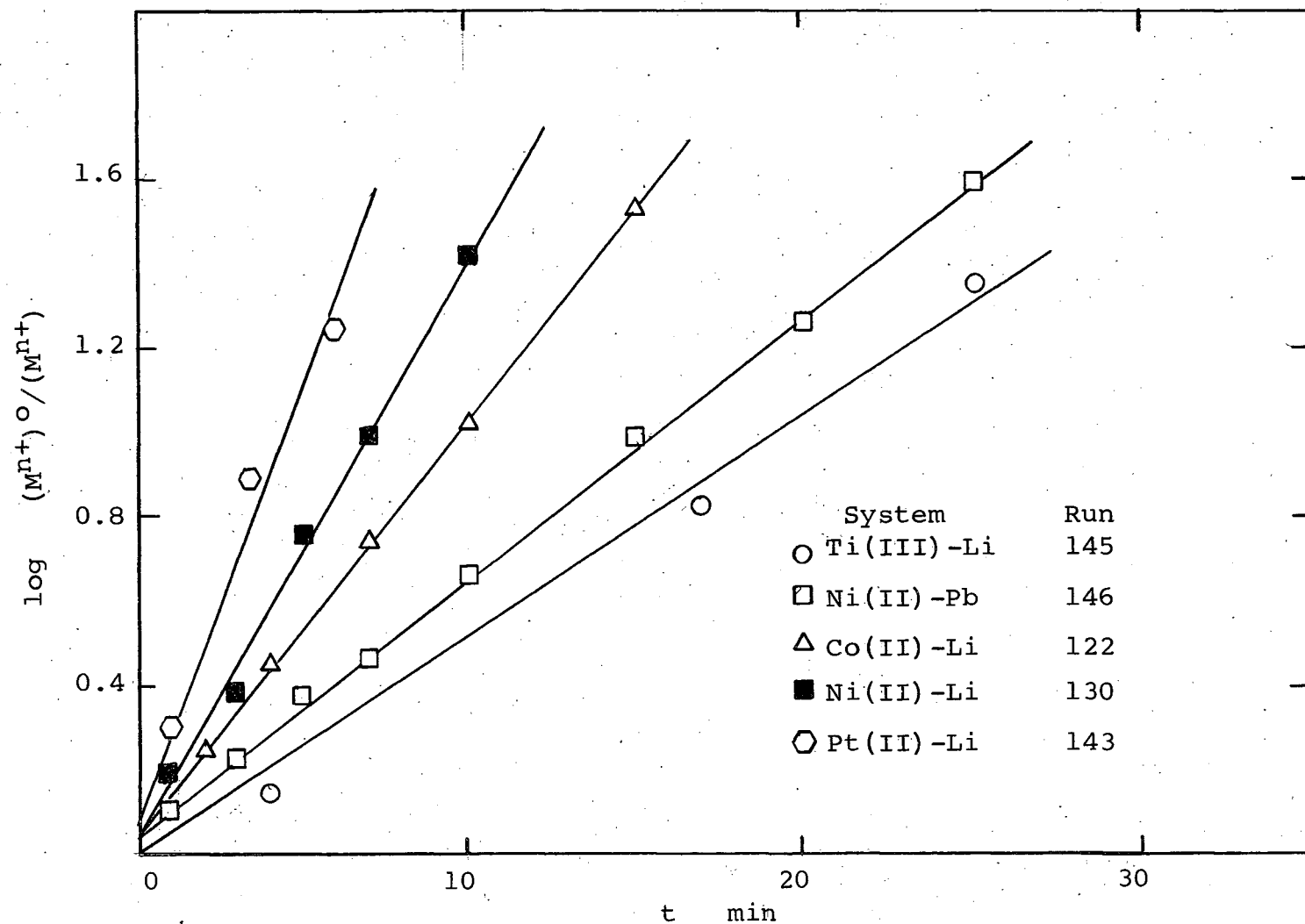


Figure 19: First Order Rate Plots for Metal Ion Reductions
Group 2 (400°C, 112 rpm, 20 gm salt, 100 gm alloy)

TABLE XVII
BOUNDARY LAYER THICKNESSES δ_s
FOR VARIOUS SOLUTES

Solute	k min ⁻¹	D x 10 ⁶ cm ² sec ⁻¹	δ_s cm
Pb ⁺⁺	0.032	12.6	0.010
Cd ⁺⁺	0.030	12.1	0.011
Ag ⁺	0.063	32	0.013
In ⁺⁺⁺	0.017	6.1	0.009
Cr ⁺⁺⁺	0.011	5.6	0.013

Two runs for Cd⁺⁺ (125 and 126) at different salt heights indicate an inverse dependence of the rate constant on salt height.

The observed results infer that the reductions of Ag⁺, Cd⁺⁺ and In⁺⁺⁺ with Li and the reduction of Cr⁺⁺⁺ with Pb are controlled by the diffusion of the respective metal ions in the salt phase.

Reduction of Pt⁺⁺, Ti⁺⁺⁺, Co⁺⁺, Ni⁺⁺ and Cr⁺⁺⁺

The rates listed in Table XVI for these solutes are somewhat higher than those predicted based on transport in the salt phase.

In each of these reductions precipitated metal was observed in the solidified salts at the end of the runs. Fairly

large volumes of metallic sponge were noted in some cases during dissolution of the salts out of the crucibles.

"Blank" runs were performed in pyrex crucibles for each of the cases in which metal was observed. These tests were carried out in an identical manner to the kinetic experiments, with the exception that no stirring was applied. The crucibles and contents were quenched in an air-blast part way through the reductions; solidification was complete in approximately 30 seconds. The salts were broken up and an examination was made of the interfacial region. Photographs were taken after spraying the salts with acrylic plastic to prevent moisture contamination.

Co⁺⁺ Reduction

The run was quenched after 5 min. at 400°C. A photograph of the salt phase is shown in Figure 20. The main portion of the salt was a turquoise-blue homogeneous phase. A dendritic growth of reduced Co metal (checked with a magnet after dissolution of the salt in water) is clearly shown in the picture. A large mass of Co was also observed floating on the salt surface at the beginning of the quench.

A logical explanation for metal on the melt surface is the following. Since the salts may contain some moisture,

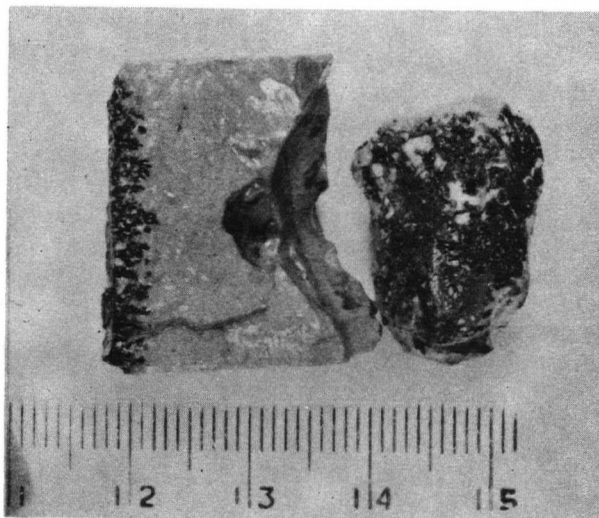


Figure 20: Salt from Co^{++} Reduction by
Lithium Blank Run

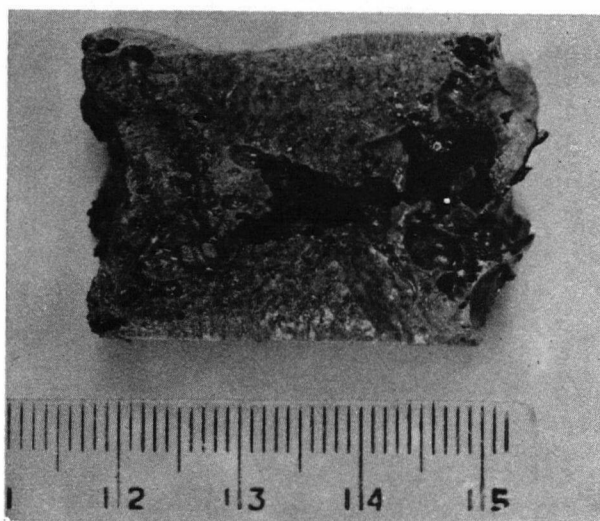


Figure 21: Salt from Ni^{++} Reduction by
Lithium Blank Run

reaction of Li with this moisture would produce hydrogen. A very small weight of hydrogen could have sufficient volume to float metal sponge from the interface to the salt surface. This explanation is substantiated by the observation that no metal was present on the surface of a Ni^{++} salt reacted with pure lead (to be discussed).

The reduction rates for three runs increased with increasing alloy lithium concentration; the relation between k and $[\text{Li}]^0$ is linear. This indicates that the rate may be controlled by diffusion of Li in the alloy, but the results are not conclusive. The variation in k may be caused by experimental error or by variations in the amount of deposited cobalt.

Ni^{++} Reduction

Nickel ion reduction experiments were conducted using both Li (in lead) and Pb as reducing agents. The rate of the reduction with Li was more than twice as high as those with Pb. However even the latter runs are faster than would be predicted from a pure diffusion mechanism. Precipitated nickel was observed in both cases.

Blank runs for reduction of Ni^{++} with Li were frozen at 1 1/2 minutes and at 4 minutes. The appearance of the salt was similar in both cases; the salt from the 4 minute quench is

shown in Figure 21. Some reduced Ni is present on the surface, but no distinct separation of reduced metal from salt in the interface vicinity occurred. Rather, the whole salt mass was a dark grey colour.

A seven gram sample of the seemingly homogeneous salt phase was dissolved in water and filtered through a Gooch crucible. The undissolved material was weighed, dissolved in dilute nitric acid and the resulting solution analyzed for Ni and Pb. The precipitate weighed 34 mgm (0.5% of total sample), and contained $70 \pm 10\%$ Ni and 9% Pb. Thus the grey colour is produced primarily by a fine dispersion of reduced Ni.

The salt sample of a reduction of Ni^{++} with Pb blank run, shown in Figure 22 had a much different appearance, and in fact was very similar to the Co^{++} reduction (with Li). The deposited Ni metal at the interface does not appear as extensive as was the cobalt, and the reduction rate for nickel is not as high. The identification of the material as Ni was confirmed with a magnet. No metal was observed on the salt surface, as mentioned previously, and as expected if no H_2 was generated in this case.

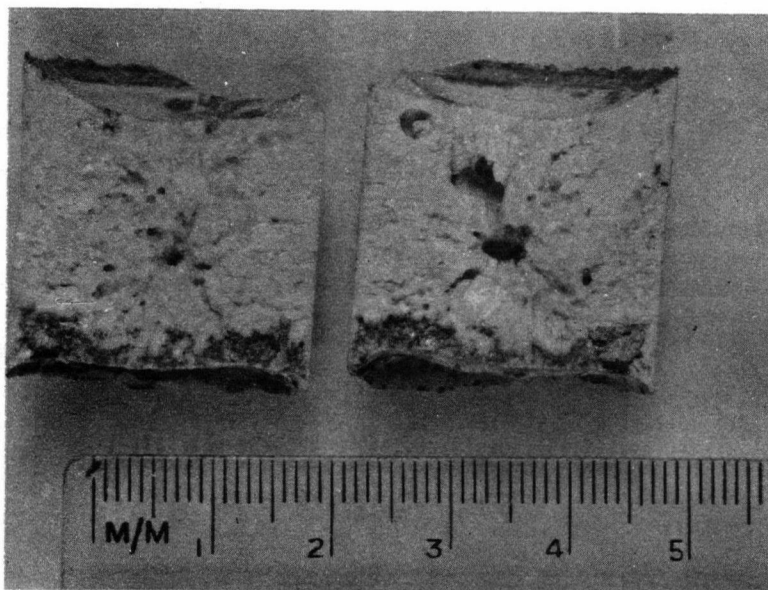


Figure 22: Salt from Ni^{++} Reduction by Lead
Blank Run

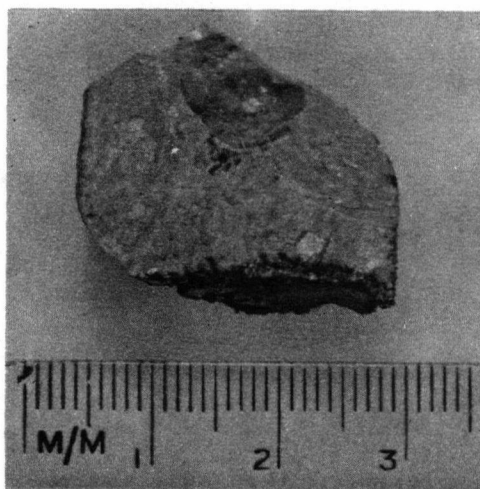


Figure 23: Salt from Ti^{+++} Reduction by
Lithium Blank Run

Ti⁺⁺⁺ Reduction

The initial concentration of Ti⁺⁺⁺ was somewhat lower than the average solute concentrations generally used, since the solubility in this system appears to be $< 2 \times 10^{-4}$ moles cm⁻³ at 400°C. The rate constant for the reduction of Ti⁺⁺⁺ with Li was 0.05 min⁻¹, or approximately three times as fast as the In⁺⁺⁺ reduction.

The salt sample, frozen after 10 minutes, is shown in Figure 23. The appearance of the salt is similar to the Co case, with deposited metal at the interface. The salt was light grey. That the deposited material was metallic Ti, and not Ti subhalides, was confirmed by water dissolution. The grey material was insoluble. The greyness of the salt was caused by a relatively small amount of Ti metal dispersed throughout the phase.

Cr⁺⁺⁺ Reduction

Reaction of Cr⁺⁺⁺ in LiCl-KCl with Li resulted in complete reduction of Cr⁺⁺⁺ to the metallic state. The rate constant of this run for the first seven minutes was approximately 0.043 min⁻¹; this value indicates that the reaction rate was significantly faster than expected from a simple diffusion mechanism. A test frozen at 10 minutes showed the presence of

metallic Cr. The salt did not break cleanly from the alloy, but when the alloy was placed in water, a black precipitate, assumed to be Cr metal, was observed. The main portion of the salt was homogeneous, and mauve in colour. Metal was observed on the salt surface.

Pt⁺⁺ Reduction

The reaction rate for the reduction of Pt⁺⁺ with Li was the highest observed in the entire study. The initial (Pt) was lower than for some of the other solutes because of limited solubility. The salt sample, frozen after four minutes, is shown in Figure 24. The salt did not break away cleanly from the alloy, but Pt metal can be seen at the interface. However the main portion of the salt was grey, indicating the presence of reduced Pt. Water dissolution resulted in a precipitate which was also insoluble in HCl (Note that PtCl₂ is relatively insoluble in water, but dissolves readily in the presence of HCl).

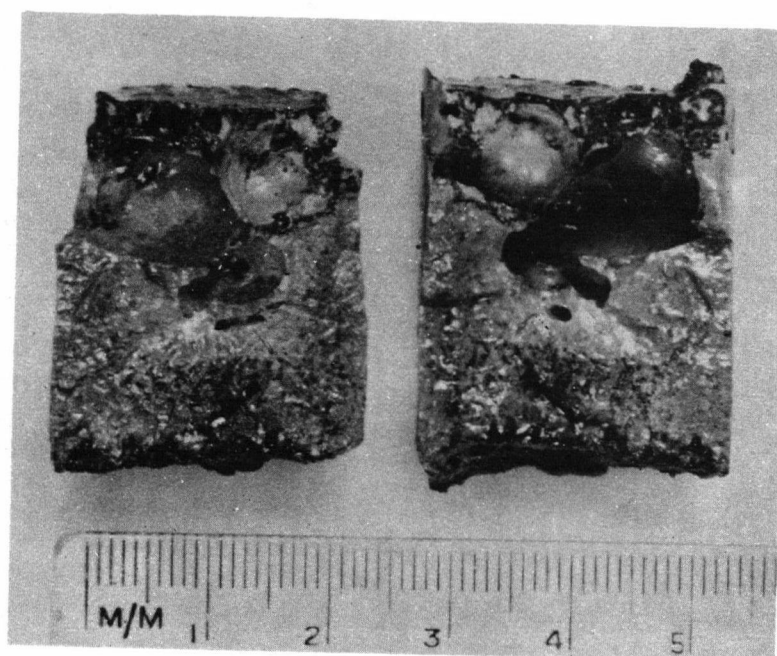


Figure 24: Salt from Pt^{++} Reduction by
Lithium Blank Run

To summarize, the reductions of these ions with either Li or Pb were fast compared to the reductions of Cd^{++} , Pb^{++} , In^{+++} and Ag^+ . Reduced metal was observed in two forms:

- (a) metal was found at the salt-metal interface during the reductions of Co^{++} , Cr^{+++} and Ti^{+++} with Li and the reduction of Ni^{++} with Pb.
- (b) metal was dispersed throughout the salt phase in the reductions of Ni^{++} and Pt^{++} with Li.

Chronopotentiometry

The basic chronopotentiometric data obtained in this study are presented in Appendix C. Listed are average transition times (for one to three tests) determined at various current densities and concentrations for each solute studied.

Table XVIII is a summary of the present results.

The procedures used for determining transition times from the recorded potential-time curves are discussed in Appendix B.

The results will now be detailed for each solute.

Solvent

Chronopotentiograms for the purified solvent were determined. A typical solvent potential-time curve is shown in Figure 25a. An examination of this curve resulted in the data given in Table XIX.

TABLE XIX

RESIDUAL TRANSITION TIME OF SOLVENT

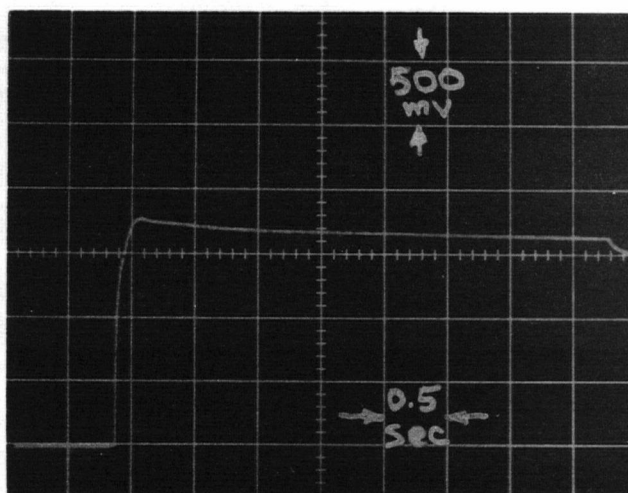
E(v.) vs. Ag(I) - Ag(0)	τ sec	$i \tau^{1/2}$ amp cm ⁻² sec ^{1/2}
- 0.5	-	negligible
- 1.0	0.03	0.22×10^{-2}
- 1.5	0.09	0.38×10^{-2}

TABLE XVIII

SUMMARY OF PRESENT CHRONOPOTENTIOMETRIC RESULTS

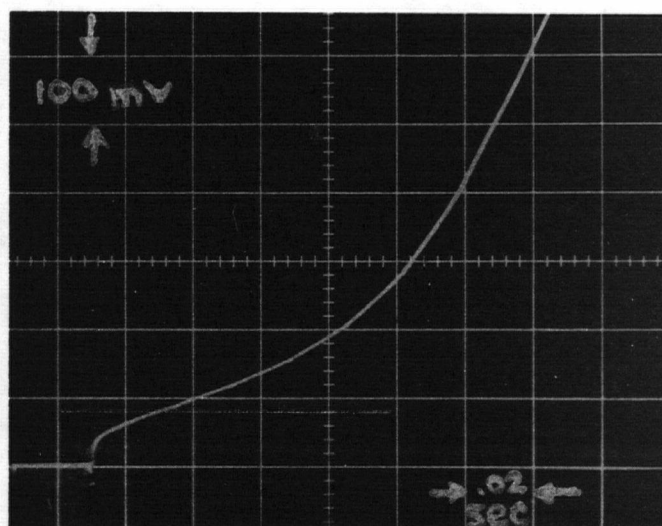
Ion	T °C	C	$i\tau^{1/2} \times 10^2$	$D \times 10^6$
		M cm ⁻³	amp cm ⁻² sec ^{1/2}	cm ² sec ⁻¹
Ag(I)	400	4.95 x 10 ⁻⁵	2.31 ± 0.10	29.8 ± 1.5
	400	8.75	4.46 ± 0.15	34.5 ± 2.3
	400	1.40 x 10 ⁻⁴	7.70 ± 0.25	40.5 ± 2.7
Pb(II)	400	6.21 x 10 ⁻⁵	3.67 ± 0.05	12.0 ± 0.3
	400	8.52	5.09 ± 0.05	12.3 ± 0.3
	400	2.45 x 10 ⁻⁴	15.30 ± 0.05	13.4 ± 1.0
	445	1.10 x 10 ⁻⁵	0.81 ± 0.02	18.7 ± 0.7
	445	1.70	1.29 ± 0.05	19.8 ± 1.3
	445	2.38	1.77 ± 0.02	19.1 ± 0.5
	403	2.38	1.01 ± 0.02	6.2 ± 0.25
In(III)	403	5.07	2.11 ± 0.05	6.0 ± 0.3
	429	5.07	2.48 ± 0.06	8.3 ± 0.45
	451	5.07	2.63 ± 0.12	9.3 ± 1.0
	402	2.26	1.31 ± 0.02	11.6 ± 0.4
Co(II)	402	4.70	2.72 ± 0.10	11.5 ± 0.9
	453	4.70	3.29 ± 0.10	16.9 ± 0.9
	493	4.70	3.65 ± 0.10	20.8 ± 1.0
	402	7.20	4.61 ± 0.15	14.1 ± 1.1
Ni(II)	400	2.10	1.34 ± 0.06	14.0 ± 1.4
	400	6.70	4.16 ± 0.12	13.3 ± 0.8
Pt(II)	400	1.58	1.00 ± 0.02	13.7 ± 0.7
	400	2.35	1.37 ± 0.04	11.6 ± 0.8
	400	3.28	1.90 ± 0.02	11.6 ± 0.2
Fe(II)	400	1.01 x 10 ⁻⁴	5.59 ± 0.05	10.5 ± 0.4
	400	2.46 x 10 ⁻⁵	1.60 ± 0.04	14.6 ± 0.8
	400	3.75	2.65 ± 0.06	17.2 ± 0.8
	400	5.06	3.45 ± 0.10	16.0 ± 1.0
	400	5.06*	3.60 ± 0.10	
Cr(III)	400	2.60	0.51 ± 0.02	5.4 ± 0.05
	400	8.45	1.73 ± 0.08	5.8 ± 0.45
Cr(II)	400	1.58	1.13 ± 0.05	17.6 ± 1.6
	400	3.32	2.38 ± 0.10	17.7 ± 1.5
	400	5.2**	2.65 ± 0.06	

* } Solubility limit apparently reached (see text).
 ** }



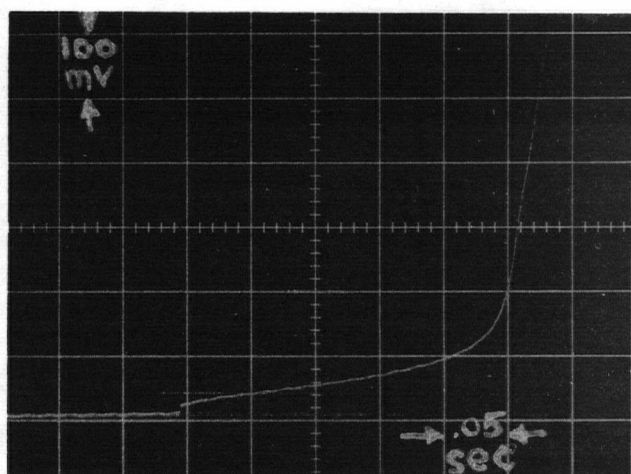
(a) Solvent

$T = 400^{\circ}\text{C}$
 $i = 1.26 \times 10^{-2} \text{ a cm}^{-2}$
 W electrode



(b) Silver(I)

$T = 400^{\circ}\text{C}$
 $C = 8.75 \times 10^{-5} \text{ M cm}^{-3}$
 $i = 1.51 \times 10^{-1} \text{ a cm}^{-2}$
 $\tau = 0.085 \text{ sec}$



(c) Lead(II)

$T = 400^{\circ}\text{C}$
 $C = 6.21 \times 10^{-5} \text{ M cm}^{-3}$
 $i = 7.44 \times 10^{-2} \text{ a cm}^{-2}$
 $\tau = 0.23 \text{ sec}$

Figure 25: Typical Chronopotentiograms for Solvent, Silver(I) and Lead(II)

The solvent thus has a residual transition time, probably caused by hydroxyl ion, water, silicate and heavy metal ion contaminations. Laitinen et al³³ have suggested that a transition time of 0.01 - 0.09 sec. should be assigned to the melt. In the present work, few solutes were examined at potentials more than 0.5 v. negative to a Ag(I)-Ag(0) reference, so no corrections were applied for this effect. At low transition times in some tests slight deviations from linearity of $\tau^{1/2}$ vs $1/i$ plots were observed, undoubtedly due to the residual τ of the melt.

Silver(I)

Figure 26 is a graph of $\tau^{1/2}$ vs. $1/i$ for silver; a typical chronopotentiogram is shown in Figure 25b.

The diffusion coefficients measured at three concentrations varied from 29.8 to 40.5 $\times 10^{-6}$ cm² sec⁻¹. A calculation of the diffusion layer thickness for $C = 1.40 \times 10^{-4}$ moles cm⁻³, $i = 6.88 \times 10^{-2}$ amp cm⁻² and $\tau = 1.25$ sec. (the conditions for the lowest current density at this concentration) showed that this thickness was about 20% of the electrode dimensions. Thus the high value of D (40.5 $\times 10^{-6}$ cm² sec⁻¹) may be a result of a non-linear diffusion contribution leading to larger transport of the reducible species to the electrode than accounted for by linear diffusion alone.

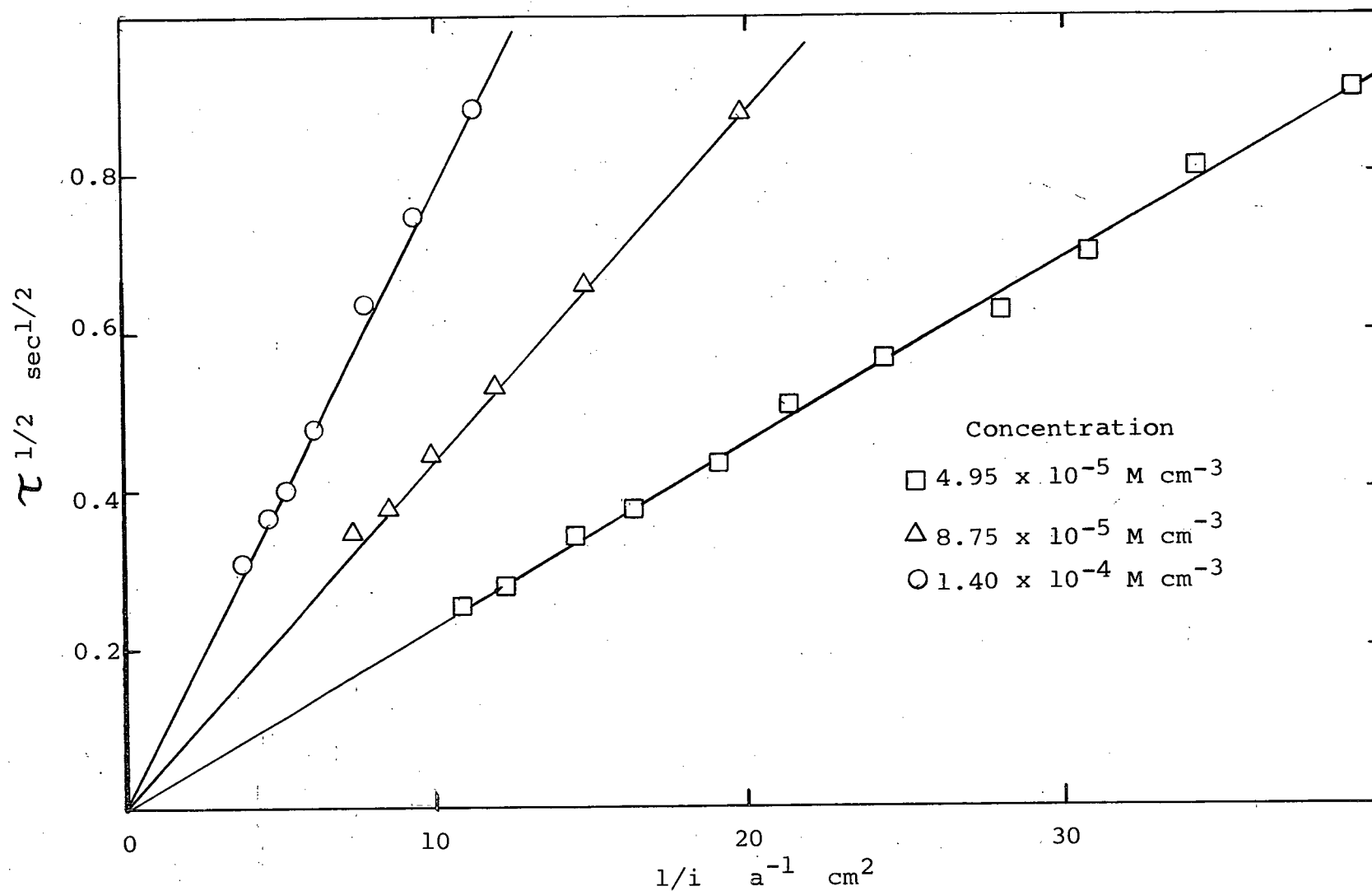


Figure 26: Chronopotentiometric Results for Silver(I) at 400°C

The best average value of the diffusion coefficient for Ag is probably $32 \pm 3 \times 10^{-6} \text{ cm}^2 \text{ sec}^{-1}$. The literature values for Ag show a good deal of scatter; the present result agrees most closely with that of Delimarskii et al.³⁴ (see Table XXI).

Measurements of the slopes of several potential versus $\log (\tau^{1/2} - t^{1/2})$ plots gave 0.145 v., compared to the theoretical Nernst slope of 0.134 v. for a reversible, one-electron reduction.

Lead(II)

Figures 27 and 28 are plots of $\tau^{1/2}$ versus $1/i$ for lead at 400°C and 445°C respectively. The average values of the diffusion coefficients are $12.6 \pm 1.5 \times 10^{-6} \text{ cm}^2 \text{ sec}^{-1}$ at 400°C, and $19.2 \pm 1.5 \times 10^{-6} \text{ cm}^2 \text{ sec}^{-1}$ at 445°C. These two values indicate an activation energy (admittedly crude) of 7.5 k cal mole⁻¹, in good agreement with the value of 7.9 k cal mole⁻¹ obtained by Thalmyer et al.³⁵.

The potential versus $\log (\tau^{1/2} - t^{1/2})$ slopes for eight tests averaged $0.070 \pm .007$ v. This value may be compared with the result of Inman and Bockris³⁶ of 0.069 v. for the reduction of Pb(II) onto a liquid lead cathode. This data indicates that Pb(II) reduces reversibly from LiCl-KCl eutectic.

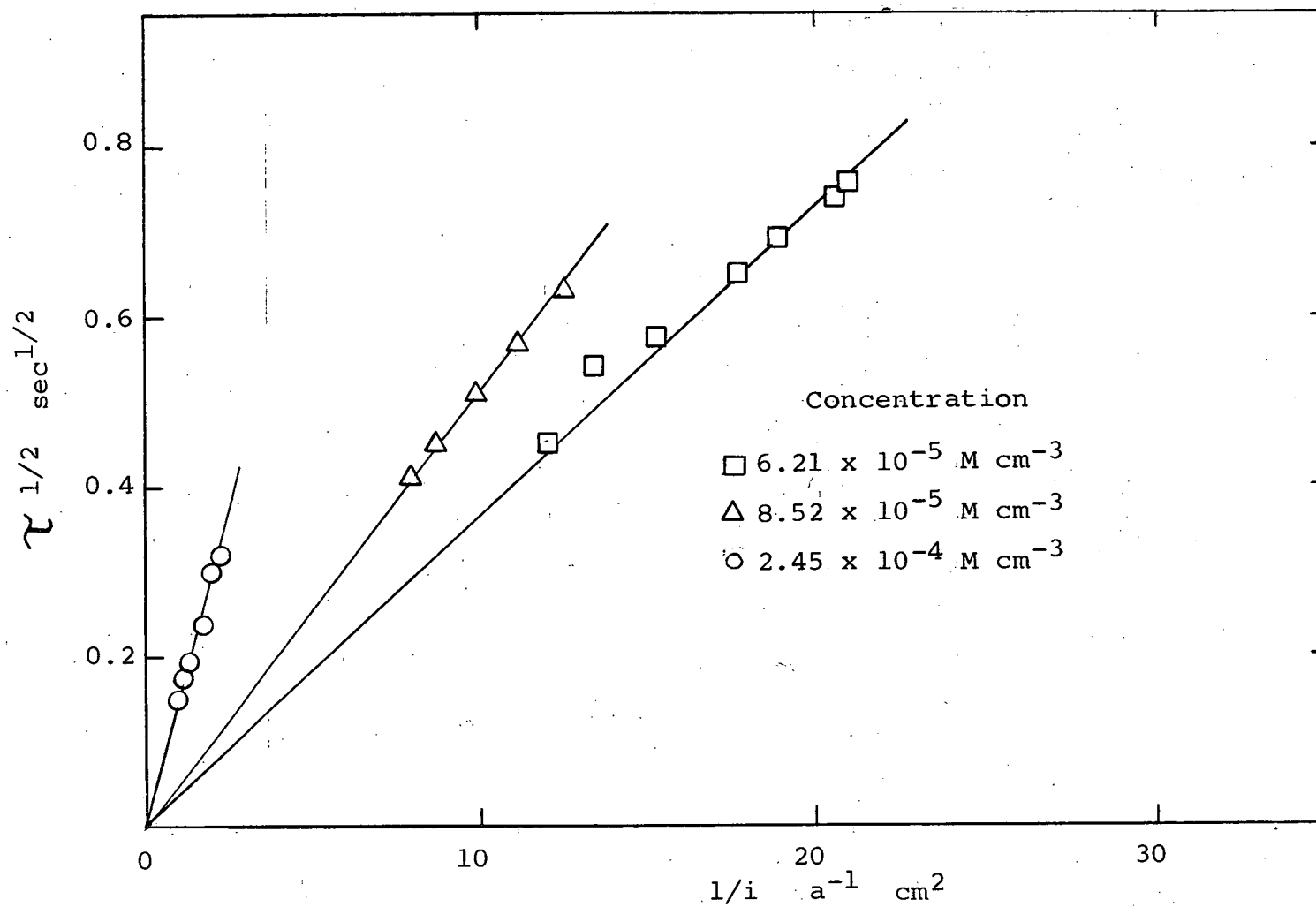


Figure 27: Chronopotentiometric Results for Lead(II) at 400°C

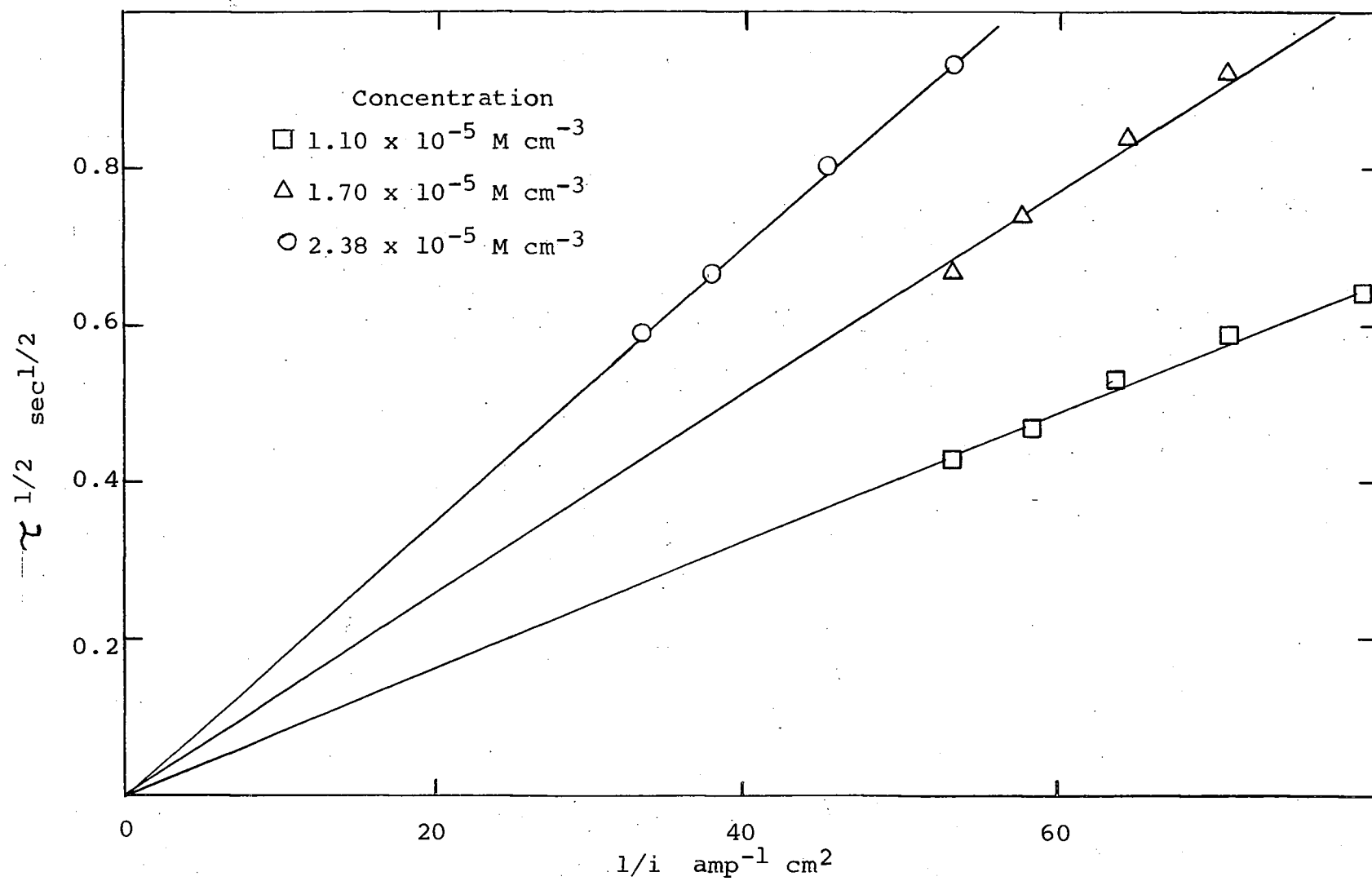


Figure 28: Chronopotentiometric Results for Lead(II) at 445°C

Indium(III)

Two waves were observed for the reduction of trivalent indium solutions; typical chronopotentiograms are shown in Figure 29. The potential of the first wave, -0.25v vs. 0.6M Ag(I) - Ag(0), agrees reasonably well with the potential difference of -0.15 v. estimated from the data of Laitinen et al³⁰. The second wave was observed at 0.52 v. less noble than the first.

Measurements for 15 tests showed that $\tau_2/\tau_1 = 1.25 \pm 0.1$. For two consecutive electrochemical reductions (see Appendix A):

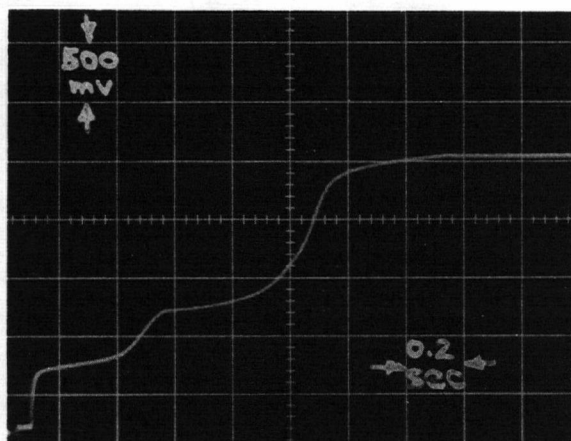
$$\frac{\tau_2}{\tau_1} = 2 \left(\frac{n_2}{n_1} \right) + \left(\frac{n_2}{n_1} \right)^2$$

Theoretical values of this ratio for various combinations of n_1 and n_2 are listed in Table XX.

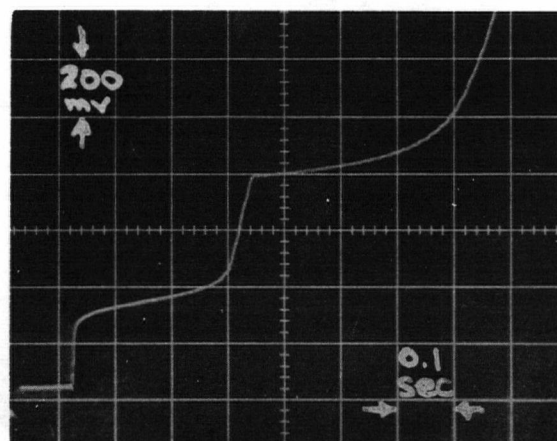
TABLE XX

τ_2/τ_1 VALUES

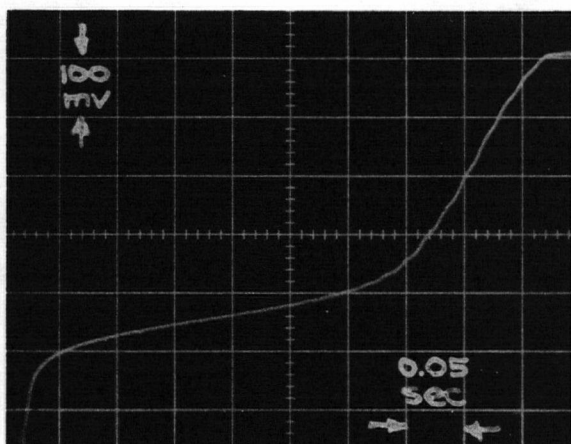
n_1	n_2	τ_2/τ_1
1	1	3
1	2	8
2	1	1.25



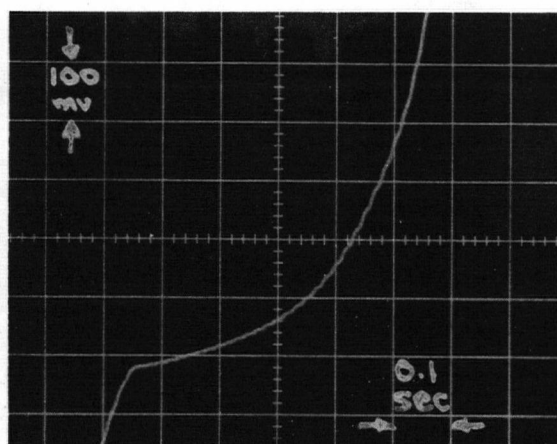
(a) Two In waves plus solvent
 $\tau_1 = 0.33$ sec



(b) Two In waves
 $\tau_1 = 0.274$ sec
 $\tau_2 = 0.35$ sec
 $\tau_1/\tau_2 = 1.28$



(c) First wave only
 $\tau_1 = 0.355$ sec



(d) Second wave only
 $\tau_2 = 0.37$ sec

Figure 29: Typical Chronopotentiograms for In(III)
 (402°C, 2.38×10^{-5} M cm⁻³, 1.90×10^{-2} amp cm⁻²)

The present results are consistent with $n_1 = 2$ and $n_2 = 1$. The slopes of E versus $\log (\tau_1^{1/2} t^{1/2} / t^{1/2})$, for both species soluble in the melt, averaged $0.071 \pm .004$ v., in good agreement with the theoretical value of 0.067 v. for a reversible two-electron reduction.

The two waves are thus due to the following reactions:



Clark et al³⁷ have prepared pure InCl, so it is entirely possible for In^+ to exist in fused salts, even though no In(I) species are stable in aqueous solution³⁸.

Figure 30 shows the plots of $\tau_i^{1/2}$ versus $1/i$ for indium(III). The measured diffusion coefficient for In(III) is $6.1 \pm 0.4 \times 10^{-6} \text{ cm}^2 \text{ sec}^{-1}$ at 400°C . Results at two other temperatures led to an activation energy of $8.8 \pm 2 \text{ k cal mole}^{-1}$.

Cobalt(II)

Graphs of $\tau^{1/2}$ versus $1/i$ for divalent cobalt are shown in Figure 31. The diffusion coefficient of Co(II) at 400°C was determined as $12.1 \pm 1.5 \times 10^{-6} \text{ cm}^2 \text{ sec}^{-1}$. Measurements were also made of the activation energy so comparison could be made with the diffusion coefficient determined by Laitinen and Gaur³⁹,

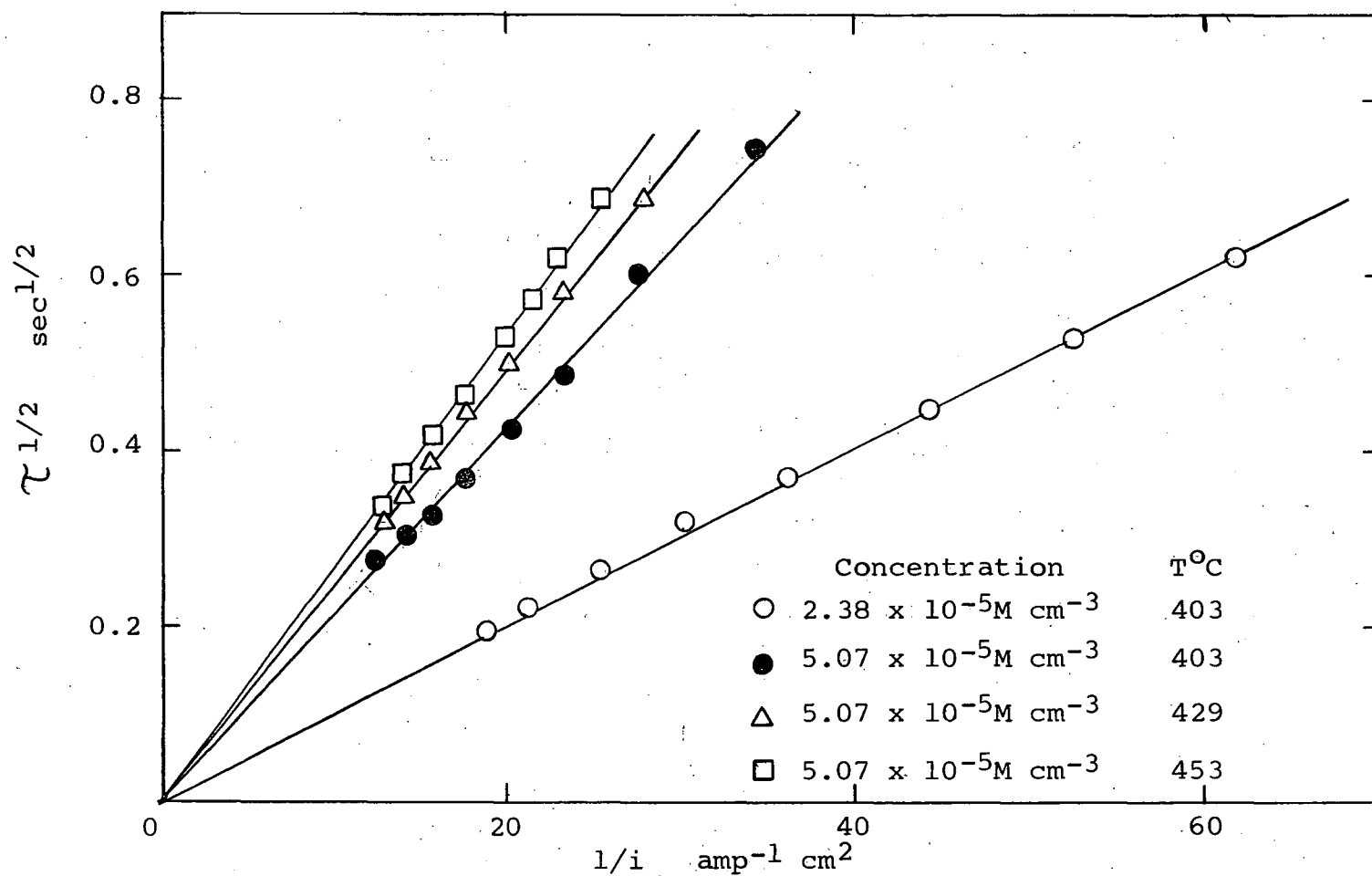


Figure 30: Chronopotentiometric Results for Indium(III)

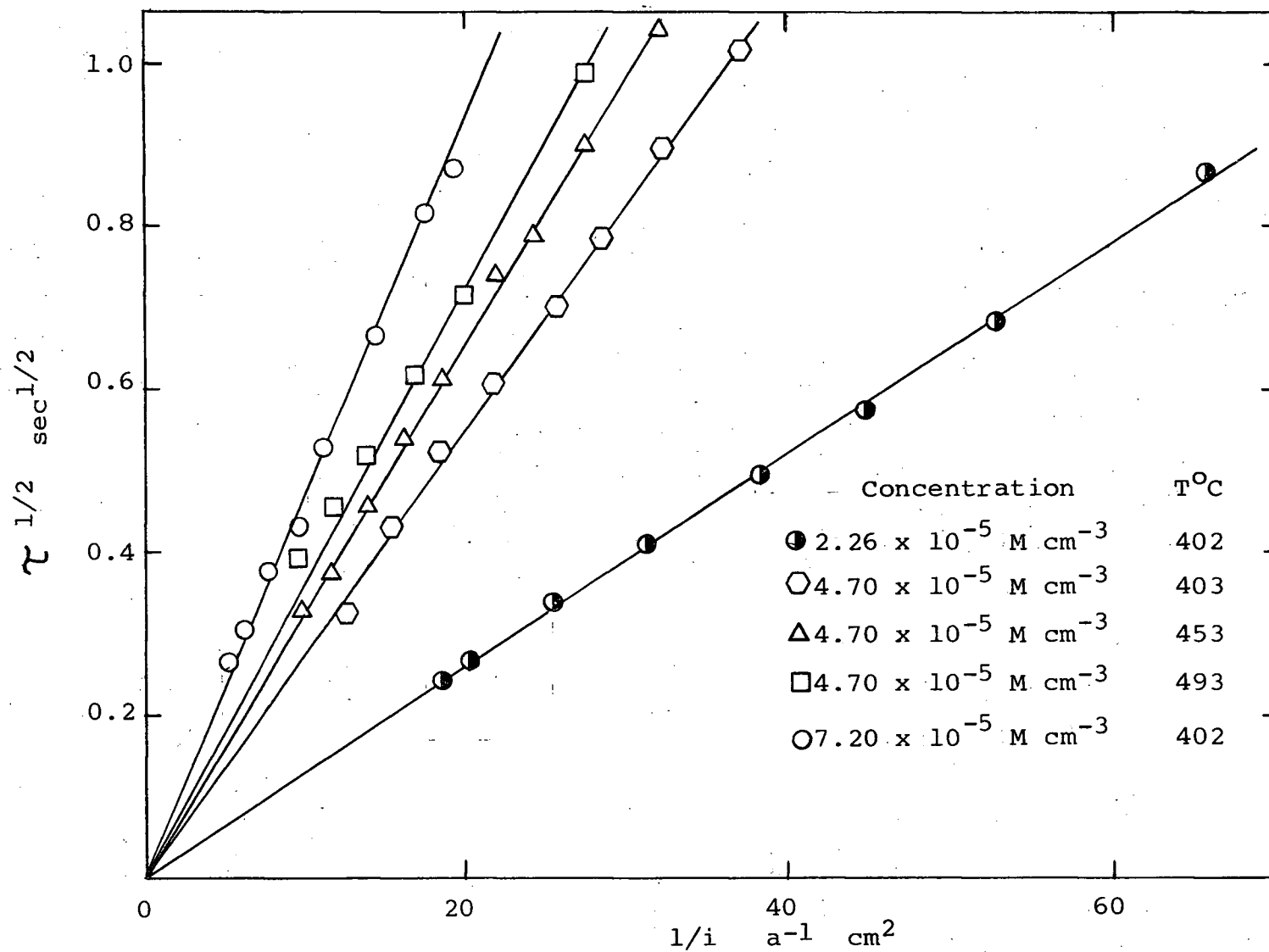
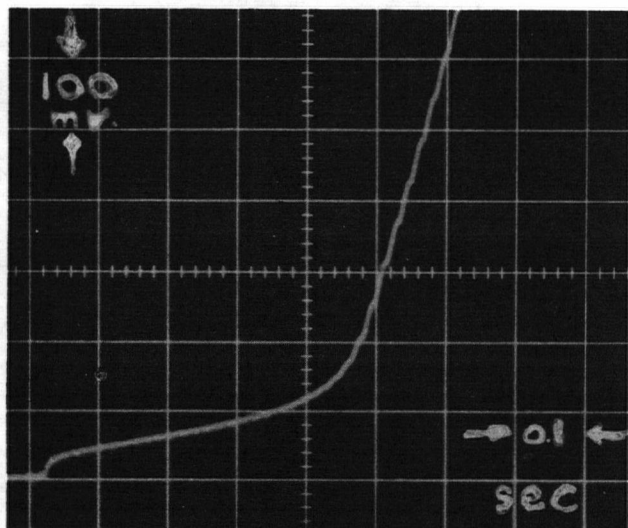
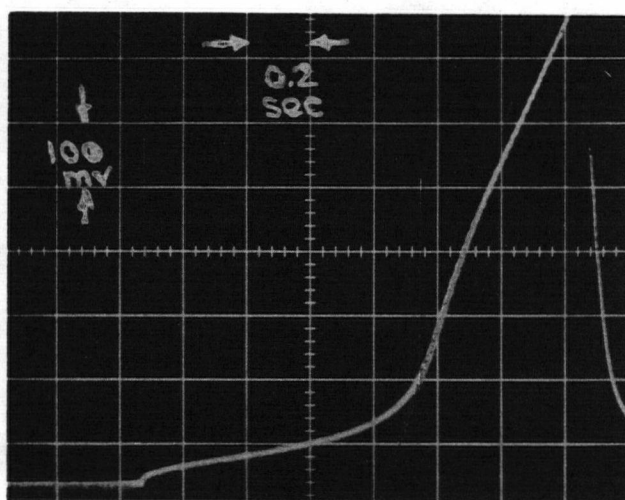


Figure 31: Chronopotentiometric Results for Cobalt(II)



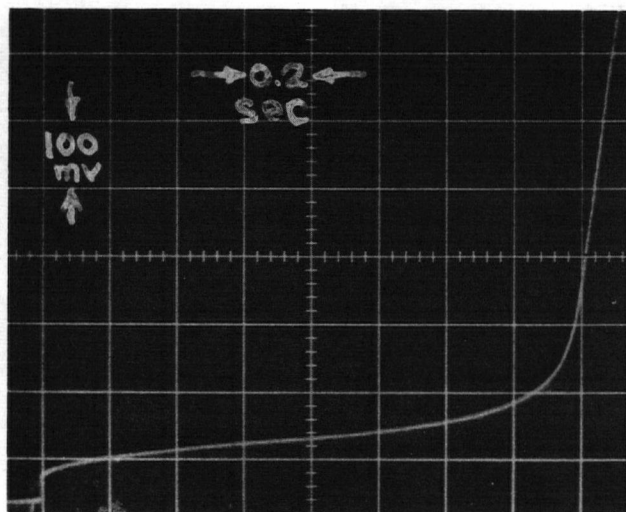
(a) Cobalt(II)

$$\begin{aligned} T &= 400^{\circ}\text{C} \\ i &= 4.87 \times 10^{-2} \text{ a cm}^{-2} \\ C &= 7.20 \times 10^{-5} \text{ M cm}^{-3} \\ \tau &= 0.43 \text{ sec} \end{aligned}$$



(b) Nickel(II)

$$\begin{aligned} T &= 400^{\circ}\text{C} \\ i &= 4.38 \times 10^{-2} \text{ a cm}^{-2} \\ C &= 6.70 \times 10^{-5} \text{ M cm}^{-3} \\ \tau &= 0.88 \text{ sec} \end{aligned}$$



(c) Platinum(II)

$$\begin{aligned} T &= 400^{\circ}\text{C} \\ i &= 2.37 \times 10^{-1} \text{ a cm}^{-2} \\ C &= 1.01 \times 10^{-4} \text{ M cm}^{-3} \\ \tau &= 1.58 \text{ sec} \end{aligned}$$

Figure 32: Typical Chronopotentiograms for Cobalt(II), Nickel(II) and Platinum(II)

$D_{450^{\circ}\text{C}} = 24.2 \times 10^{-6} \text{ cm}^2 \text{ sec}^{-1}$. E was found to be 6.8 ± 1 k cal mole $^{-1}$, and $D_{450^{\circ}\text{C}}$ was $17. \pm 1 \times 10^{-6} \text{ cm}^2 \text{ sec}^{-1}$.

The slopes of potential versus $\log (\tau^{1/2} - t^{1/2})$ plots were on the average 15% higher than the theoretical Nernst slope for a reversible 2-electron reduction.

Figure 32 shows typical chronopotentiograms for Co(II), Ni(II), and Pt(II).

Nickel(II)

Diffusion coefficients measured from the plots of $\tau^{1/2}$ versus $1/i$ in Figure 33 had an average value of $13.7 \pm 1.5 \times 10^{-6} \text{ cm}^2 \text{ sec}^{-1}$.

Potential versus $\log (\tau^{1/2} - t^{1/2})$ slopes are in the same range as those for cobalt, i.e., about 15% higher than theoretical.

Platinum(II)

Measurements for divalent Pt in LiCl-KCl, plotted in Figure 34, gave an average value of $11.8 \pm 1.5 \times 10^{-6} \text{ cm}^2 \text{ sec}^{-1}$ for its diffusion coefficient. Pt(II) reduction appears to be a reversible process, since the average slope of E versus $\log (\tau^{1/2} - t^{1/2})$ plots was determined as $0.073 \pm .007 \text{ v.}$

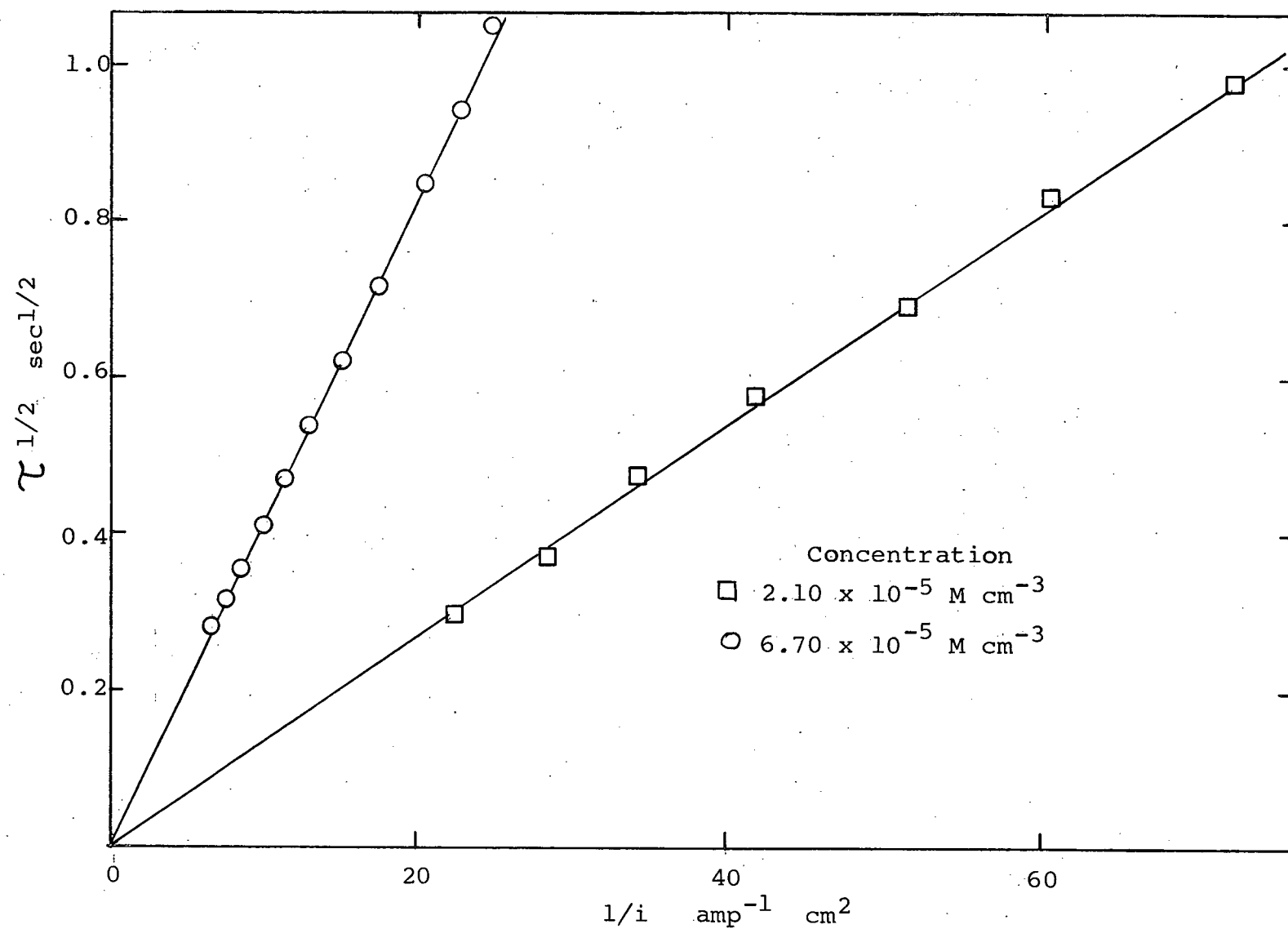


Figure 33: Chronopotentiometric Results for Nickel(II) at 400°C

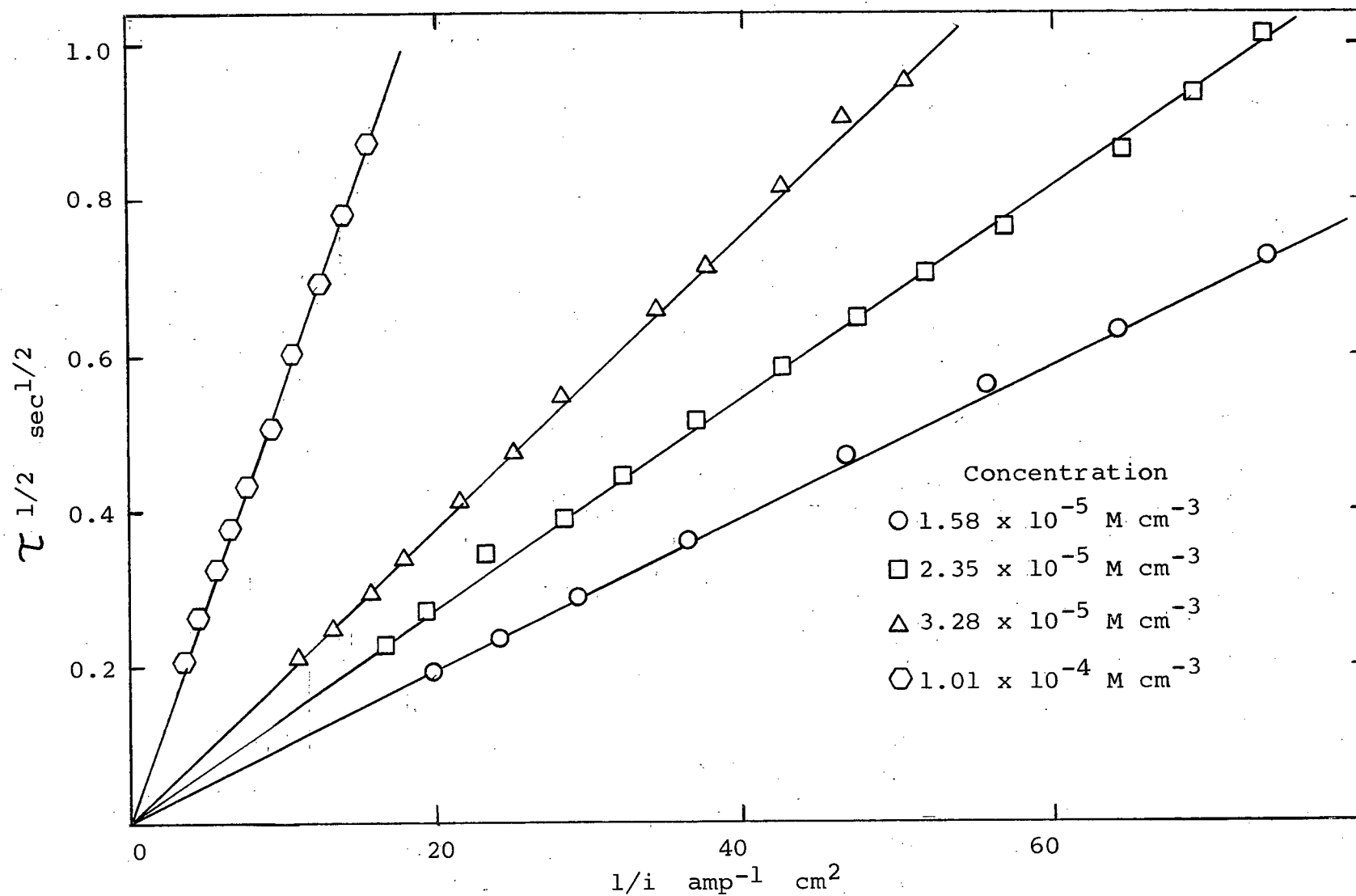


Figure 34: Chronopotentiometric Results for Platinum(II) at 400°C

Following tests at $C = 1.01 \times 10^{-4}$ moles cm^{-3} , sufficient PtCl_2 was added to produce a concentration of about 4×10^{-4} moles cm^{-3} . Argon was bubbled through the solution for 24 hours, and the solution was then sampled and frozen. Analysis indicated a maximum concentration of Pt(II) of 1.56×10^{-4} moles cm^{-3} . Undissolved PtCl_2 was observed on the surfaces of the frozen mass and in the addition tube. The solubility of Pt(II) in LiCl-KCl eutectic at 400°C is therefore approximately $1.5 \pm 0.1 \times 10^{-4}$ moles cm^{-3} . However this value should be treated with caution; the sample analysis may be high due to drawn up undissolved PtCl_2 .

Iron(III)

Tests with trivalent iron in solution resulted in only one wave, that for Fe(II) reduction, since the standard potential of the Fe(III)-Fe(II) couple⁴⁰ is 0.085 v. more noble than the Pt(II)-Pt(0) reference potential.

Iron(II)

Four successive anodizations were carried out, with chronopotentiometric tests conducted after each. Figure 35 shows the plots of $\tau^{1/2}$ versus $1/i$ for the first three concentrations. From these curves, a diffusion coefficient of $15.9 \pm 1.5 \times 10^{-6} \text{ cm}^2 \text{ sec}^{-1}$ was determined. A typical chronopotentiogram is shown in Figure 36a.

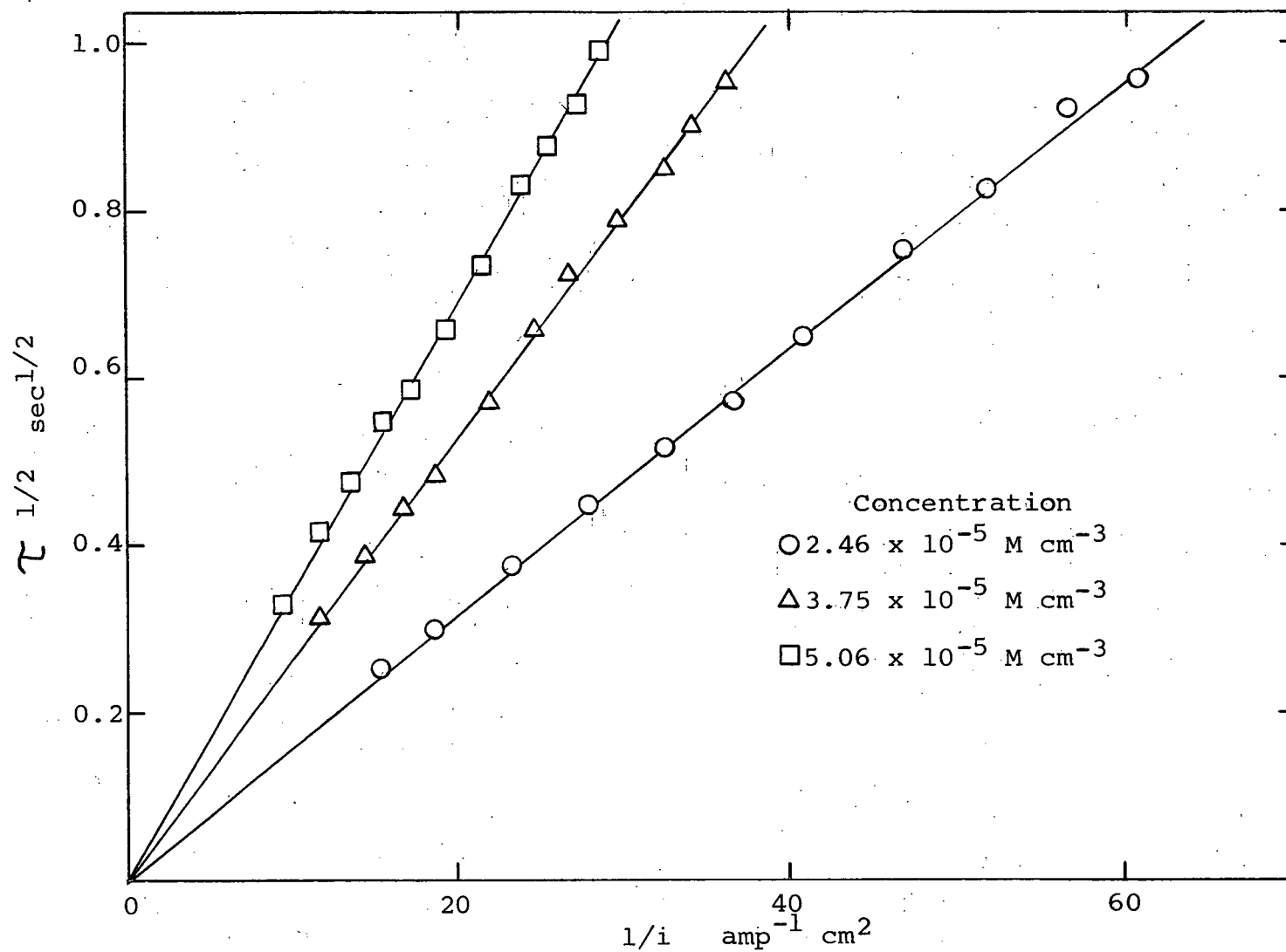
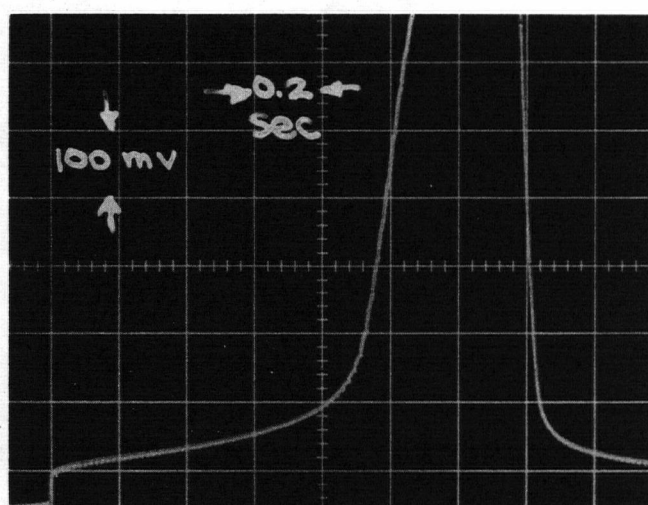
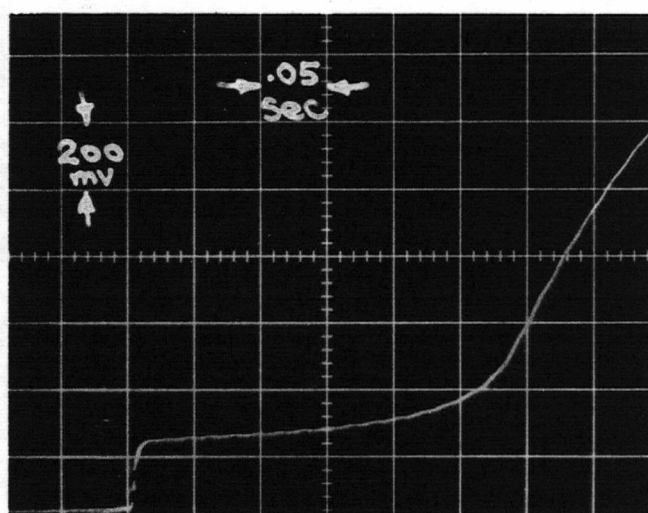


Figure 35: Chronopotentiometric Results for Iron(II) at 400°C



(a) Iron(II)

$$\begin{aligned} T &= 400^{\circ}\text{C} \\ i &= 1.65 \times 10^{-2} \text{ a cm}^{-2} \\ C &= 2.46 \times 10^{-5} \text{ M cm}^{-3} \\ \tau &= 0.92 \text{ sec} \end{aligned}$$



(b) Chromium(II)

$$\begin{aligned} T &= 400^{\circ}\text{C} \\ i &= 4.22 \times 10^{-2} \text{ a cm}^{-2} \\ C &= 3.32 \times 10^{-5} \text{ M cm}^{-3} \\ \tau &= 0.334 \text{ sec} \end{aligned}$$

Figure 36: Typical Chronopotentiograms for Iron(II) and Chromium(II)

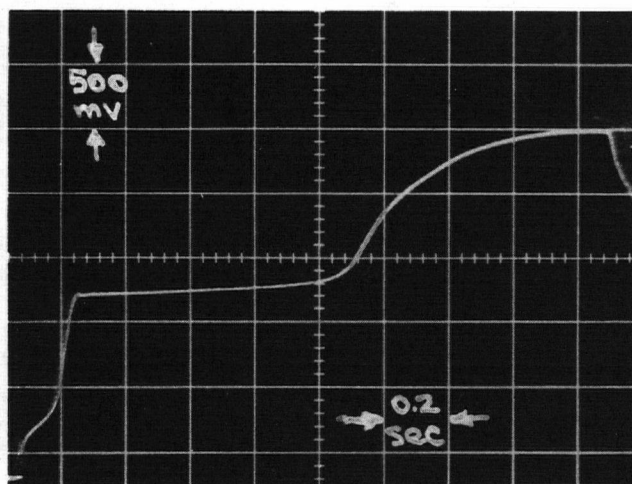
The time of the fourth anodization should have been sufficient to raise the bulk concentration to about 8×10^{-5} moles cm^{-3} . However tests resulted in approximately the same value of $i\tau^{1/2}$ as was obtained before this anodization, indicating that the solubility limit had been reached. The solubility so determined for Fe(II) in LiCl-KCl at 400°C is estimated as 5×10^{-5} moles cm^{-3} . The point should be made that the diffusion coefficient calculated for the third concentration may be low, since the analysis could have been in error because of undissolved FeCl_2 (as in the Pt case). However an average D from the first two concentrations is identical to the average from three concentrations.

The E versus $\log (\tau^{1/2}-t^{1/2})$ slopes averaged 0.073 ± 0.006 v. for four tests.

The divalent iron solutions appear to be quite stable in the present experimental set-up. Analysis of the samples showed no detectable amounts of Fe(III).

Chromium(III)

Two waves were seen in the reduction of Cr^{3+} onto a Pt electrode: typical curves are shown in Figure 37. The potential of the second wave was 1.1 v. more negative than the first, comparable to the potential difference between the Cr(III)-Cr(II)



(a) Chromium(III)

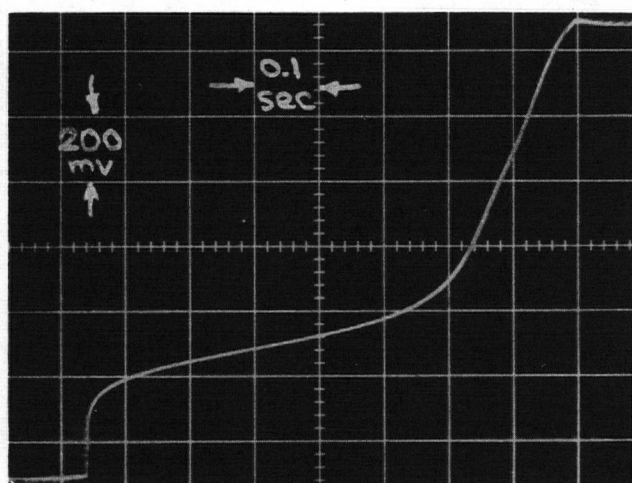
$$T = 400^{\circ}\text{C}$$

$$i = 5.25 \times 10^{-2} \text{ a cm}^{-2}$$

$$C = 8.45 \times 10^{-5} \text{ M cm}^{-3}$$

$$\tau_1 = 0.09 \text{ sec}$$

$$\frac{\tau_2}{\tau_1} = 8.5$$



(b) Chromium(III)

$$T = 400^{\circ}\text{C}$$

$$i = 2.25 \times 10^{-2} \text{ a cm}^{-2}$$

$$C = 8.45 \times 10^{-5} \text{ M cm}^{-3}$$

$$\tau_1 = 0.59 \text{ sec}$$

Figure 37: Typical Chronopotentiograms for Chromium(III)

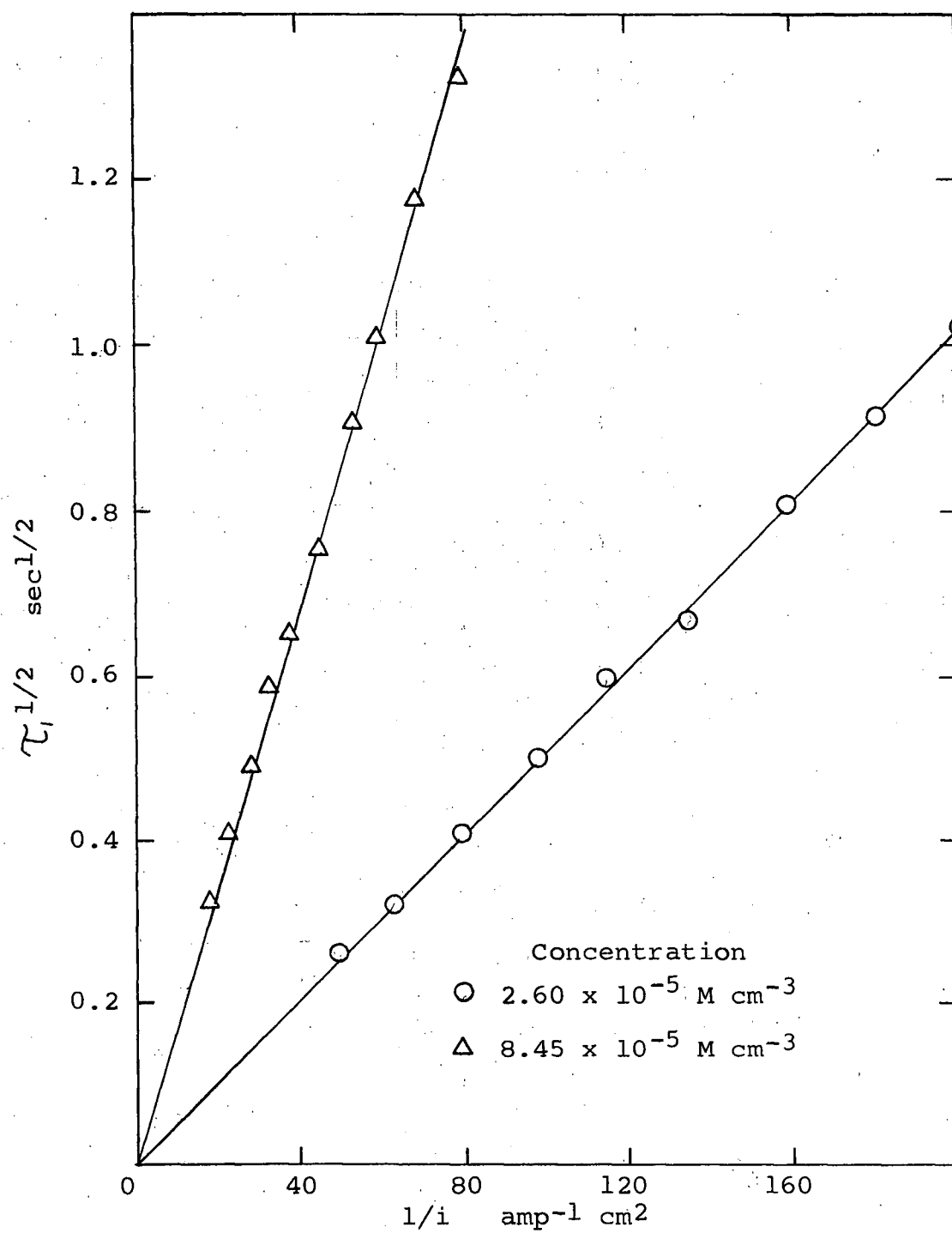


Figure 38: Chronopotentiometric Results for Chromium(III)

and Cr(II)-Cr(0) couples³⁰, 0.9 v. The potential of Cr(III)-Cr(II) is more noble than Ag(I)-Ag(0) by about 0.22 v.

An average of five determinations showed that $\tau_2/\tau_1 = 8.1 \pm 0.5$, in good agreement with the theoretical value of 8 for $n_1 = 1$ and $n_2 = 2$.

The diffusion coefficient of Cr(III) at 400°C is $5.55 \pm 0.3 \times 10^{-6} \text{ cm}^2 \text{ sec}^{-1}$, determined from Figure 38.

Three determinations of the slopes of E versus $\log (\tau^{1/2} - t^{1/2}/t^{1/2})$ plots gave $0.145 \pm .003 \text{ v.}$, reasonably close to the theoretical value of 0.134 v. for a reversible 1-electron reduction.

Chromium(II)

The diffusion coefficient of Cr(II), evaluated from the $\tau^{1/2}$ versus $1/i$ plots of Figure 39 for two concentrations, is $17.6 \pm 1.6 \times 10^{-6} \text{ cm}^2 \text{ sec}^{-1}$. A typical chronopotentiogram is shown in Figure 36b.

The apparent solubility limit of Cr(II) in LiCl-KCl is approximately $3.7 \times 10^{-5} \text{ moles cm}^{-3}$, indicated by a constant $i\tau^{1/2}$ phenomenon similar to that observed for Fe(II).

Slopes of potential versus $\log (\tau^{1/2} - t^{1/2})$ plots averaged $0.076 \pm 0.008 \text{ v.}$

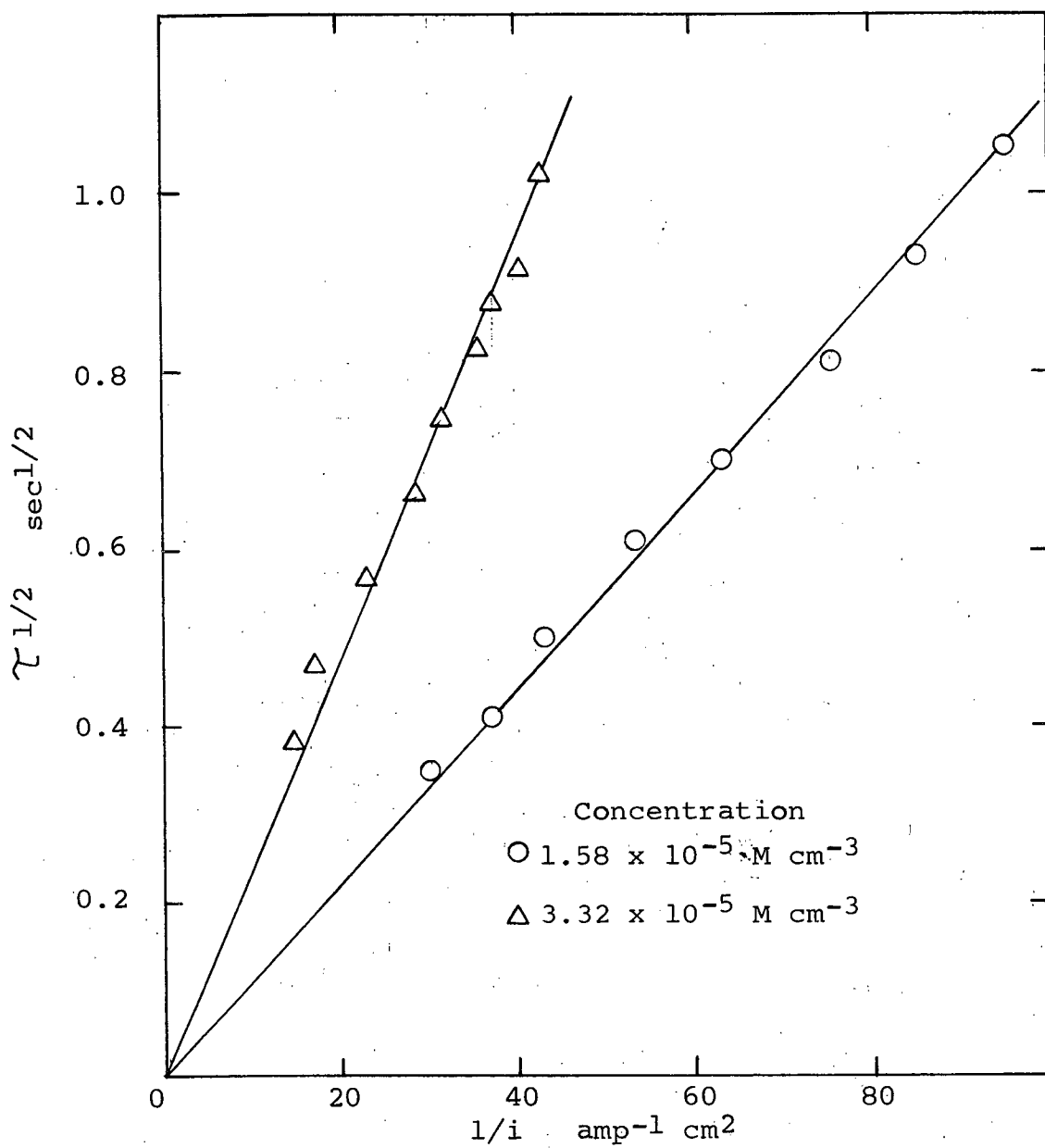


Figure 39: Chronopotentiometric Results for Chromium(II)

Titanium(III) and Molybdenum(V)

Chronopotentiometric data for these solutes was incomplete. The results are presented in Appendices E and F.

DISCUSSION

Diffusion in LiCl-KCl

A summary of ionic diffusion coefficients in molten LiCl-KCl eutectic, including both those measured in this work and those from the literature, is given in Table XXI. The most striking feature of these values is the marked dependence of D on the charge of the diffusing species, illustrated in Figure 40.

Diffusion in liquid metals, and self-diffusion in some molten salts such as NaCl,⁴¹ is found to approximately obey the Stokes-Einstein equation

$$D = kT/6\pi r\eta \quad (24)$$

where r is the radius of the diffusing species and η is the medium viscosity. However Stokes-Einstein behaviour is invalid for simple ions in LiCl-KCl, as shown by the comparison of diffusion coefficients with ionic radii made in Table XXII; ions with the largest radii (e.g., Ag^+ , Tl^+) have the highest diffusion coefficients. Equation 24 may be valid if the diffusing species is significantly enlarged due to complex formation.

TABLE XXI

IONIC DIFFUSION COEFFICIENTS IN LiCl-KCl

Ion	T°C	E kcal mole ⁻¹	D x 10 ⁶ cm ² sec ⁻¹	Reference
Ag(I)	400	5.8	24	35
	400		32	present study
	450		26, 21, 33, 40	33, 39, 42, 34
	500		46	43
Cu(I)	450		35	33
	500		67	43
Tl(I)	450		38.8	39
Pb(II)	400	7.9	8.9	35
	400	7.5	12.6	present study
	450		21.8, 22, 17	42, 44
	500		20.3	43
Cd(II)	400	6.5	12.1	35
	450		17, 21, 18	33, 42, 44
	500		27.5	43
Co(II)	400	6.8	12.3	present study
	450		24.2	39
Pt(II)	400		11.9	present study
	450		15	45
Pd(II)	450		14	45
Ni(II)	400		13.7	present study
	500		41.4	43
Fe(II)	400		15.9	present study
Cr(II)	400		17.6	present study
Bi(III)	400	9.8	6.3	35
	450		6, 28, 8	33, 42, 45
Cr(III)	400		5.6	present study
In(III)	400	8.8	6.1	present study
Sb(III)	450		12	45
U(IV)	400	7.7	4.9	35

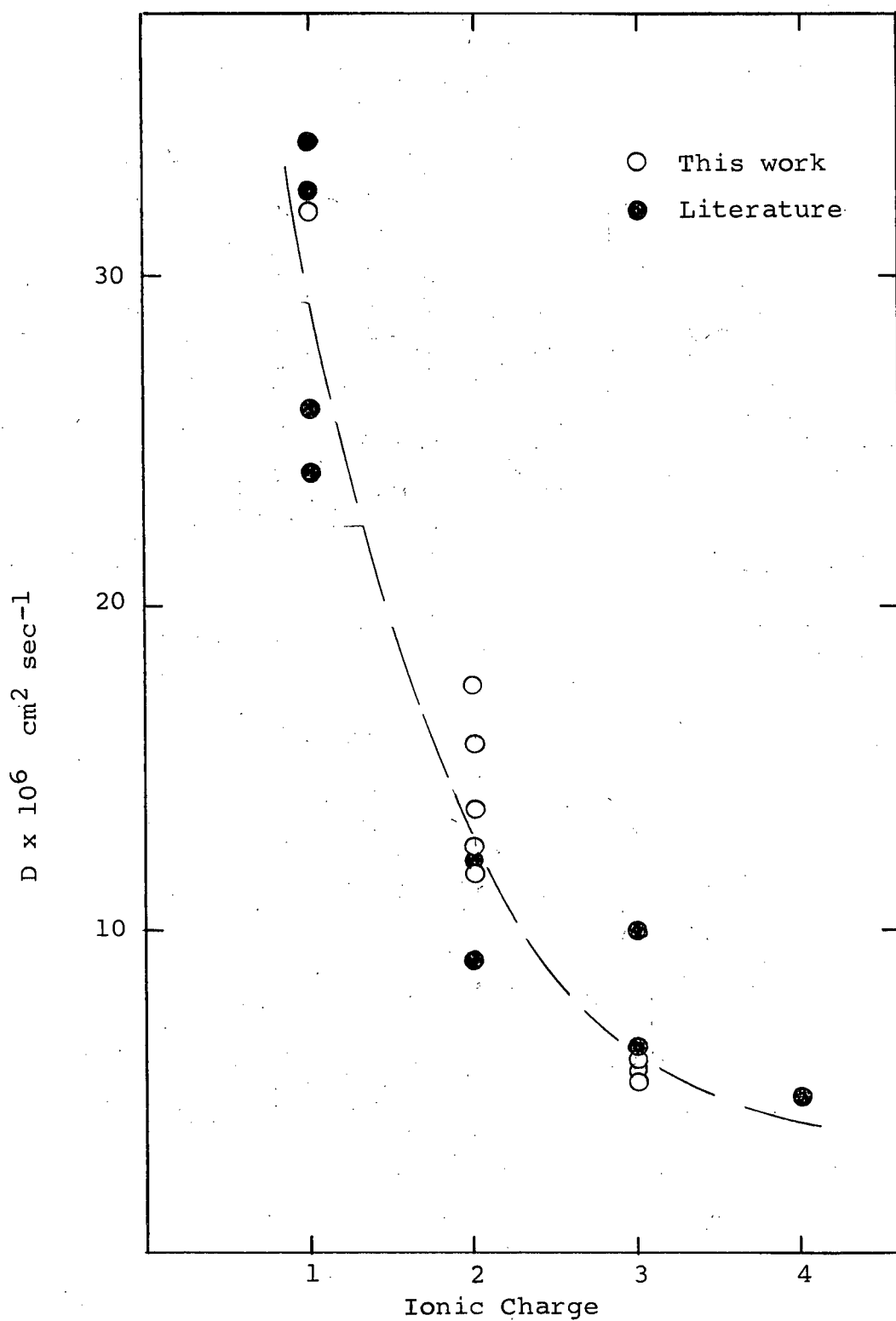


Figure 40: Dependence of Diffusion Coefficients of Ions in LiCl-KCl on Ionic Charge

TABLE XXII
METAL ION DATA

Ion	Radius $\text{\AA}$	Atomic Mass	$D_{400} \times 10^6$ $\text{cm}^2 \text{sec}^{-1}$
Ag ⁺	1.26	107.87	32
Li ⁺	0.60	6.94	
Na ⁺	0.95	22.99	
K ⁺	1.33	39.10	
Tl ⁺	1.44	204.37	35
Cu ⁺		63.54	33
Pb ⁺⁺	1.21	207.19	12.6
Co ⁺⁺	0.72	58.93	12.3
Ni ⁺⁺	0.69	58.71	13.7
Fe ⁺⁺	0.75	55.85	15.9
Pt ⁺⁺	0.52	195.09	11.9
Pd ⁺⁺	0.50	106.4	11
Cd ⁺⁺	0.97	112.4	12.1
Bi ⁺⁺⁺	1.20	208.98	6.3
Cr ⁺⁺⁺	0.65	52.00	5.6
In ⁺⁺⁺	0.81	114.82	6.1
U ⁺⁺⁺⁺	0.89	238.03	4.9

The absorption spectra of transition metal chlorides in LiCl-KCl indicate the existence of complex ions; a partial list is given in Table XXIII.

TABLE XXIII
COMPLEX SPECIES IN LiCl-KCl⁴⁶

Solute	Complex Species
Ti(III)	TiCl_6^{3-}
Cr(III)	CrCl_6^{3-}
Fe(II)	FeCl_4^{2-}
Co(II)	CoCl_4^{2-}
Ni(II)	NiCl_4^{2-}
Cu(II)	CuCl_4^{2-}

Deviations from ideal activity behaviour observed by Yang and Hudson⁴⁷ for several solutes in LiCl-KCl have been interpreted in terms of complex formation. PbCl_2 and AgCl form nearly ideal solutions, suggesting that complex formation is slight. Significant negative deviations for CdCl_2 , MgCl_2 and ZnCl_2 may indicate more stable complexes for these solutes.

A consideration of the available data indicates that more highly charged ions are more likely to form complex ions.

However the effect of complex ion formation on diffusion cannot be significant unless the degree of complexing is large. In fact an explanation of diffusion coefficient trends on this basis would require that ion complexing be either complete or irreversible; the latter seems unlikely in view of electrochemical measurements in fused salts.

Solid salts have volume expansions on melting of the order of 20%, compared to 5% or less for liquid metals. This overall expansion, not accompanied by a corresponding increase in nearest neighbour separations, is interpreted in terms of the formation of a random distribution of free volume, or holes, in the liquid salt. Diffusion processes can be interpreted in terms of the hole theory by assuming that heats of activation reflect the amount of work required to create a solute sized hole and the work involved in the jump process; Bockris and Hooper⁴⁸ have shown that the latter is probably quite small. The average hole diameter calculated for molten KCl at 800°C is about $2.1 \text{ \AA}$, significantly larger than the simple ionic radius for the largest solute ion studied in LiCl-KCl (Tl^+ , $r = 1.44 \text{ \AA}$). The assumption of complex ion formation is thus required to rationalize the present data in terms of the hole theory.

Diffusion data in other systems is sparse; Table XXIV lists the available known diffusion coefficients. Data for the NaCl-KCl system indicates the same charge effect observed for LiCl-KCl, since the coefficients for divalent ions lie in the

TABLE XXIV

IONIC DIFFUSION IN FUSED SALTS OTHER THAN LiCl-KCl

Solvent	Solute	T°C	$D \times 10^6$ $\text{cm}^2 \text{sec}^{-1}$	E kcal/mole	Ref.
NaCl-KCl	Pb ⁺⁺	701	24		49
	Pb ⁺⁺	710	70		
	Zn ⁺⁺	710	23		
	Ag ⁺	710	45		50
	Ni ⁺⁺	710	14		
	Cd ⁺⁺	710	37		
	Pb ⁺⁺	720	48±17		51
LiNO ₃ -NaNO ₃ -KNO ₃	Zn ⁺⁺	160	1.5	9.5	
	Cd ⁺⁺	160	1.5	13	52
	Pb ⁺⁺	160	1.8	13	
	Ni ⁺⁺	160	1.2	10	
NaNO ₃ -KNO ₃	Pb ⁺⁺	263	2.3		
	Cd ⁺⁺	263	5.1		36
	Ag ⁺	263	7.2		
	Ag ⁺	297	13.0		
	Ag ⁺	300	10.6		53

same range ($14-40 \times 10^{-6} \text{ cm}^2 \text{ sec}^{-1}$ at $\sim 700^\circ\text{C}$) while D_{Ag^+} is somewhat higher. The values for four divalent solutes in the

Li-Na-K nitrate melt are each within 20% of $1.5 \times 10^{-6} \text{ cm}^2 \text{ sec}^{-1}$ at 160°C . Data for $\text{NaNO}_3\text{-KNO}_3$ again indicates that lower charged ions have higher diffusion coefficients.

The general conclusion may be made that ionic diffusion in fused salts, particularly LiCl-KCl eutectic melts, is primarily influenced by the charge of the diffusing species.

Reversibility of Metal Ion Reductions in LiCl-KCl

The transition metal ions exhibit, in many cases, substantial activation polarization during their deposition from aqueous solution⁵⁴. Thus it is expected that these same solutes would be the most likely ions to show irreversibility upon deposition from fused salts.

The present results indicate that these reductions, and those for non-transition metals, are reversible. The slightly higher than theoretical Nernst slopes for some of the tests are most likely attributable to impurity reduction or electrode contamination, especially in view of the experimental evidence for reversible reductions listed in Table XXV.

TABLE XXV

REDUCTION SYSTEMS WITH EXPERIMENTALLY
OBSERVED REVERSIBILITY

Ion	Solvent	Electrode	T°C	Method	Ref.
Pb(II)	LiCl-KCl	Liquid Pb	400	Chronopotentiometry	36
Cd(II)	LiCl-KCl	Pt	450	Polarography	55
Bi(III)	"	"	"	"	
Cr(III)	"	"	"	"	
Cr(II)	"	"	"	"	
Pt(II)	LiCl-KCl	Pt	450	Impedance	56
Ni(II)	"	"	"	"	
Co(II)	"	"	"	"	
Pb(II)	LiCl-KCl	W	500	Polarography	43
Cd(II)	"	"	"	"	
Ni(II)	"	"	"	"	
Cu(I)	"	"	"	"	
Ag(I)	"	"	"	"	
Pb(II)	PbCl ₂	Liquid Pb	530	Polarization	57
"	PbCl ₂ -KCl	"	600	Curves	
Cd(II)	CdCl ₂	Liquid Cd	590		
"	CdCl ₂ -KCl	"	590		
Sn(II)	SnCl ₂	Liquid Sn	350		
Zn(II)	ZnCl ₂	Liquid Zn	490		
	ZnCl ₂ -KCl	"	490		

Reduction Experiments

The reduction experiments can be divided into three basic types according to the deportment of the reduced metal.

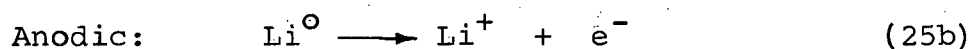
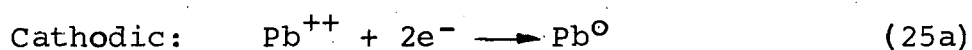
- (1) The metal dissolves in the lead alloy.
- (2) The metal forms as a new phase at the alloy-salt interface.
- (3) Some of the metal is dispersed throughout the salt phase.

Reductions with Alloy Dissolution

The reductions of Pb^{++} , Cd^{++} , In^{+++} and Ag^+ with Li, the reduction of Cr^{+++} with Pb and the reduction of Li^+ with Na are all of the first type and appear to occur by boundary layer diffusion without complications.

Pb^{++} Reduction

The reduction of Pb^{++} with Li was most extensively examined. In this system the electrochemical effect, illustrated by previously discussed experiments, indicates that the interface reaction can be described by two half-cell reactions:



The cathodic reaction can then occur on all metallic surfaces

in electrochemical contact with the anodic process, while the latter occurs only where there is a source of Li^0 , i.e., on the alloy surface.

The rate expression for Pb^{++} reduction can be written in the form

$$\frac{d(\text{Pb}^{++})}{dt} = k (\text{Pb}^{++}) \quad (26)$$

$$\text{where } k = \frac{DA}{\delta V_s} = \frac{D}{\delta h_s}$$

and A is the total area of the cathodic surface.

The extra cathodic area (e.g., crucible - salt contact) will be less active in cases where the potential drop due to the crucible resistance is an appreciable fraction of the reaction driving force. The observations of Grimble et al³, described in the Introduction, might be explained on this basis.

Reduction of Ag^+ , Cd^{++} , In^{+++} and Cr^{+++}

The similarity of boundary layer thicknesses for these reductions to those for the reduction of Pb^{++} indicates that the rate-controlling mechanism in each case is the boundary layer diffusion of each species in the salt phase.

The value of δ for Cr^{+++} reduction is somewhat higher than for the others, possibly since this reduction involves no metal phase diffusion. The fact that the rate of the Cr^{+++} reaction is similar to rates for the other cases in this group is additional evidence that these reactions are salt phase transport controlled.

Nature of the Boundary Layers

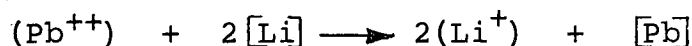
Salt Phase

The effect of agitation on the salt-phase boundary layer is shown in Table XXVI.

TABLE XXVI
EFFECT OF AGITATION ON δ_s

rpm	k min ⁻¹	δ_s cm
0	0.014	0.0175
64	0.014	0.0175
112	0.022	0.0112
224	0.053	0.0046

The negligible effect below 64 rpm can be attributed to the effectiveness of natural convection. The reduction



involves an appreciable change in phase densities in the boundary

layers. In the salt, one mole of lead (M.W.207) is replaced by two moles of lithium (M.W. 7) so that the interfacial salt region becomes less dense than the bulk, thus contributing to convection. The exothermic heat of reaction, concentrated in the interfacial region, would contribute to natural convection in a similar manner. A comparison of boundary layer thicknesses for 25 mm and 5 mm crucibles shows that δ for the small tubes is only a factor of two larger, indicating that density and thermal effects do indeed provide a significant amount of convection.

The effect of agitation above 64 rpm fits the relation

$$\delta \propto 1/(\text{rpm})^{0.8} \quad (27)$$

Temperature effects are probably small in view of the correspondence between the activation energies of diffusion and reaction.

As mentioned previously, δ depends on $D^{0.3}$.

The salt phase boundary layer thickness under the conditions of this study is, then, largely a function of the flow conditions.

Alloy Phase

Very little data was obtained which would lead to values of δ for the metal phase. If the Li^+ reduction experiments are controlled by alloy diffusion of Na, then δ is approximately 0.003 to 0.006 cm*. The validity of this value can be examined with respect to the following evidence:

- (1) the viscosity of molten lead, 2.32 cp. at 400°C⁵⁹, is less than half that for LiCl-KCl⁶⁰, 5.50 cp, at the same temperature.
- (2) the alloy phase was unstirred (δ for unstirred salt is about 0.017 cm).
- (3) the density changes during the reaction are such that the boundary region becomes less dense than the bulk alloy.

In view of this information the calculated values of δ seem somewhat low.

To summarize, reductions of type (1), i.e., those in which the reduced metal dissolves in the lead alloy, are rate-controlled by diffusion of the ionic species across a boundary layer in the salt phase. The values of the salt phase

* Calculated using $D_{\text{Na}} = 10 \times 10^{-6} \text{ cm}^2 \text{ sec}^{-1}$ at 400°C and 3.3 w/o, determined by reference 58.

boundary layer thickness δ_s are in the range 0.005 to 0.02 cm; δ_s is largely dependent on agitation conditions, and slightly dependent on the diffusion coefficient D . These reductions appear to occur electrochemically.

Reductions with Reduced Metal at the Interface

The reductions of Co^{++} , Cr^{++} and Ti^{+++} with Li and the reduction of Ni^{++} with Pb each resulted in the deposition of metal at the salt-alloy interface. Also, the rates of these reactions are higher than those in which the reduced metal dissolves in the alloy.

Since these reactions are probably electrochemical, the deposited metal effectively increases the cathodic area* by acting as a conduction path for electrons, and rates are increased in much the same manner as the use of stainless steel crucibles resulted in increased Pb^{++} reduction rates. The interfacial area may be increased to the extent that diffusion in the salt phase ceases to be rate-controlling. The Co^{++} runs in particular show that the metal deposit has a very large surface area; the rates at three different initial alloy lithium

* This assumes that the deposited metal forms dendrites or sponge extending well beyond the normal boundary layer thickness, a condition substantiated by observation (e.g., Fig. 20).

concentrations indicate that diffusion of Li in the alloy may be the rate-determining step.

The solubilities of Co, Ni, Pt and Cr in liquid lead at 400°C are tabulated in Table XXVII. Although no data is available for the solubility of Ti in lead, the value is assumed to be very small.

TABLE XXVII
SOLUBILITIES OF METALS IN LIQUID LEAD (400°C)

Element	w/o	Solubility moles in 100 gm Pb	Ref.
Co	0.044	7.5×10^{-4}	61
Ni	0.20	3.4×10^{-3}	62
Pt	13	6.7×10^{-2}	59
Cr	0.01*	2×10^{-4}	63

* Solubility is 0.01 at 900°C

Each of the reduction processes involved the reaction of approximately 3 to 4×10^{-3} moles of metal. In the cases of Cr and Ti, the metal solubilities are much too small for the produced metal to dissolve in the alloy phase, so metallic Cr and Ti are nucleated at the interface.

About 20% of the reduced Co and all of the reduced Ni should dissolve in the lead phase. Calculations can be made to determine the steady state diffusion fluxes in the two phases for these two systems. The following assumptions are made:

- (1) the alloy surface region rapidly becomes saturated with the reduced metal.
- (2) the diffusion coefficients of Co and Ni in liquid lead are $2.5 \times 10^{-5} \text{ cm}^2 \text{ sec}^{-1}$ (estimated from the data of Niwa et al⁶⁴ for diffusion of Sn, Bi, Sb, and Cd in lead)
- (3) the boundary layer thickness in the alloy phase is about 0.006 cm (as estimated previously).

Table XXVIII lists the calculated fluxes; Figure 41 illustrates the concentration gradients.

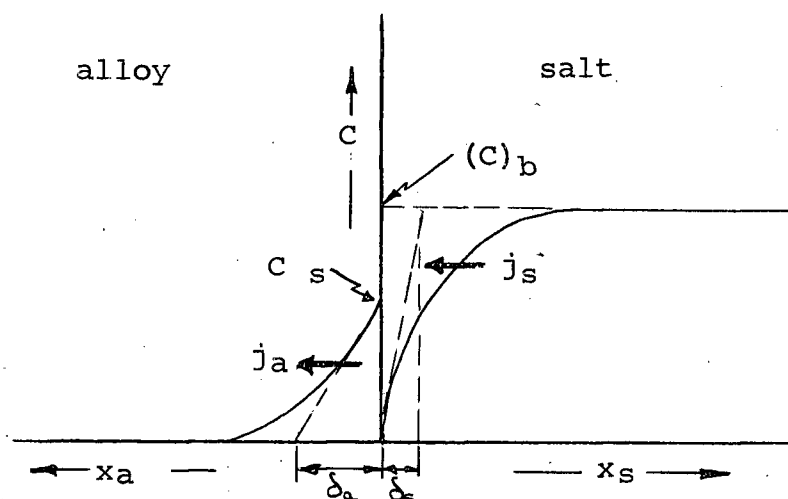


Figure 41: Concentration Gradients Assumed for Flux Calculation

TABLE XXVIII
THEORETICAL FLUX CALCULATIONS

Ion or Element	Flux (moles sec ⁻¹ cm ⁻²)	
	j_a	j_s
Co	3.1×10^{-7}	3.5×10^{-7}
Ni	1.4×10^{-6}	3.3×10^{-7}

The salt-phase fluxes are probably accurate to within 10-20%, since salt phase diffusion coefficients and boundary layer thicknesses have been determined in this work. The alloy phase fluxes are, unfortunately, subject to greater error; diffusion coefficients and values of δ could only be estimated.

The calculations show that the alloy flux for Co reduction is smaller than the salt phase flux; the reverse holds for Ni reduction.

The presence of Co metal is not then surprising, in view of the small flux and the fairly low solubility. It is more difficult to explain the behaviour of Ni. Perhaps the steady state flux calculations are not valid; for many experiments in this study the initial reduction rates are abnormally fast, because the method of initiating the reactions causes a

certain amount of phase mixing. The appearance of Ni at the interface cannot be rationalized in any other way.

The conclusion can be made that the appearance of reduced metal at the interface for these reductions is caused by low metal solubility in the alloy phase. The mechanism of reduction of Ni^{++} with Pb is not fully understood, but probably combines alloy surface nickel saturation with slow mass transfer of Ni in the alloy.

Reductions with Salt Phase Metal Dispersion

The lithium reductions of Ni^{++} and Pt^{++} (and Ti^{+++} to a small degree) were very interesting cases, since reduced metal was dispersed throughout the salt phase. The Pt^{++} reaction also had reduced metal at the interface. In view of the unusual behaviour of these reductions, a speculative discussion of possible mechanisms was thought to be worthwhile. Possible homogeneous reduction mechanisms may involve electronic conduction or metal solubility in the salt.

Solutions* of metals in their own salts are of two general classes:

* These are true solutions, not colloidal suspensions.

- (1) the dissolving metal imparts its metallic character to the melt, thus providing some degree of electronic conductivity. The solution is pictured as a random mixture of anions and electrons within a cation "lattice", with the electrons in shallow traps (analogous to F centers in solids, but the electrons are not restricted entirely to the anion volume).

The dissolution process may be



This type of solution is exhibited by the alkali metal chlorides and some alkaline earth and lanthanide chlorides. The degree of electronic conductivity in systems of this type is not really appreciable. For example, the specific conductance of a 4 mole % Na in NaCl solution at 850°C is only 50% larger than that of pure NaCl. This can be contrasted to a solution of Na in liquid NH₃ at -34°C, where the addition of 2 - 2.5 mole % Na increases the conductivity by more than 15 times.

- (2) the metal may dissolve in such a way as to lose its characteristic properties, i.e., by an oxidation-reduction reaction with its salt, with the formation

* For detailed reviews on solutions of metals in salts see Corbett⁶⁵ and Bredig⁶⁶.

of a subhalide which provides no mobile electrons for conduction. Most of the transition and heavy metals show this type of behaviour. Conductivity measurements on these systems usually indicate slight decreases of overall conductivity on addition of metal. Conflicting evidence for solutions of Pb in PbCl_2 has been presented. Herzog and Klemm⁶⁷ indicated by moving boundary experiments that an equilibrium exists between Pb^0 , Pb^{++} and electrons, with the electron mobility ~ 5 times that of the chloride ion relative to Pb^{++} . However Duke and Laity⁶⁹ reported that the conductivity of PbCl_2 does not change on saturation with metal at 600°C (0.02 mole%), indicating that if electrons are present they are not "mobile".

Table XXIX is a selected list of metal solubilities in fused chlorides.

Experimental evidence indicates that solutions of metals in salts are specific, i.e., the apparent solution, if any, of a metal in a salt of a different metal can be considered as a oxidation-reduction reaction superimposed on the solution phenomenon.

TABLE XXIX
SOLUBILITIES OF METALS IN FUSED SALTS

Metal	Salt	T°C	Solubility mole %	Ref.
Li	LiCl	640	0.5	32
		1000	2.0	
Na	NaCl	950	8	69
K	KCl	770	15	70
Li + K	LiCl-KCl	350	1	71
		550	3	
Ag	AgCl	520	0.012	72
Ni	NiCl ₂	980	9.1(eutectic)	73
Pb	PbCl ₂	600	0.020	74
		700	0.052	
		800	0.123	
Bi	BiCl ₃	202	28.0	75
Cd	CdCl ₂	550	14.0	76

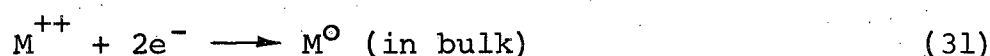
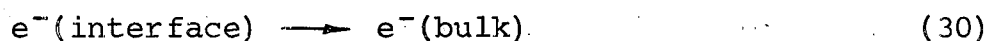
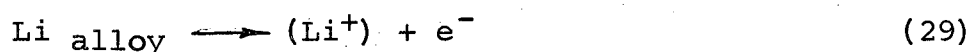
Heymann and Weber⁷⁷ discovered that, although Bi, Sb, Tl, Sn, Au, Cd and Pb are insoluble in liquid NaBr, in the presence of sodium metal the intermetallics Na₃Bi, Na₃Sb, NaSn and NaAu are transferred to the salt. At the temperatures of the experiments (700-800°C) no transfer of a Na-Pb intermetallic was noted. However Heymann attributed this difference in the case of lead to the melting points of the intermetallic compounds. For those cases in which transfer was observed the intermetallics have high melting points, close to the experimental temperatures, and thus the intermetallic compound is

presumably stable in the liquid. In the sodium-lead system the intermetallics have low melting points, and so probably do not exist in the liquid state at 800°C.

The solubility of combined Li and K in LiCl-KCl has been estimated by Bredig⁷¹ as 1 mole % at 350°C; this value seems high for the present experimental conditions since no K metal is present, and Li metal is not at unit activity in the alloy. The actual solubility of Li in LiCl-KCl is thus expected to be significantly less than 1 mole%. In view of the magnitudes of the previously discussed electronic conductivities, and also in view of the fact that the rates measured for the reductions of Pb^{++} , Cd^{++} , Ag^+ and In^{+++} are consistent with diffusion control with no homogeneous reaction, the mechanism of homogeneous reduction observed for Ni(II) and Pt(II) probably does not involve electronic conductivity.

Even though the solubility of Li is small, it is conceivable that the homogeneous reduction may be due to a solubility phenomenon. As shown by the Na reduction experiments the rates of transfer of alkali metals in the systems examined are quite high. The mechanism may involve a continuous flux of Li into the salt; homogeneous reaction with Ni^{++} could prevent saturation of the metal-melt system. The solubility of Li in

the salt may not have to be very significant at all for this mechanism to proceed. However if Li dissolves according to reaction 28, a knowledge of the electron location and mobility would be required to assess the mechanism. For example, the following reactions may occur:

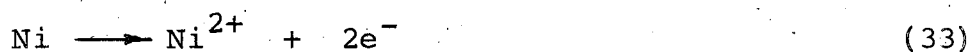


Platinum and nickel nucleations are suspected of being energetically easier than for other metal nucleation in aqueous solutions; if the same were true in fused salts, then reaction (31) above may occur for Ni and Pt and not for the other solutes examined here.

Johnson et al⁷³ have demonstrated the high solubility of Ni in NiCl_2 , and postulated that the freezing point depression data indicated the possibility of



Bredig⁶⁶ states that another possibility is



The homogeneous reduction may then involve the reaction of Li (or an electron) with Ni^{++} to produce Ni^+ , which, on the above basis, may be stable. Upon cooling, the monovalent species would disproportionate to produce Ni metal. The corresponding M^+ ions for Cr, Mn, Fe and Co are definitely less stable according to data for the respective M-MX_2 systems.⁷⁸ However Cu^+ has a well-known stability; if the above mechanism involving Ni^+ has any validity then the Li reduction of CuCl_2 should show a similar homogeneous reduction.

The observations of Heymann indicate another possible mechanism. At the temperatures involved in this work, intermetallic compounds of Li and Pb may be stable in the liquid alloy, and may transfer to the salt phase. As an uncharged solute, the intermetallic could have quite a high diffusion rate. The mechanism would then involve the reduction of Ni^{++} by Li from the soluble intermetallic compound. Interestingly enough, the insoluble portion of the Ni salt contained about 10 w/o lead. Also analyses of an experiment conducted with LiCl-KCl salt and a Pb-Li alloy indicated the presence of 0.02 to 0.09 w/o Pb in the salt phase; this may have been contamination of some type, or it may have been caused by Li-Pb solution.

The platinum mechanism may be similar to that for Ni. Certainly the solubility of Pt in lead (~ 13 w/o) is much too high to cause precipitation of metal at the interface.

The above discussion is, admittedly, largely speculative. However the author feels that the apparent homogeneous reduction is the most intriguing aspect of this work, and indicates some interesting problems for future work.

In summary, the mechanism of homogeneous reduction observed during the reaction of Ni^{++} and Pt^{++} with Li is not understood, but it may involve the solubility of either Li or a Li-Pb intermetallic compound in the salt.

CONCLUSIONS

Diffusion of the reducing ionic species across a salt-phase boundary layer was shown to be the rate-controlling step for the reductions of Pb^{++} , Cd^{++} , Ag^+ and In^{+++} by lithium, and of Cr^{+++} by lead. Values of δ_s , the salt-phase boundary layer thickness, for these reactions were estimated to be in the range 0.005 to 0.02 cm, and were found to be dependent primarily on agitation conditions and to a lesser extent on diffusion coefficients.

Insolubility of the reduced metal in the molten alloy resulted in deposition of metal at the salt-alloy interface during the reductions of Co^{++} , Cr^{+++} and Ti^{+++} by lithium. Metal deposition in the case of Ni^{++} reduction by lead is probably caused by alloy surface saturation combined with slow alloy-phase mass transfer.

Apparent homogeneous reaction in the salt occurs during the reductions of Ni^{++} and Pt^{++} by lithium. The mechanisms have not been deduced but may involve solubility of either lithium or a Li-Pb intermetallic compound in the salt.

The interface reactions are primarily electrochemical in nature .

In all cases where the reduction rates were different from those predicted from a boundary layer diffusion model, the rates were higher than these predictions indicating that the chemical reactions at the interface are never rate-controlling. Chronopotentiometric measurements indicate that these reduction reactions are reversible under the conditions described in this work.

Ionic diffusion in LiCl-KCl eutectic is influenced primarily by the ionic charge of the diffusing species, as shown by the diffusion coefficients of Ag^+ , Pb^{++} , Co^{++} , Ni^{++} , Fe^{++} , Cr^{++} , Cr^{+++} and In^{+++} measured in this study.

SUGGESTIONS FOR FUTURE WORK

The mechanisms of Ni(II) and Pt(II) reductions have yet to be determined; the following measurements are suggested as possible methods of elucidating these mechanisms:

- (1) a determination of the possible transfer of a Li-Pb intermetallic compound to LiCl-KCl eutectic at temperatures in the region of 400°C. The techniques for measuring metal solubilities in molten salts are well documented^{65,66}.
- (2) electrical conductance and Hall measurements on the Ni-NiCl₂ system would indicate the mechanism of metal solution.
- (3) measurements of the solubility of Li in LiCl-KCl could be made, although the procedure would be difficult in view of the probable low value. Electronic measurements might indicate the solution mechanism.
- (4) the lithium reduction of CuCl₂ may elucidate the role, if any, of monovalent species such as Ni⁺ and Cu⁺ in homogeneous reduction.

The occurrence of interfacial metal deposition during the lead reduction of Ni(II) might be explained on the basis of a series of tests to determine the rate-controlling step of the

reaction. If diffusion of Ni in the alloy is slow then the alloy surface may become saturated and result in Ni nucleation at the surface.

Other measurements which could be made include reduction rates and mechanisms in other fused salt systems (e. g., NaCl-KCl), and diffusion coefficients in LiCl-KCl, other salts and molten lead (primarily for Li and Na).

Perhaps the most interesting area for future work suggested by the present thesis is that of homogeneous reactions in molten salts. The reactions of direct relation to this work are those involving the reduction of Ni(II) or Pt(II) by lithium in solution in the salt. A course of study should start with simple, low-melting systems if possible. As an example the experiment might involve injecting a dilute solution of NiCl_2 in NaCl into a solution of Na dissolved in NaCl, then following the reaction in some manner. The rates of these reactions are presumably fast, and a technique other than sampling would have to be applied.

APPENDIX A

THEORY OF CHRONOPOTENTIOMETRY

Consider the reduction of a metal ion M^{n+} in a constant current electrolysis in the presence of a supporting electrolyte. The concentration of M^{n+} is assumed to be uniform throughout the solution initially.

The concentration of M^{n+} at any distance perpendicular to the electrode surface at any time t after the start of the electrolysis, assuming semi-infinite linear diffusion, is given by the solution to Fick's second law for the following boundary conditions (assuming D is independent of concentration):

$$C(x,0) = C \quad (1)$$

and

$$\left[\frac{\partial C(x,t)}{\partial x} \right]_{x=0} = \frac{i}{nFD} \quad (2)$$

where $C(x,t)$ = concentration of M^{n+} (moles cm^{-3}) at x at t

C = bulk concentration of M^{n+}

x = perpendicular distance from the electrode surface (cm)

t = time after start of electrolysis (sec)

n = number of electrons involved in the reaction (mole^{-1})

i = current density (amp cm^{-2})

F = Faraday (coulombs)

D = diffusion coefficient of M^{n+} ($\text{cm}^2 \text{ sec}^{-1}$)

The solution to this equation is²³:

$$C(x,t) = C - \frac{2it^{1/2}}{nF\pi^{1/2} D^{1/2}} \exp\left[-\frac{x^2}{4Dt}\right] + \frac{ix}{nFD} \operatorname{erfc}\left[\frac{x}{2D^{1/2} t^{1/2}}\right] \quad (3)$$

Figure A-1 shows the variations of concentration of the electrolyzed substance at various times t .

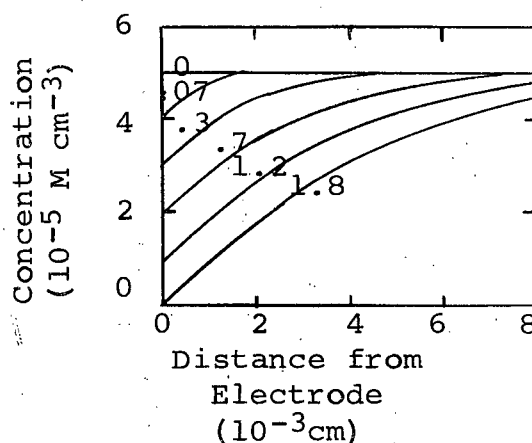


Figure A-1: Variations of Concentration of the Electrolyzed Substance.
(The number on each curve is the time, in seconds, elapsed since the beginning of electrolysis)

For a reversible electrode process in which the reduced species is insoluble in the melt, the potential of the indicator electrode is given by the Nernst equation:

$$E = E^{\circ} + \frac{RT}{nF} \ln \left[C - \frac{2it^{1/2}}{nF\pi^{1/2} D^{1/2}} \right] \quad (4)$$

where E° is the standard electrode potential of the $M^{n+} - M$ electrode system (volts)

$$\text{As } C \longrightarrow \frac{2it^{1/2}}{nF\pi^{1/2} D^{1/2}},$$

$$E \longrightarrow \infty$$

In other words, after a finite time τ , defined as the transition time, the surface concentration reaches zero.

$$\tau^{1/2} = \frac{nF\pi^{1/2} D^{1/2} C}{2i} \quad (5)$$

Substituting C from equation (5) into equation (4) gives:

$$E = E_{\text{const.}} + \frac{RT}{nF} \ln (\tau^{1/2} - t^{1/2}) \quad (6)$$

TABLE A-I: CHRONOPOTENTIOMETRIC FUNCTIONS FOR REVERSIBLE PROCESSES (FROM DELAHAY²⁴)

Process	τ Function	Potential Function
Single Electrochemical React.		$E = E_{1/2} + \frac{RT}{nF} \ln (\tau^{1/2} - t^{1/2})$
a) reduced species insoluble in melt ($a_R = 1$)	$\tau^{1/2} = \frac{n\pi^{1/2} F C_D^{1/2}}{2i}$	
b) both species soluble in melt	(for both (a) and (b))	$E = E_{1/2} + \frac{RT}{nF} \ln \left(\frac{\tau^{1/2} - t^{1/2}}{t^{1/2}} \right)$
Consecutive Electrochemical Reactions involving two different species	$\tau_1^{1/2} = \frac{n_1 \pi^{1/2} F C_1 D_1^{1/2}}{2i}$ $(\tau_1 + \tau_2)^{1/2} - \tau_1^{1/2} = \frac{n_2 \pi^{1/2} C_2 D_2^{1/2}}{2i}$	First wave: either of the above
Stepwise Electrode Processes	$\tau_1^{1/2} = \frac{n_1 \pi^{1/2} F C_1 D_1^{1/2}}{2i}$ $\tau_2 = \tau_1 \left[2 \left(\frac{n_2}{n_1} \right) + \left(\frac{n_2}{n_1} \right)^2 \right]$	$E_1 = E_{1/2} + \frac{RT}{n_1 F} \ln \left(\frac{\tau_1^{1/2} - t^{1/2}}{t^{1/2}} \right)$

Chronopotentiometric functions derived by Delahay and co-workers²⁴ for various electrochemical situations are summarized in Table A-I.

A theoretical chronopotentiometric curve is shown in Figure A-2 and one experimentally measured is shown in Figure A-3.

Theoretically the potential rise at $t = \tau$ is infinite. In practice the potential never becomes infinite but reaches a value at which reduction of the electrolyte occurs. The slope of the $E-t$ curve at $t = \tau$ may not be as steep as theoretically predicted because of surface roughness, i.e., different points on the surface reach zero concentration at slightly different times.

There is also usually a sharp potential rise near $t = 0$ due to the charging of the electric double layer at the electrode surface.

For practical chronopotentiometry the quantities of equation (5) must be adjusted so that τ is:

- (1) very much larger than the time required to charge the double layer (i.e., τ should be at least in the millisecond range).

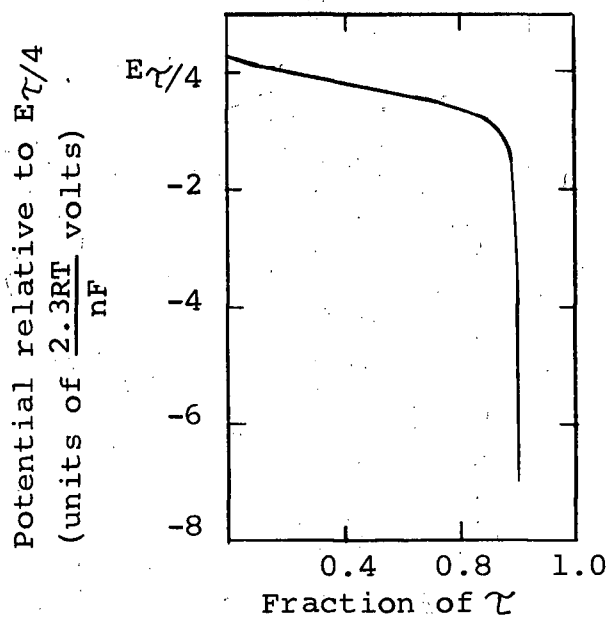


Figure A-2: Theoretical Cathodic Chronopotentiogram

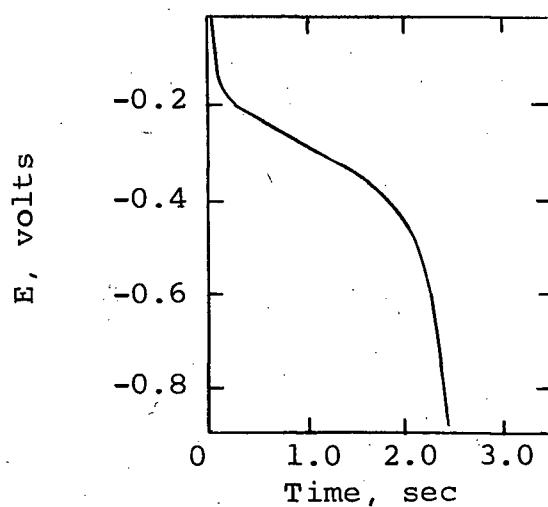


Figure A-3: A Typical Cathodic Chronopotentiogram

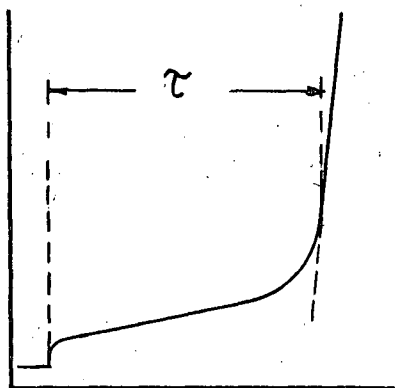
- (2) small enough so that convection does not disturb the conditions of semi-infinite linear diffusion. In fused salts, Laitinen and Ferguson³³ have shown that τ should be less than five seconds; the ideal range is 0.1 to two seconds.

APPENDIX B

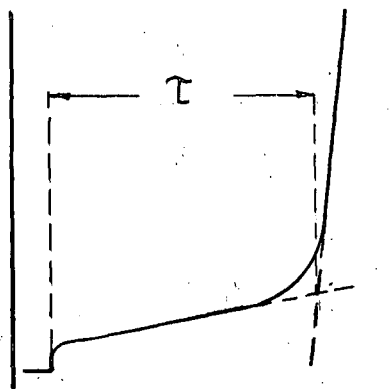
MEASUREMENT OF TRANSITION TIMES

The transition time τ is defined as the time interval between the start of a constant current electrolysis and the complete concentration polarization of the electrode. Chronopotentiometric waves may be distorted both at low times and at times near τ . The initial distortion, or potential rise, is due generally to double layer charging and in most cases is not very significant (i.e., if $\tau \gg$ time for double layer charging); it may also be caused by impurities. At times near τ , a slow rise of potential indicates either surface roughness or impurities in the melt.

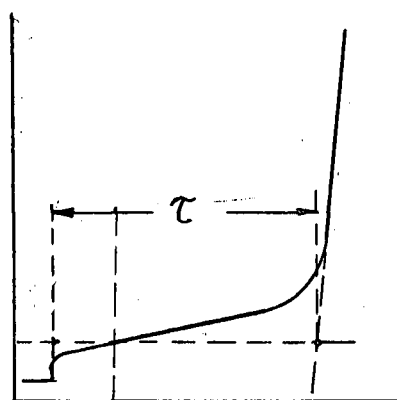
Three empirical methods for determining τ from chronopotentiometric curves are illustrated in the following sketches for an ideal experimental curve.



Method 1



Method 2



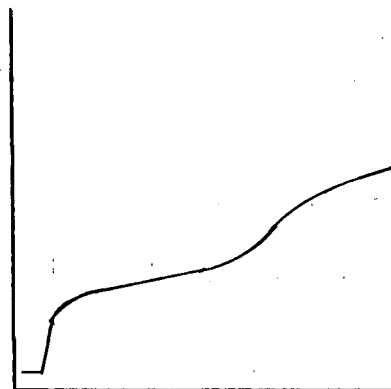
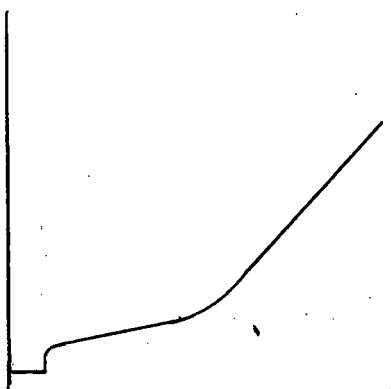
Method 3

Measurements of τ , for a Pt test with ideal shape, were made by each of the three methods

<u>Method</u>	<u>τ (sec)</u>
1	0.768
2	0.764
3	0.768

As can be seen, the difference between these methods is insignificant.

However if these three methods are applied to the following curves the differences become appreciable.



Method 3 gives an abnormally small value of τ ; τ by Method 2 is somewhat larger. However the best and most consistent results are obtained by using Method 1. For example, from one such curve $\tau_1 = 0.480$, $\tau_2 = 0.308$ and $\tau_3 = 0.248$ sec.

Thus the following procedure was used. Zero time was taken at the point where the potential first changed, if the time interval for the initial rising portion was small. Otherwise a parallel line was drawn to this initial portion, and zero time determined as the point of departure of the experimental curve from this line. The time $t = \tau$ was taken as the point at which the experimental curve coincided with a line drawn parallel to the final rising portion of the curve.

This procedure gave the most consistent results throughout the study.

APPENDIX C

CHRONOPOTENTIOMETRIC DATA

SILVER

Reference Electrode: Ag(I) - Ag(0)

i amp. cm^{-2}	τ_{av} sec.
$C = 4.95 \times 10^{-5} \text{ M cm}^{-3}$	
$T = 400^{\circ}\text{C}$	
Ind.Electrode: 0.035"D. W	
2.56×10^{-2}	0.820
2.92	0.646
3.25	0.492
3.57	0.390
4.10	0.323
4.68	0.256
5.20	0.188
5.50	0.179
6.10	0.148
7.00	0.115
8.11	0.078
9.19	0.068

$C = 8.75 \times 10^{-5} \text{ M cm}^{-3}$
 $T = 400^{\circ}\text{C}$
 Ind.Electrode: 0.035"D. W

3.93×10^{-2}	1.24
5.06	0.766
6.74	0.434
8.43	0.279
10.12	0.197
11.78	0.144
13.45	0.119

i amp. cm^{-2}	τ_{av} sec.
$C = 1.40 \times 10^{-4} \text{ M cm}^{-3}$	
$T = 400^{\circ}\text{C}$	
Ind.Electrode: 0.050"D. W	
6.86×10^{-2}	1.236
8.83	0.779
1.06×10^{-1}	0.562
1.27	0.432
1.42	0.298
1.60	0.225
1.87	0.159
2.17	0.132
2.55	0.092

LEAD (II)

Reference Electrode: Ag(I) - Ag(0)

i amp. cm^{-2}	τ_{av} sec.
------------------------------	----------------------------

$$C = 6.21 \times 10^{-5} \text{ M cm}^{-3}$$

$$T = 400^{\circ}\text{C}$$

Ind.Electrode: 0.035"D. W

4.80×10^{-2}	0.590
4.85	0.551
5.28	0.487
5.68	0.420
6.57	0.322
7.44	0.298
8.35	0.199

$$C = 8.52 \times 10^{-5} \text{ M cm}^{-3}$$

$$T = 400^{\circ}\text{C}$$

Ind. Electrode: 0.035"D. W

8.00×10^{-2}	0.396
9.00	0.320
10.2	0.255
11.4	0.202
12.5	0.167

$$C = 2.45 \times 10^{-4} \text{ M cm}^{-3}$$

$$T = 400^{\circ}\text{C}$$

Ind.Electrode: 0.035"D.W

4.82×10^{-1}	0.103
5.22	0.087
5.83	0.072
6.39	0.057
7.06	0.048
7.65	0.039
8.81	0.030
10.10	0.022

i amp. cm^{-2}	τ_{av} sec.
------------------------------	----------------------------

$$C = 1.10 \times 10^{-5} \text{ M cm}^{-3}$$

$$T = 445^{\circ}\text{C}$$

Ind.Electrode: Pt foil

1.26×10^{-2}	0.409
1.41	0.339
1.57	0.275
1.72	0.215
1.88	0.179

$$C = 1.70 \times 10^{-5} \text{ M cm}^{-3}$$

$$T = 445^{\circ}\text{C}$$

Ind.Electrode: Pt foil

1.24×10^{-2}	1.10
1.42	0.849
1.56	0.709
1.73	0.556
1.88	0.440

$$C = 2.38 \times 10^{-5} \text{ M cm}^{-3}$$

$$T = 445^{\circ}\text{C}$$

Ind.Electrode: Pt foil

1.88×10^{-2}	0.876
2.20	0.648
2.64	0.446
3.00	0.352

INDIUM (III)

Reference Electrode: Ag(I) - Ag(0)

Indicator Electrode: 0.035"D. W

i	τ_{av}
amp. cm ⁻²	sec.

C = 2.38×10^{-5} M cm⁻³
T = 403°C

1.62 x 10 ⁻²	0.387
1.90	0.278
2.25	0.201
2.74	0.138
3.28	0.096
3.90	0.069
4.60	0.048
5.26	0.039

C = 5.07×10^{-5} M cm⁻³
T = 403°C

2.90 x 10 ⁻²	0.560
3.58	0.360
4.27	0.240
4.94	0.180
5.62	0.140
6.34	0.110
7.06	0.090
7.82	0.07

i	τ_{av}
amp. cm ⁻²	sec.

C = 5.07×10^{-5} M cm⁻³
T = 429°C

3.57 x 10 ⁻²	0.480
3.91	0.400
4.27	0.345
4.61	0.28
4.94	0.25
5.62	0.20
6.31	0.15
7.00	0.12
7.71	0.10

C = 5.07×10^{-5} M cm⁻³
T = 451°C

3.45 x 10 ⁻²	0.64
3.91	0.48
4.23	0.38
4.59	0.33
4.92	0.28
5.59	0.21
6.27	0.175
7.00	0.14
7.82	0.11

COBALT (II)

Reference Electrode: Ag(I) - Ag(o)

Indicator Electrode: 0.035"D. W

i amp. cm^{-2}	τ_{av} sec.	i amp. cm^{-2}	τ_{av} sec.
$C = 2.26 \times 10^{-5} \text{ M cm}^{-3}$ $T = 402^{\circ}\text{C}$		$C = 4.70 \times 10^{-5} \text{ M cm}^{-3}$ $T = 453^{\circ}\text{C}$	
1.52×10^{-2}	0.760	3.13×10^{-2}	1.14
1.89	0.467	3.65	0.800
2.23	0.348	4.12	0.617
2.61	0.247	4.57	0.553
3.20	0.162	5.35	0.378
3.90	0.113	6.18	0.291
4.91	0.071	7.17	0.209
5.35	0.060	8.58	0.142
		1.01×10^{-1}	0.106
$C = 4.70 \times 10^{-5} \text{ M cm}^{-3}$ $T = 402^{\circ}\text{C}$		$C = 4.70 \times 10^{-5} \text{ M cm}^{-3}$ $T = 493^{\circ}\text{C}$	
2.70×10^{-2}	1.03	3.62×10^{-2}	0.975
3.11	0.809	4.31	0.710
3.51	0.616	5.02	0.508
3.90	0.492	5.89	0.373
4.57	0.368	7.20	0.266
5.43	0.281	8.62	0.180
6.43	0.182	1.01×10^{-1}	0.151
7.78	0.109		
8.25	0.096		
$C = 7.20 \times 10^{-5} \text{ M cm}^{-3}$ $T = 402^{\circ}\text{C}$			
5.21×10^{-2}	0.756		
5.80	0.660		
6.79	0.434		
8.83	0.274		
1.02×10^{-1}	0.192		
1.29	0.143		
1.59	0.087		
1.87	0.060		

NICKEL (II)

Reference Electrode: Ag(I) - Ag(0)

Indicator Electrode: 0.035"D. W

Temperature: 400°C

i amp. cm^{-3}	τ_{av} sec.
$C = 2.10 \times 10^{-5} \text{ M cm}^{-3}$	
1.39×10^{-2}	0.950
1.66	0.70
1.95	0.48
2.39	0.33
2.94	0.23
3.49	0.125
4.38	0.076

i amp. cm^{-3}	τ_{av} sec.
$C = 6.70 \times 10^{-5} \text{ M cm}^{-3}$	
3.60×10^{-2}	1.42
4.04	1.11
4.38	0.890
4.91	0.718
5.74	0.520
6.65	0.389
7.73	0.295
8.83	0.224
1.00×10^{-1}	0.171
1.15	0.127
1.30	0.101
1.49	0.079

PLATINUM (II)

Reference Electrode: Pt(II) - Pt(0)

Indicator Electrode: Pt foil

Temperature: 400°C

i amp. cm^{-2}	τ_{av} sec.	i amp. cm^{-2}	τ_{av} sec.
$C = 1.58 \times 10^{-5} \text{ M cm}^{-3}$		$C = 3.28 \times 10^{-5} \text{ M cm}^{-3}$	
1.05×10^{-2}	0.882	1.79×10^{-2}	1.10
1.16	0.724	1.97	0.908
1.36	0.532	2.14	0.818
1.56	0.403	2.34	0.666
1.79	0.319	2.65	0.515
2.14	0.222	2.91	0.437
2.74	0.131	3.52	0.297
3.44	0.084	4.00	0.230
4.16	0.060	4.63	0.170
5.09	0.038	5.55	0.115
$C = 2.35 \times 10^{-5} \text{ M cm}^{-3}$		6.37	0.088
1.36×10^{-2}	1.02	7.57	0.062
1.45	0.876	8.91	0.047
1.56	0.748	$C = 1.01 \times 10^{-4} \text{ M cm}^{-3}$	
1.76	0.592	6.32×10^{-2}	0.768
1.93	0.500	6.87	0.654
2.11	0.420	7.17	0.616
2.33	0.342	8.07	0.482
2.70	0.266	9.25	0.366
3.11	0.196	1.09×10^{-1}	0.256
3.52	0.151	1.28	0.193
4.15	0.114	1.49	0.145
5.12	0.072	1.76	0.104
5.92	0.055	2.12	0.070
		2.67	0.044

IRON (II)

Reference Electrode: Pt(II) - Pt(0)

Indicator Electrode: Pt foil

Temperature: 400°C

i amp. cm^{-2}	τ_{av} sec.
$C = 2.46 \times 10^{-5} \text{ M cm}^{-3}$	
1.65×10^{-2}	0.926
1.77	0.856
1.93	0.680
2.14	0.558
2.46	0.414
2.76	0.322
3.11	0.267
3.58	0.196
4.33	0.139
5.39	0.088
6.52	0.064

 $C = 3.75 \times 10^{-5} \text{ M cm}^{-3}$

2.40×10^{-2}	1.224
2.54	1.084
2.77	0.904
2.94	0.812
3.10	0.724
3.37	0.624
3.73	0.530
4.07	0.436
4.55	0.324
5.32	0.240
6.03	0.197
6.99	0.149
8.59	0.098

i amp. cm^{-2}	τ_{av} sec.
$C = 5.06 \times 10^{-5} \text{ M cm}^{-3}$	
3.48×10^{-2}	0.980
3.68	0.852
3.93	0.760
4.22	0.686
4.66	0.540
5.20	0.430
5.73	0.352
6.35	0.304
7.35	0.228
8.54	0.173
1.08×10^{-1}	0.108

 $C \sim 5.06 \times 10^{-5} \text{ M cm}^{-3} *$

3.53×10^{-2}	0.984
3.96	0.794
4.34	0.676
4.75	0.612
5.40	0.492
5.77	0.382
6.05	0.353
7.00	0.258
8.43	0.185
1.06×10^{-1}	0.120

* Solution anodized for approximately one hour at 100 ma before this series.

CHROMIUM (III)

Reference Electrode: Pt(II) - Pt(0)

Indicator Electrode: Pt foil

Temperature: 400°C

i	τ_{av}
amp. cm ²	sec.

$$C = 2.60 \times 10^{-5} \text{ M cm}^{-3}$$

4.98 x 10 ⁻³	1.06
5.56	0.838
6.28	0.660
7.22	0.518
7.38	0.453
8.69	0.345
1.04 x 10 ⁻²	0.250
1.25	0.175
1.61	0.108
1.98	0.007

i	τ_{av}
amp. cm ²	sec.

$$C = 8.45 \times 10^{-5} \text{ M cm}^{-3}$$

1.25 x 10 ⁻²	1.75
1.45	1.40
1.68	1.056
1.88	0.836
2.25	0.588
2.61	0.437
2.95	0.340
3.51	0.243
4.24	0.170
5.26	0.113
6.65	0.074

CHROMIUM (II)

Reference Electrode: Pt(II) - Pt(0)
Indicator Electrode: Pt foil
Temperature: 400°C

i amp. cm^{-2}	τ_{av} sec.
------------------------------	---------------------

$$C = 1.58 \times 10^{-5} \text{ M cm}^{-3}$$

1.05×10^{-2}	1.10
1.18	0.864
1.32	0.670
1.58	0.488
1.87	0.370
2.33	0.252
2.66	0.171
3.34	0.134
4.39	0.090

$$C = 3.32 \times 10^{-5} \text{ M cm}^{-3}$$

2.33×10^{-2}	1.04
2.49	0.844
2.66	0.774
2.84	0.680
3.13	0.558
3.50	0.444
4.22	0.334
5.33	0.218
6.53	0.150

i amp. cm^{-2}	τ_{av} sec.
------------------------------	---------------------

$$C \sim 5.22 \times 10^{-5} \text{ M cm}^{-3} *$$

2.58×10^{-2}	1.06
2.72	1.00
2.86	0.84
3.18	0.714
3.63	0.538
4.15	0.392
5.01	0.279
6.05	0.200
7.27	0.165
8.55	0.12
1.04×10^{-1}	0.088

* Solution anodized for approximately one hour at 150 ma before this series.

APPENDIX D

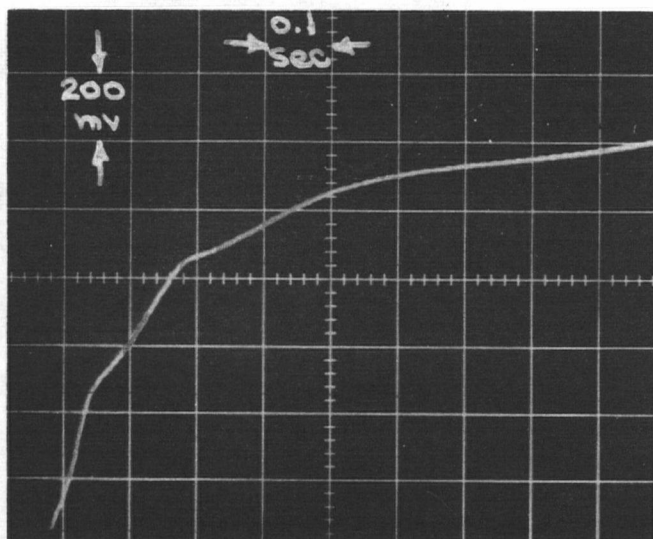
CHRONOPOTENTIOMETRY OF Mo(V)

A limited number of chronopotentiometric tests were conducted in LiCl-KCl at 400°C, with MoCl₅ added as solute. These tests were done using gold electrodes* since it was thought that the Mo(V) potential could be quite noble.

Chronopotentiograms under these conditions showed four waves; some typical curves are shown in Figure D-1.

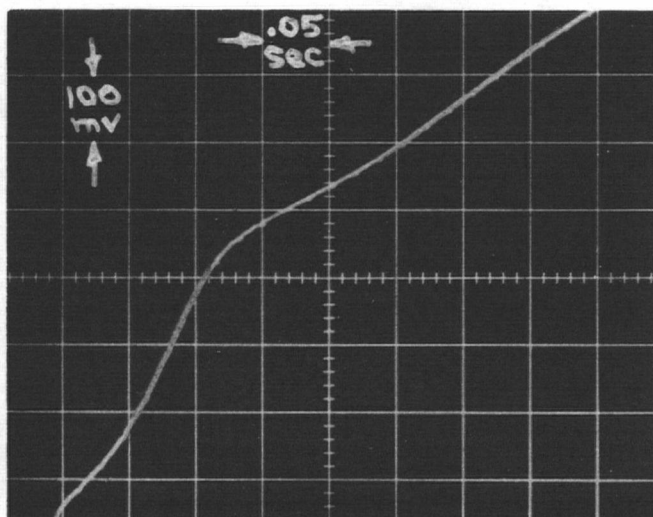
Measurements of the reduction potentials for each wave, with approximate values of the transition times, are shown in Table D-I. Selis⁷⁹ reported the standard potential of the Mo(III) - Mo(II) couple as -0.603 v. versus 1M. Pt(II) - Pt(0). The potential of Au(I) - Au(0) is 0.21 v. on the Pt scale, so that the Mo(III) - Mo(II) potential is about -0.81 v. on the Au scale. The value measured for wave 3 in this work

* Chronopotentiograms of the solvent only indicated a maximum potential rise with a gold indicator electrode of -1.45 v. versus Au(I) - Au(0). When a platinum electrode was used, the potential rose to -2.6 v. versus Au(I) - Au(0). The proposed explanation of the low value for Li deposition onto Au is that the Li does not deposit at unit activity, but forms an intermetallic compound with Au, so depositing at a more noble potential.



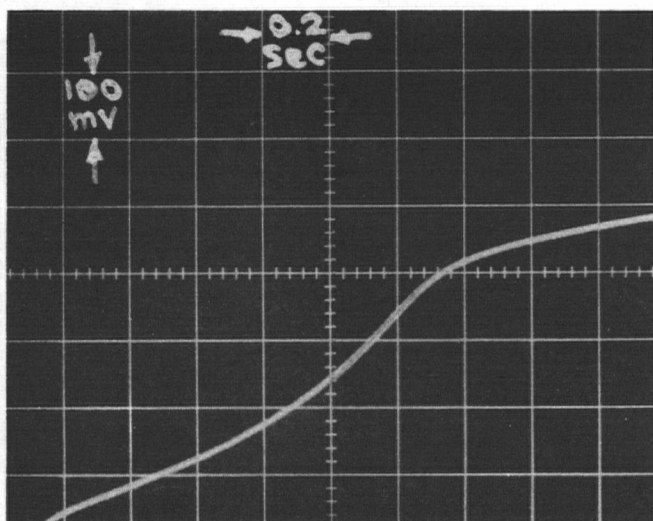
(a) Test 11

$$\begin{aligned} T &= 400^{\circ}\text{C} \\ i &= 2.65 \times 10^{-2} \text{ a cm}^{-2} \\ C &= 1.60 \times 10^{-5} \text{ M cm}^{-3} \end{aligned}$$



(b) Test 15

$$\begin{aligned} T &= 400^{\circ}\text{C} \\ i &= 1.60 \times 10^{-2} \text{ a cm}^{-2} \\ C &= 1.60 \times 10^{-5} \text{ M cm}^{-3} \end{aligned}$$



(c) Test 22

$$\begin{aligned} T &= 400^{\circ}\text{C} \\ i &= 5.07 \times 10^{-3} \text{ a cm}^{-2} \\ C &= 1.60 \times 10^{-5} \text{ M cm}^{-3} \end{aligned}$$

Figure D-1: Typical Chronopotentiograms for MoCl_5

is then in good agreement with the Mo(III) - Mo(II) potential.

TABLE D-I

REDUCTION POTENTIALS FOR MoCl_5

Test 11: $i = 2.65 \times 10^{-2} \text{ amp cm}^{-2}$

Wave	Potential (V) vs. Au(I) - Au(0)	τ sec
1	-0.04	0.024
2	-0.45	0.045
3	-0.84	0.052
4	-1.10	0.40

Data from the chronopotentiometric tests are shown in Table D-II. Although some scatter exists, the following calculations were made. Using $i\tau_1^{1/2} = 4 \times 10^{-3} \text{ amp cm}^{-2} \text{ sec}^{1/2}$ and the equation:

$$i\tau_1^{1/2} = \frac{n_1 \pi^{1/2} F C D_1^{1/2}}{2}$$

$$D_1^{1/2} = \frac{2.93 \times 10^{-3}}{n_1} \text{ cm sec}^{-1/2}$$

$$\text{For } n_1 = 1, D_1 = 8.6 \times 10^{-6} \text{ cm}^2 \text{ sec}^{-1}$$

$$n_1 = 2, D_1 = 2.2 \times 10^{-6} \text{ cm}^2 \text{ sec}^{-1}$$

TABLE D-II

Mo(V) CHRONOPOTENTIOMETRIC DATA

Conditions: 400°C

Au electrodes

 $C \approx 1.6 \times 10^{-5}$ moles cm^{-3}

Test	τ_1 sec	i amp cm^{-2}	$i\tau_1^{1/2}$ amp cm^{-2} sec $^{1/2}$
14	0.048	1.95×10^{-2}	4.28×10^{-3}
15	0.059	1.60	3.89
16	0.108	1.26	4.14
17	0.154	1.05	4.12
18	0.226	8.75×10^{-3}	4.16
19	0.280	7.03	3.73
20	0.450	5.78	3.88
22	0.860	5.07	4.70
23	0.700	5.78	4.78
24	0.092	1.26×10^{-2}	3.83
25	0.159	8.75×10^{-3}	3.49
26	0.218	7.03	3.28
27	0.274	5.78	3.03
28	0.414	5.04	3.19
29	0.478	4.52	3.12
30	0.610	4.00	3.13
31	0.175	8.75	3.66

Average $i\tau^{1/2} = 3.79 \times 10^{-3} \pm 0.8$

Plots were made of potential versus $\log(\tau_1^{1/2} - t^{1/2}/t^{1/2})$ and potential versus $\log(\tau_1^{1/2} - t^{1/2})$ for Test 30. Both were linear; the slope of the former was 0.084 v., the latter was 0.140 v. Recall that for reversible reductions with $n = 1, 2$ or 3 these slopes would be 0.134 v., 0.067 v. and 0.045 v.

The transition time ratios for the four waves were:

$$\tau_4/\tau_3 = 7.7$$

$$\tau_3/\tau_2 = 1.15$$

$$\tau_2/\tau_1 = 1.87$$

Theoretical values for successive reactions are:

$$n_1 = 1, n_2 = 1 \quad \tau_2/\tau_1 = 3$$

$$n_1 = 1, n_2 = 2 \quad \tau_2/\tau_1 = 8$$

$$n_1 = 2, n_2 = 1 \quad \tau_2/\tau_1 = 1.25$$

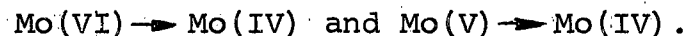
Consider these results if the only initial species were Mo(V). In view of the reduction potential for the third wave, and of the experimental τ_4/τ_3 ratio, the third and fourth waves are undoubtedly those for the $\text{Mo(III)} \rightarrow \text{Mo(II)}$ and $\text{Mo(II)} \rightarrow \text{Mo}$ reductions, respectively. Thus the first two waves should be $\text{Mo(V)} \rightarrow \text{Mo(IV)}$ and $\text{Mo(IV)} \rightarrow \text{Mo(III)}$; τ_2/τ_1 would then be 3, and a plot of E versus $\log(\tau_1^{1/2} - t^{1/2}/t^{1/2})$ would have a slope of 0.134 v. From the results it is obvious that the system is much more complicated than assumed here.

The following reactions may be considered as possible explanations:

- (1) disproportionation of Mo(V), i.e.,



The first wave would then be a combination of



- (2) oxidation of Au, i.e.,



In either of these cases, the reaction of Mo(V) would produce at least two additional products. Theoretical treatments of complex systems such as this are not available, and any further considerations are beyond the scope of this thesis.

APPENDIX E

CHRONOPOTENTIOMETRY OF Ti(III)

One series of chronopotentiometric tests in LiCl-KCl eutectic at 400°C was performed with TiCl_3 added as solute, and using Pt electrodes. The results were somewhat inconclusive but may add some knowledge to the electrochemical behaviour of Ti in this fused salt.

Previous Work

Bockris et al⁸⁰ studied solutions of titanium chlorides in LiCl-KCl polarographically. At 400°C they obtained the polarographic wave for the reduction of Ti(III) to Ti(II), but no wave for the Ti(II)-Ti(0) reduction was seen at potentials less negative than that for decomposition of the melt. However, under the same conditions Okada et al⁸¹ have obtained polarograms for both of these reduction processes.

Redox potential measurements of the Ti(III)/Ti(II) couple in LiCl-KCl were carried out by Menzies et al⁸² and by Smirnov⁸³. Both used essentially the same technique, but values differed by 0.6 v. at 500°C. Menzies et al found the standard potential at infinite dilution to be -1.55 v. on the chlorine scale.

Recently Baboian et al⁸⁴ have applied the methods of potentiometry and polarography to a study of Ti(II) and Ti(III) in LiCl-KCl at 450°C and 550°C. The following electrode potentials were determined (versus M. Pt(II)/Pt):

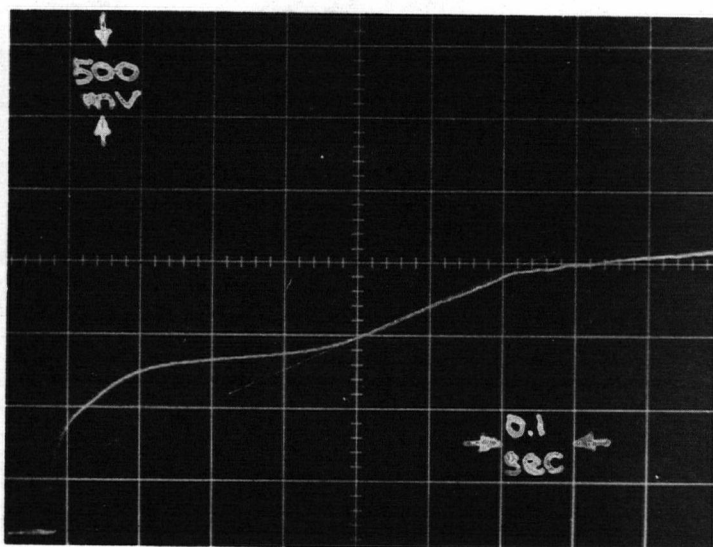
$$\left. \begin{array}{ll} \text{Ti(II)/Ti} & - 1.74 \text{ v.} \\ \text{Ti(III)/Ti(II)} & - 1.43 \text{ v.} \end{array} \right\} \text{ at } 450^{\circ}\text{C}$$

Polarographic waves for oxidation and reduction of Ti(II), and for reduction of Ti(III), were observed. In addition a solubility limit for TiCl_2 in LiCl-KCl at 450°C of 5×10^{-5} mole fraction was detected, which may explain the absence of an observable polarographic wave for Ti(II) reduction in the work of Bockris et al.

Henrie⁸⁵ has suggested that reaction of Ti ions with SiO_2 could take place in these systems. Baboian et al noted that their Ti(II) solutions seemed quite stable for some time, that no trace of glass attack was observed, and that no silicon-containing residues were detected in the melt.

Present Study

A typical chronopotentiogram obtained at 400°C in LiCl-KCl for Ti(III) is shown in Figure E-1. The unusual portion of the curve, occurring just after the initial sharp potential



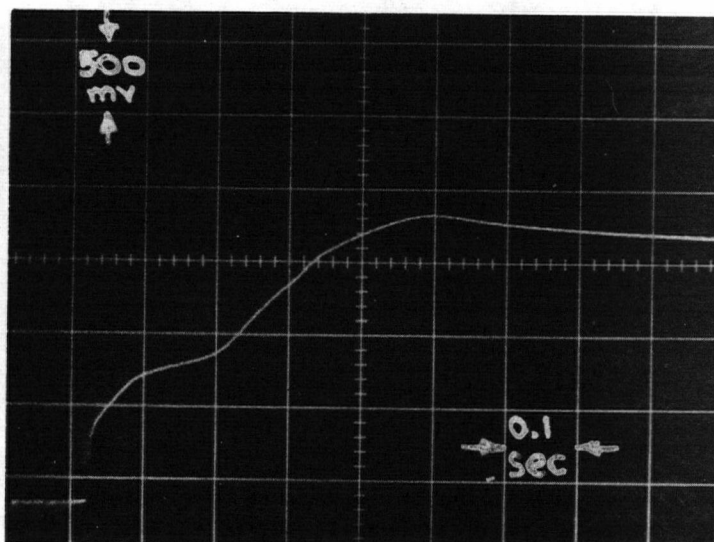
(a) Test 31

$$T = 400^{\circ}\text{C}$$

$$i = 3.80 \times 10^{-2} \text{ amp cm}^{-2}$$

$$C = 2.70 \times 10^{-5} \text{ M cm}^{-3}$$

$$\tau_t = 0.20 \text{ sec}$$



(b) Test 35

$$T = 400^{\circ}\text{C}$$

$$i = 2.88 \times 10^{-2} \text{ amp cm}^{-2}$$

$$C = 2.70 \times 10^{-5} \text{ M cm}^{-3}$$

$$\tau_t = 0.41 \text{ sec}$$

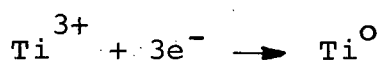
Figure E-1: Typical Chronopotentiograms for Ti(III)

rise, could not be resolved into a more distinct and separate wave. Measurements made of the total transition time are listed in Table E-I.

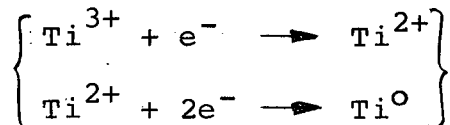
Using the values of $C = 2.70 \times 10^{-5}$ moles cm^{-3} and $i\tau^{1/2} = 1.68 \times 10^{-2}$ amp cm^{-2} $\text{sec}^{1/2}$,

$$D^{1/2} = (7.28 \times 10^{-3})/n \text{ cm sec}^{-1/2}$$

For $n = 3$, i.e., for either



or



$$D = 5.9 \times 10^{-6} \text{ cm}^2 \text{ sec}^{-1}$$

This value corresponds very well with diffusion coefficients for Cr(III) and In(III) in LiCl-KCl at 400°C.

Substituting a value of $n = 1$ results in $D \sim 50 \times 10^{-6} \text{ cm}^2 \text{ sec}^{-1}$, i.e., much too high for Ti(III) diffusion. Therefore the wave observed is not due to a Ti(III) - Ti(II) reduction alone.

The following observations support the mechanism of a stepwise reduction of Ti(III) to Ti(II) to Ti:

TABLE E-I

Ti(III) CHRONOPOTENTIOMETRIC DATA

Conditions: 400°C

Pt electrodes

$C = 2.70 \pm 0.2 \times 10^{-5}$ moles cm^{-3}

Test	τ sec.	i amp cm^{-2}	$i\tau^{1/2}$ amp cm^{-2} sec $^{1/2}$
26	0.27	3.80×10^{-2}	1.97×10^{-2}
27	0.25	3.80	1.90
28	0.12	4.56	1.58
29	0.11	4.56	1.51
30	0.15	3.80	1.44
31	0.20	3.80	1.70
32	0.26	3.22	1.64
33	0.67	2.14	1.75
34	0.54	2.58	1.89
35	0.41	2.88	1.84
42	0.24	3.22	1.58
43	0.54	2.14	1.57
44	0.47	2.14	1.46
45	0.41	2.58	1.64
Average: $1.68 \pm 0.2 \times 10^{-2}$			

(1) the potential difference between the "two" waves is roughly 0.3-0.4 v., comparable to the value of 0.31 v. measured by Baboian.

(2) theoretically $\tau_2/\tau_1 = 8$; for test 32, $\tau_t = 0.26$ sec
 $= \tau_1 + \tau_2 = 9\tau_1$

$$\therefore \tau_1 = 0.029 \text{ sec}$$

$$\text{and } \tau_1^{1/2} = 0.17 \text{ sec}^{1/2}$$

Using this value of $\tau_1^{1/2}$, $i = 3.22 \times 10^{-2}$, and $n = 1$,

D was calculated as $5.7 \times 10^{-6} \text{ cm}^2 \text{ sec}^{-1}$, in good

agreement with that determined for $n = 3$, and τ_t .

Thus it seems most likely that the observed wave is actually a combination of two.

APPENDIX F

REDUCTION DATA

In the accompanying Tables the data for the reduction tests are summarized, with all the pertinent experimental conditions. The following points apply to all runs:

- (a) Crucibles
 - (1) quartz
 - (2) quartz-sleeved stainless steel
 - (3) stainless steel

All crucibles were $1.05 \pm .02$ " I. D.

- (b) Stirrers situated 8 - 10 mm above salt-metal interface.

- (c) M_s = Mass of salt

M_a = Mass of alloy

TABLE F - I

LEAD REDUCTION EXPERIMENT CONDITIONS

Run No.	T°C	Stir.	rpm	(Pb) ^o w/o	M _S gm	[Li] ^o w/o	M _a gm	Cruc.	k min ⁻¹	Comments
66	380	-	0	5.6	20	0	60	3	0	No Li in alloy
86	373	-	0	4.1	20	0.22	100	3	.040	
87	374	-	0	4.8	20	0.12	100	3	.034	
88	374	-	0	3.8	20	0.23	100	3	.061	
89	374	-	0	0	20	0.26	50	3	0	No Pb chloride in salt
90	378	-	0	6.2	20	0.21	50	3	.068	
91	378	-	0	6.1	20	0.27	60	3	.072	
92	378	-	0	6.3	20	0.57	70	3	.068	
93	379	-	0	7.7	20	0.64	80	3	.058	
94	376	-	0	7.7	20	0.38	100	3	.073	
95	378	-	0	1.22	20	0.25	100	3	.093	
97	373	-	0	3.64	20	0.35	100	2	.015	
98	375	-	0	3.75	20	0.30	100	3	.066	
99	376	-	0	3.84	20	0.26	100	1	.014	
100	377	-	0	4.74	20	0.28	90	2	.021	SS strips, A=8cm ²
101	379	-	0	4.38	20	0.27	90	2	.027	SS strips, A=12cm ²
102	377	-	0	4.23	20	0.31	90	2	.034	SS strips, A=16cm ²
103	377	-	0	3.72	20	0.28	90	2	.009	
104	377	glass	64	3.64	20	0.25	100	3	.071	
105	375	glass	64	3.60	20	0.24	100	2	.010	
106	380	-	0	3.69	20	0.30	100	2	.028	SS strips, A=10cm ²
107	380	-	0	3.86	20	0.30	100	2	.016	
108	380	-	0	3.68	20	0.24	100	2	.014	
109	370	-	0	3.60	20	0.25	85	2	.027	Current determination
110	375	-	0	4.77	20	0.23	50	2	.012	

TABLE F-I CON'T.

Run No.	T°C	Stir.	rpm	(Pb) ^o w/o	M _S gm	[Li] ^o w/o	M _a gm	Cruc.	k min ⁻¹	Comments
112	376	SS	112	4.63	20	0.19	100	2	.020	
113	376	SS	112	4.33	20	0.17	100	2	.022	
114	376	SS	224	4.40	20	0.19	100	2	.053	
117	390	SS	112	4.85	20	0.24	100	2	.025	
118	405	SS	112	5.18	20	0.25	100	2	.032	
119	426	SS	112	5.03	20	0.29	100	2	.035	
120	450	SS	112	4.67	20	0.19	100	2	.041	
137	385	SS	112	4.75	20	0.24	100	2	.020	
138	375	SS	112	1.57	20	0.17	100	2	.029	
139	375	SS	112	2.95	20	0.18	100	2	.03	
140	375	SS	112	6.80	20	0.16	100	2	.023	
141	375	SS	112	4.75	20	0.08	100	2	.023	
142	375	SS	112	4.75	30	0.17	100	2	.015	

TABLE F-II

LEAD REDUCTION DATA

Run	t min	(Pb) w/o	Run	t min	(Pb) w/o	Run	t min	(Pb) w/o
66	0	5.56	88	8	1.47	93	0	7.65
	1	5.54		11	0.89		1	6.93
	3	5.56		12	0.77		2	6.28
	6	5.63		15	0.62		6	3.36
	10	5.37		20	0.26		8	2.70
	15	5.33					10	2.50
	24	5.44	90	0	6.20		17	1.58
	30	5.38		1	5.36		26	0.82
	49	5.55		2	4.62		30	0.74
	69	5.39		4	3.18		40	0.11
	111	5.53		6	2.90			
				8	2.44	94	0	7.75
86	0	4.13		10	2.05		1	6.32
	1	3.30		12	1.95		2	5.65
	2	2.92		15	1.52		4	3.73
	4	2.58		17	1.27		6	2.01
	6	2.16		20	1.11		8	1.94
	8	1.69		24	0.93		10	1.49
	10	1.51					12	0.58
	13	1.24	91	0	6.10		15	0.82
	15	0.97		1	5.06		20	0.34
	21	0.59		2	4.54			
	25	0.21		4	3.02	95	0	1.22
				6	2.64		1	0.94
87	0	4.80		8	1.96		2	0.82
	1	4.27		10	1.83		4	0.53
	2	4.00		12	1.33		6	0.30
	4	3.50		15	1.06		8	0.25
	6	3.23		17	0.83		10	0.30
	8	3.25		25	0.68		12	0.15
	10	2.74					15	0.10
	12	2.40	92	0	6.32		21	0.05
	15	1.77		1	5.24			
	20	1.06		2	3.54	97	0	3.64
				4	2.65		1	3.13
				6	2.02		2	2.99
88	0	3.8		8	1.71		4	2.71
	1	3.64		10	0.86		6	2.60
	2	3.04		12	0.93		8	2.44
	4	2.08		15	0.81		10	2.21
	6	2.02						

TABLE F-II CON'T.

Run	t min	(Pb) w/o	Run	t min	(Pb) w/o	Run	t min	(Pb) w/o
97	12	2.16	101	0	4.38	104	4	1.81
	15	2.00		2	3.40		6	1.40
	20	1.72		5	2.95		8	0.99
	30	1.39		7	2.46		10	0.74
				10	2.00		13	0.47
98	0	3.75		13	1.77		15	0.41
	1	3.29		15	1.72		18	0.25
	2	2.63		18	1.33		20	0.18
	4	2.18		21	1.37		48	0.05
	6	1.72		25	0.90			
	8	1.43		41	0.34	105	0	3.60
	10	0.93		109	0.06		2	2.98
	12	0.59					4	2.96
	15	0.52	102	0	4.23		6	2.89
	17	0.41		2	3.53		9	2.77
	20	0.24		4	2.48		12	2.56
				7	2.02		15	2.40
99	0	3.84		9	1.77		20	2.15
	2	3.47		12	1.53		30	1.61
	5	2.73		15	1.25		51	1.07
	7	2.50		18	0.85			
	10	2.19		21	0.68	106	0	3.69
	13	2.02		25	0.53		2	2.86
	15	2.04		36	0.16		4	2.51
	20	1.73		103	0.03		6	2.10
	26	1.58					9	1.64
	32	1.29	103	0	3.72		12	1.48
	46	0.79		2	3.40		15	1.16
	112	0.20		5	3.18		20	0.81
				8	3.00		25	0.71
100	0	4.74		10	2.87		37	0.49
	2	4.02		13	2.73		50	0.19
	5	3.76		15	2.59			
	8	3.28		20	1.74	107	0	3.86
	10	3.17		25	2.14		2	3.07
	12	2.57		35	2.08		4	2.76
	15	1.78		49	1.36		6	2.60
	19	1.97		102	0.37		8	2.36
	25	1.74					10	2.23
	35	0.98	104	0	3.64		13	1.98
	45	0.89		1	3.08		15	1.91
	106	0.14		2	2.43		20	1.52

TABLE F-II CON'T.

Run	t min	(Pb) w/o	Run	t min	(Pb) w/o	Run	t min	(Pb) w/o
107	25	1.20	113	0	4.33	119	5	3.34
	42	0.72		2	3.82		8	2.79
				5	3.40		11	2.15
108	0	3.68		10	2.66		15	1.58
	2	3.26		20	1.55		20	0.90
	4	3.11		30	1.09		25	0.51
	6	2.86		40	0.46			
	9	2.64		51	0.24	120	0	4.67
	12	2.25		60	0.20		2	4.09
	15	2.27					3	3.59
	20	1.85	114	0	4.40		5	3.10
	25	1.55		2	3.54		8	2.11
	32	1.20		5	2.75		11	1.81
	58	0.62		10	1.82		15	0.94
				21	1.15		20	0.41
109	0	3.61		30	0.62			
	5	2.65		40	0.27	137	0	4.75
	11	1.89					3	3.80
	16	0.81	117	0	4.85		6	3.25
	26	0.71		2	4.05		10	2.72
	44	0.21		4	3.58		16	2.23
	60	0.05		8	2.93		23	1.67
				13	2.27		30	1.08
110	0	4.77		18	1.73		40	0.70
	2	4.18		24	1.18		63	0.17
	5	3.77		32	0.64			
	10	3.29		41	0.44	138	0	1.57
	20	2.52					2	1.09
	30	1.90	118	0	5.18		4	0.92
	40	1.52		2	4.66		7	0.71
	53	1.02		3	4.02		12	0.54
	70	0.50		6	3.46		20	0.41
				10	2.57		29	0.17
112	0	4.63		15	1.86		40	0.09
	2	4.08		20	1.23			
	5	3.48		25	0.70	139	0	2.95
	10	2.80		30	0.44		2	2.29
	20	1.78		40	0.28		3	2.38
	30	1.15					6	2.08
	40	0.73	119	0	5.03		10	1.71
	50	0.55		2	4.06		15	1.06
	61	0.22		3	3.84		20	0.61

TABLE F-II CON'T.

Run	t min	(Pb) w/o	Run	t min	(Pb) w/o	Run	t min	(Pb) w/o
139	27	0.13	141	0	4.75	142	0	4.75
	39	0.05		2	3.91		2	3.54
				5	3.23		6	2.89
140	0	6.80		10	2.37		10	2.61
	2	5.03		15	1.30		15	2.40
	5	4.36		20	0.74		20	1.83
	10	3.42		26	0.31		26	0.78
	15	2.92		34	0.13		30	0.35
	20	2.11						
	26	1.41						
	35	0.47						
	47	0.23						

TABLE F-III

Li(I) REDUCTION DATA

Conditions: T = 400°C
 Stirred, 112 rpm, glass stirrer
 20 gm salt (LiCl-KCl)
 100 gm alloy

Run 148
 $[\text{Na}]^o = 1.02 \text{ w/o}$

t min	(Na) w/o
0	0
1	1.45
2	1.20
3	1.74
4.5	2.12
6	2.09
8	2.37
10	2.15
15	2.33
22	2.60

Run 149
 $[\text{Na}]^o = 0.49 \text{ w/o}$

t min	(Na) w/o
0	0
1	0.38
2	0.71
3	0.73
5	1.15
7	1.26
9	1.22
12	1.52
16	1.68
21	1.93
41	1.95

Run 149: $[\text{Na}]^e = 0.085 \text{ w/o}$
 $[\text{Li}]^e = 0.110 \text{ w/o}$

TABLE F-IV

METAL REDUCTION CONDITIONS

All Experiments: 400°C
 112 rpm, glass stirrer
 100 gm alloy
 20 gm salt (30 gm, Run 126)

Solute	Run	(M^{n+}) ^o w/o	$M \text{ cm}^{-3*}$ $\times 10^4$	$[Li]^{o}$ w/o	k min^{-1}	Metal Obsvd.
Ag(I)	144	1.50	2.31	0.30	0.063	No
Cd(II)	125	1.85	2.73	0.30	0.030	No
Cd(II)	126	1.25	1.84	0.31	0.022	No
In(III)	128	1.90	2.75	0.25	0.017	No
Cr(III)	150	1.00	3.19	0	0.011	No
Cr(III)	131	0.79	2.52	0.25	0.04	Yes
Co(II)	121	1.03	2.90	0.26	0.093	Yes
Co(II)	122	1.03	2.90	0.31	0.105	Yes
Co(II)	124	1.03	2.90	0.37	0.118	Yes
Ni(II)	130	0.86	2.44	0.23	0.143	Yes
Ni(II)	146	0.86	2.44	0	0.057	Yes
Ni(II)	147	0.70	1.99	0	0.052	Yes
Ti(III)	145	0.43	1.49	0.24	0.050	Yes
Pt(II)	143	1.20	1.02	0.23	0.22	Yes

$$* \text{ } M \text{ cm}^{-3} = \frac{\text{w/o}}{100} \times \frac{g}{M}$$

TABLE F-V

METAL REDUCTION DATA

Run	t min	(M) w/o	Run	t min	(M) w/o	Run	t min	(M) w/o
121	0	1.03	126	45	0.12	144	2	0.95
	1.5	0.82		60	0.04		3	0.81
	2.8	0.52					4	0.70
	5	0.31	128	0	1.90		5	0.62
	10	0.12		2	1.63		7	0.47
	15	0.05		5	1.44		10	0.30
	20	0.02		10	1.29		12	0.22
	30	0.01		15	1.06		15	0.15
				22	0.72			
122	0	1.03		31	0.49	145	0	0.43
	2	0.58		44	0.29		4	0.33
	4	0.36		65	0.14		17	0.07
	7	0.18		97	0.06		25	0.02
	10	0.10						
	15	0.03	130	0	0.86	146	0	0.86
	20	N.D.		1.5	0.47		1	0.67
				3	0.35		3	0.52
124	0	1.03		5	0.15		5	0.41
	1	0.72		7.3	0.09		7	0.31
	3	0.49		10.3	0.03		10	0.20
	5	0.46		15	0.05		15	0.09
	11	0.04		22	N.D.		20	0.05
	13	0.03					25	0.02
	18	N.D.	131	0	0.79			
				1	0.71	147	0	0.70
125	0	1.85		2.5	0.65		1	0.52
	1	1.72		4	0.60		3	0.46
	3	1.50		6	0.49		5.3	0.36
	6	1.21		7.5	0.35		8	0.29
	10	0.94		11	0.06		11.5	0.12
	15	0.80		14	0.06		15	0.19
				16	0.03		20	0.04
126	0	1.25					25	0.02
	1	1.20	143	0	1.2			
	3	1.13		1.5	0.59			
	6	0.94		3.5	0.16			
	10	0.78		6	0.07			
	15	0.63						
	20	0.46	144	0	1.50			
	30	0.26		1	1.12			

TABLE F-V CON'T.

Run	t min.	(Pb) w/o	equiv. (Cr ³⁺) w/o
150	0	0	1.00
	5	0.31	0.85
	10.5	0.63	0.68
	20	0.92	0.54
	31	1.14	0.43
	45	1.18	0.41
	64	1.57	0.21
	82	1.77	0.11
	119	2.01	0
	142	1.99	0

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