

AN ABSTRACT OF THE THESIS OF

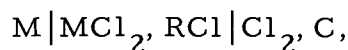
DRANNAN CARSON HAMBY for the DOCTOR OF PHILOSOPHY  
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(Major) (Date)

Title: THE THERMODYNAMIC PROPERTIES OF MOLTEN  
MIXTURES OF SOME TRANSITION METAL HALIDES WITH  
SOME ALKALI HALIDES

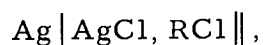
Abstract approved: *Redacted for Privacy*  
Dr. Allen B. Scott

Thermodynamic properties including the activity coefficient, and the partial molar free energy, enthalpy, and entropy of mixing have been determined for the solutes  $\text{NiCl}_2$  and  $\text{CoCl}_2$  in the solvents  $\text{KCl}$ ,  $\text{NaCl}$ ,  $\text{LiCl}$  and 1:1  $\text{NaCl-KCl}$ . The values of the properties were established by measuring the reversible emf's of cells of the type:



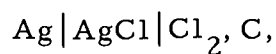
where R represents an alkali metal cation. Cell emf's were determined over a range of concentration from approximately  $10^{-4}$  to  $5 \times 10^{-1}$  mole fraction of solute and temperatures ranging from the melting points of the solvents to  $900^\circ\text{C}$ . The experimentally determined entropy of mixing has been compared with calculated values based on several microstate models.

Reference electrodes of the type:



which utilized solid porcelain as a bridge, were immersed in the same melts, and allowed continuous monitoring of chlorine electrode potentials as solute concentrations varied.

In a preliminary study of electrode designs the AgCl formation cell,



was studied as a function of temperature. Several electrode designs were tested for both the chlorine and metal electrodes. The relationship between cell emf and temperature was found to be in agreement with that established by Senderoff and Mellors.

The Thermodynamic Properties of Molten  
Mixtures of Some Transition Metal  
Halides With Some Alkali Halides

by

Drannan Carson Hamby

A THESIS

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Typed by Clover Redfern for Drannan Carson Hamby

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To

Bev, Marcy, and Mark

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# THE THERMODYNAMIC PROPERTIES OF MOLTEN MIXTURES OF SOME TRANSITION METAL HALIDES WITH SOME ALKALI HALIDES

## I. INTRODUCTION

The work reported in this thesis concerns the equilibrium properties of cobalt and nickel electrodes in mixtures of the divalent chlorides of these metals with the alkali metal chlorides, KCl, NaCl, and LiCl. The thermodynamic properties of these liquid mixtures have been of equal concern. Interest in these systems is grounded both in the more practical aspects of electrochemical separations and in a desire to compare experimentally determined thermodynamic quantities with values calculated on the basis of particular lattice models of the liquid mixtures.

The feasibility of utilizing a fused salt electrolysis to prepare essentially cobalt free (20 parts per million by weight) nickel, starting with ferronickel alloy, was demonstrated by Nissen and Scott (1964). Several advantages of molten salts over water as an electrolyte were mentioned; e. g., higher electrical conductivity, greater decomposition span, excellent possibilities for altering solute activities and the spread of standard potentials by varying solvent composition, and greater choice in selection of temperature of operation which may be useful in activity control both in the melt and in the deposit. Their solvent was a mixture of 60 wt% KCl and 40 wt% NaCl which melted

near 650° C. In a supporting study (Hamby, 1961) the present author determined the electrode potentials of nickel and cobalt in 1:1 molar NaCl-KCl over a solute concentration range of  $5 \times 10^{-4}$  to  $5 \times 10^{-2}$  mole fraction and a temperature range of 650° C to 800° C. More recently Sullivan, Barton, and Cattoir (1968) have utilized the LiCl-KCl eutectic as the solvent in a single stage electrolytic separation which yielded a nickel product containing less than 0.1 weight percent cobalt. The degree of success attained in these studies have stimulated our further investigation of fused salt solvents as electrolytic separation media.

It has been reported that activation polarization is small in fused chloride systems which are essentially free of water and hydrolysis products (Yang and Hudson, 1959a; Delimarskii and Vlasyuk, 1962). The minimum potential difference needed for decomposition of a molten transition metal chloride,  $MCl_2$ , in a molten alkali halide or mixture of alkali halides,  $RCl$ , is expected to be close to the reversible electromotive force (emf),  $E$ , for the cell



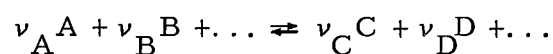
where  $N$  is the mole fraction,

$$N = \frac{n_{MCl_2}}{n_{MCl_2} + n_{RCl}} \quad (1)$$

and  $n_{MCl_2}$  and  $n_{RCl}$  are numbers of moles of transition metal and alkali metal chloride respectively. Therefore, determination of  $E$  as a function of solute concentration, solvent composition, and temperature provides basic information which is pertinent in the selection of optimum operating conditions for the electrochemical separation of the metals,  $M$ .

### The Thermodynamics of Reversible Cells Without Liquid Junction

The determination of the reversible emf's for galvanic cells is one of the classical methods for evaluation of the changes in the thermodynamic potentials,  $G$ ,  $S$ , and  $H$ , the Gibbs function, the entropy, and the enthalpy respectively, associated with the assumed cell reaction. We shall base our initial discussion on an assumed reaction



where the  $\nu$ 's are stoichiometric coefficients. The reaction as written implies a particular choice of components for the description of the system which consists of the melt, the electrodes and the reactants. The relationships between the thermodynamic potentials, and the measured quantities  $E$ ,  $P$ ,  $T$ , and  $N$  may be derived on the basis of the first and second laws of thermodynamics and an assumption concerning the number and kinds of variables necessary to specify

the state of the system. In addition to the assumed cell reaction we assume the validity of the following relationships:

- (a) For any infinitesimal process, the change in energy,  $U$ , of the system will be given by

$$dU = dq - PdV - E'dZ \quad (2)$$

where  $dq$  is the heat exchanged with the surroundings,  $P$  is the pressure exerted by the surroundings on the system,  $V$  is the system volume,  $E'$  is the terminal potential difference, TPD, for the cell and is always a positive quantity when the cell reaction proceeds in the forward direction.  $dZ$  is the amount of electricity which has passed between the terminals through an external circuit during the process.

- (b) For any infinitesimal isothermal process

$$TdS \geq dq \quad (3)$$

where the equality refers to a reversible process and the inequality to an irreversible process.

$$(c) \quad G = G(T, P, n_1, \dots, n_i, \dots, n_r) \quad (4)$$

The extent-of-reaction variable,  $\xi$ , is defined as

$$Z = nF\xi \quad (5)$$

where  $F$  is the Faraday, 96,500 coulombs, and  $n$  is an integer chosen so that  $nF$  is the quantity of electric charge that passes through the external circuit when the cell reaction has proceeded by one unit of advancement.

Then

$$dZ = nFd\xi \quad (6)$$

and substituting (6) and (3) into (2)

$$dU \leq TdS - PdV - nFE'd\xi. \quad (7)$$

The Gibbs function,  $G$ , is defined as

$$G = U + PV - TS. \quad (8)$$

It follows from (7) and (8) that at constant temperature and pressure

$$dG_{T,P} \leq -nFE'd\xi. \quad (9)$$

Dividing this equation through by  $d\xi$  indicates that the change in the Gibbs function per unit of advancement of the cell reaction at constant temperature, pressure and composition,  $\Delta\bar{\mu}$ , will always be equal to or less than  $-nFE'$ , or  $E'$  will always be equal to or less than the quantity  $E$ , the reversible cell potential, provided the assumed electrode reactions predominate.

The relationships between the thermodynamic potentials and concentration may be established through Equation (4). Differentiating Equation (4)

$$dG = \left(\frac{\partial G}{\partial T}\right)_{P, n_i} dT + \left(\frac{\partial G}{\partial P}\right)_{T, n_i} dP + \sum_i \left(\frac{\partial G}{\partial n_i}\right)_{T, P, n_j \neq n_i} dn_i \quad (10)$$

and using the definition

$$\left(\frac{\partial G}{\partial n_i}\right)_{T, P, n_j \neq n_i} = \mu_i = \text{chemical potential} \quad (11)$$

we have

$$dG = \left(\frac{\partial G}{\partial T}\right)_{P, n_i} dT + \left(\frac{\partial G}{\partial P}\right)_{T, n_i} dP + \sum_i \mu_i dn_i. \quad (12)$$

The  $dn_i$  are related to the extent of reaction variable according to

$$dn_i = \nu_i d\xi \quad (13)$$

where the  $\nu_i$  are positive for products and negative for reactants.

At constant temperature and pressure Equation (12) yields

$$dG_{T, P} = \sum_i \mu_i \nu_i d\xi \quad (14)$$

or for a reversible change

$$\Delta \bar{\mu} = \sum_i \mu_i \nu_i = -nFE. \quad (15)$$



The quantities  $\mu_i$  may be defined in terms of concentrations, activities, and activity coefficients in order to allow a convenient representation of the cell data in terms of solute concentrations.

We further define the chemical potential,  $\mu_i$ , as

$$\mu_i = \mu_i^\circ + RT \ln a_i \quad (16)$$

where  $\mu_i^\circ$  is the chemical potential of component  $i$  in its standard state,  $R$  is the gas constant,  $a_i$  is the activity of component  $i$ , and  $RT \ln a_i$  is the change in Gibbs function necessary to transfer one mole of  $i$  from its standard state to the state in which its chemical potential is  $\mu_i$ . In order to complete the definition a reference function must be chosen to provide connection between the  $\mu_i$  and experiment. For the solutes and solvents we choose the mole fraction,  $N$ , as the reference function and define the reference state according to

$$\lim_{N \rightarrow 1} \frac{a}{N} = 1 \quad (17)$$

at the temperature of the experiment and one atmosphere total external pressure. The activity coefficient,  $\gamma$ , is defined as

$$a = N\gamma. \quad (18)$$

The reference and the standard states of the solutes and solvents

according to these definitions correspond to the pure liquids with the properties of the pure liquids at the temperature of the experiment and one atmosphere total external pressure. The reference function for chlorine gas is taken to be the pressure

$$\lim_{P_{Cl_2} \rightarrow 1} \text{at 1 atm total pressure} \frac{a_{Cl_2}}{P_{Cl_2}} = 1 \quad (19)$$

and

$$a_{Cl_2} = P_{Cl_2} \gamma_{Cl_2} \quad (20)$$

The reference function for the metallic reactants is mole fraction and the reference and standard states for the metals are taken as the pure elements in their stable modification at one atmosphere total pressure, at one atmosphere pressure, and the temperature of the experiment.

Utilizing (15), (16), and (18), we obtain

$$E = -\frac{1}{nF} \sum_i \nu_i \mu_i^\circ - \frac{RT}{nF} \sum_i \nu_i \ln N_i - \frac{RT}{nF} \sum_i \nu_i \ln \gamma_i \quad (21)$$

or

$$E = E^\circ - \frac{RT}{nF} \sum_i \nu_i \ln N_i - \frac{RT}{nF} \sum_i \nu_i \ln \gamma_i \quad (22)$$

which is the Nernst Equation;  $E^\circ$  corresponds to the cell emf when all reactants and products are in their standard states.

The relationship between the temperature coefficient of the cell emf and the partial molar entropy change involved in the reaction,  $\tilde{\Delta s}$ , may be established by considering Equations (7), (8), (15), and (11). From (15) and (11)

$$E = - \frac{1}{nF} \sum_i \nu_i \left( \frac{\partial G}{\partial n_i} \right)_{T, P, n_j \neq n_i} \quad (23)$$

Differentiating with respect to temperature at constant pressure and composition and applying Equations (7) and (8) yields

$$\left( \frac{\partial E}{\partial T} \right)_{P, n_i} = - \frac{1}{nF} \sum_i \nu_i \frac{\partial^2 G}{\partial n_i \partial T} = \frac{1}{nF} \sum_i \nu_i \left( \frac{\partial S}{\partial n_i} \right)_{T, P, n_j \neq n_i} \quad (24)$$

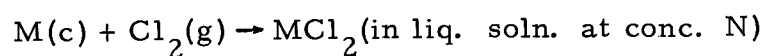
or

$$\tilde{\Delta s} = \sum_i \nu_i \left( \frac{\partial S}{\partial n_i} \right)_{T, P, n_j \neq n_i} = nF \left( \frac{\partial E}{\partial T} \right)_{P, n_i} \quad (25)$$

The partial molar enthalpy for the cell reaction is

$$\tilde{\Delta H} = \tilde{\Delta \mu} + T \tilde{\Delta s} \quad (26)$$

We now consider the cell reaction



The partial molar mixing functions for this reaction are:

$$\bar{G} = -nFE - \Delta\tilde{\mu}^\circ, \quad (27)$$

$$\bar{S} = nF\left(\frac{\partial E}{\partial T}\right)_{P, n_i} - \Delta\tilde{s}^\circ, \quad (28)$$

$$\bar{H} = -nFE + nFT\left(\frac{\partial E}{\partial T}\right)_{P, n_i} - \Delta\tilde{H}^\circ, \quad (29)$$

where  $\Delta\tilde{\mu}^\circ$ ,  $\Delta\tilde{s}^\circ$ , and  $\Delta\tilde{H}^\circ$  refer to the changes in Gibbs function, entropy, and enthalpy when the cell reaction is carried out with all reactants and products in their standard states. These mixing quantities give the changes in the functions when one mole of solute,  $MCl_2$ , is transferred from the reference state to the solution at concentration  $N$ , temperature  $T$  and one atmosphere total pressure.

Throughout this thesis the expression "ideal" when applied to the solutes  $NiCl_2$  and  $CoCl_2$  will indicate Raoult's law behavior of the solute. In this sense it is easily demonstrated that solute ideality requires

$$a = N. \quad (30)$$

Considering equations (22), (27) and (30) and the assumed cell reaction it is reasonable to define the excess partial molar free energy of mixing,  $\bar{G}^E$ , as

$$\bar{G}^E = \bar{G} - RT \ln N = RT \ln \gamma. \quad (31)$$

It is to be emphasized that the relationships above are not based

on any particular micro-model of the liquid. They were chosen mainly on the basis of convenience for data tabulation. In later sections we will suggest other choices of components which lead to different values of  $\gamma$  and we will attempt to calculate the values of the mixing functions on the basis of particular models of the liquid structure. A listing of the basic assumptions and equations involved in the statistical treatment will be deferred to a later section.

### Purpose of the Study

The introductory discussion above is adequate to allow a concise statement of the purposes of this study. They were:

- (1) To establish the reversible emf's for the cells



and



where RCl is KCl, NaCl, 1:1 molar NaCl-KCl, or LiCl, over as wide a range of solute concentration and temperature as possible.

- (2) To utilize the cell data to establish and tabulate several thermodynamic quantities including:

a. The activities and activity coefficients of the solutes as

a function of concentration and temperature.

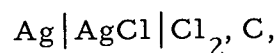
b. The mixing quantities  $\bar{S}$ ,  $\bar{H}$ ,  $\bar{G}$ .

c. The standard quantities  $\Delta\tilde{\mu}^\circ$ ,  $\Delta\tilde{s}^\circ$  and  $\Delta\tilde{H}^\circ$  for the cell reactions.

- (3) To calculate values of  $\bar{S}$  on the basis of simple lattice models of the liquid and compare these values with the experimental values.

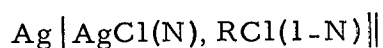
In the course of carrying out the work listed above two related problems were studied:

- (4) The reversible emf's of the AgCl formation cell,



were measured in a study aimed primarily toward evaluation of electrode designs and other measurement techniques.

- (5) Reference electrodes of the type



where the junction is an ion-conductive porcelain, were prepared and utilized in electrode reversibility tests and in polarographic tests of melt purity. The range of solute concentration over which one may convert electrode potentials based on this reference electrode to potentials based on the chlorine electrode without correcting for junction

effects was established.

### The Literature

The amount of work done on fused salt systems has grown rapidly since World War II both because of the possibility of new technological applications and because of intrinsic scientific interest in these liquids. Most of the common physicochemical measurements and techniques of study have been applied, including infrared, visible, ultraviolet and Raman spectroscopy, measurements of vapor pressure and composition, viscosity, cryoscopy, X-ray and neutron diffraction, molar volume, calorimetry, and many electrochemical techniques. Several monographs have appeared, which, taken together, provide adequate surveys of most of the areas of interest in the field up to about 1964. These include the books edited by Blander (1964) and Sundheim (1964) and a more recent elementary text by Bloom (1967). Both Blander's and Sundheim's books contain excellent surveys on the thermodynamics of fused salt solutions. Two books emphasizing electrochemistry in molten salts have been authored by the Russians Delimarskii and Markov (1961) and Lantratov, Alabyshev and Morachevskii (1965). An extensive critical compilation of molten salt data and experimental technique has been prepared by G. J. Janz (1967) and a book concerned with the thermodynamics of molten salt mixtures has been authored by J. Lumsden (1966).

In addition to these books several shorter surveys on special topics pertinent to this work have appeared since 1964. O. J. Kleppa (1965) has reviewed the equilibrium solution chemistry of simple fused salts. J. A. Plambeck (1967) has reviewed electromotive force series in molten salts and G. M. Dijkhuis, Ria Dijkhuis and G. J. Janz (1968) have reviewed molten salt formation cells. Electrode processes in molten salts have been reviewed by A. D. Graves, G. J. Hills and D. Inman (1966). Experimental techniques have been reviewed by R. A. Bailey and G. J. Janz (1966) and the topic of molten salts as solvents has been reviewed by H. Bloom and J. W. Hastie (1965). An early but excellent review on electrodes in fused salt systems by R. W. Laity (1961) also deserves mention.

It is of interest to mention that early research in the United States on cells similar to those studied in this work was carried out by J. H. Hildebrand (1927, 1932) and his students (Watchter, 1930; Salstram, 1930a, 1930b) in the 1930's. Much of the terminology established by that group is still in use today. R. Osteryoung (1954) has included a historical survey in his thesis which reviews much of the early fused-salt research.

#### Operational Criteria of Reversibility

The quantities sought in this work are the reversible  $\text{emf}'\text{s}$  and the temperature coefficients of  $\text{emf}$  for the cells of interest.



Zemansky defines a reversible process as a hypothetical one which can be performed in such a manner that, at the conclusion of the process, both the system and the surroundings may be restored to their initial states without producing any resultant changes in the rest of the universe. In the present case, our idealized goal was to construct galvanic cells without liquid junction, characterized by a single cell reaction, each consisting primarily of metallic and gas electrodes in dynamic equilibrium with a single molten salt solution and capable of a high degree of reversibility. It is essential that such cells be designed so that the cell reaction cannot proceed at an appreciable rate without flow of electric current through an external circuit and that the cell reaction may be made to proceed as slowly as desired by controlling the current in the external circuit. In such studies the terminal potential difference,  $E'$ , established between the electrodes is commonly measured by the Poggendorf method whereby  $E'$  is opposed by an external source of emf of magnitude  $E''$ . In the case  $E' > E''$  the cell reaction proceeds in the forward direction and in the case  $E' < E''$  the flow of current and the cell reaction are reversed. At the null point  $E' = E''$  there is no flow of current in the external circuit and an infinitesimal change in  $E''$ ,  $\pm dE''$ , can cause current to flow in either direction. This sequence of tests provides an operational definition of cell reversibility, namely, the value of  $E'$

should deviate only slightly<sup>1</sup> from its no-load value when current is drawn in either direction through the cell and there should be no discontinuity in a plot of  $E'$  against cell current at the null point; the plot should exhibit no hysteresis effects in the null region. Provided these conditions are satisfied, we equate  $E$ , the reversible cell potential, to  $E'$  at the null point.

Several additional experimental indications of irreversibility are suggested in the literature including the following:

- (a) Short term fluctuations occur in  $E'$ .
- (b) Apparently identically prepared electrodes in the same solution give different values of  $E'$ .
- (c) Changes in  $E'$  occur when the electrodes are shaken or moved.
- (d)  $E'$  does not rapidly return to the null value after cell current is drawn and then terminated.
- (e) The variation of  $E'$  with temperature is not reproducible.
- (f) Failure to obtain agreement for the emf of a particular cell by independent investigators.

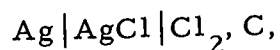
This brief discussion allows us to emphasize that experimental reversibility is a matter of degree. In the present case short term

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<sup>1</sup>A completely reversible electrode is one whose potential is unaffected when net electric current flows across its surface (Ives and Janz, 1961, p. 15).

(less than seconds) fluctuations of electrode potentials of less than 1 mv have been deemed acceptable and reproducibility of null points to within  $\pm 1$  mv when approached from opposite directions of current flow has been taken as evidence of satisfactory electrode behavior. Actually, all of the various criteria of irreversibility listed above have been applied in this study and additional comments concerning them will be made later in the Experimental and Results sections.

Due to the central importance of the chlorine electrode in this study, and to the fact that several methods of construction and pre-treatment of such electrodes are suggested in the literature (Salstrom and Hildebrand, 1930; Stern, 1956; Senderoff and Mellors, 1958; Shams El Din, 1961; Leonardi and Brenet, 1965; Yang and Hudson, 1959b; Flengas and Ingrahm, 1959), it was thought advisable to initiate this work by demonstrating the preparation of a reversible chlorine electrode. The cell chosen for initial study was the AgCl formation cell,



because it has received attention from several independent investigators (Salstrom, 1933; Senderoff and Mellors, 1958; Leonardi and Brenet, 1965; Yang and Hudson, 1959; Flengas and Ingrahm, 1959) and a direct comparison of data was possible. The investigation of this cell demonstrated the preparation of a reversible chlorine

electrode according to our operational criteria.

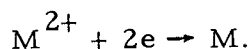
Just as the degree of reversibility must be quantitatively stated because true reversibility is impossible to achieve, certain other desirable but difficult-to-achieve features of these experiments require comment. These are: (1) freedom of the electrode from mixed reactions,<sup>2</sup> a problem related to melt purity; (2) restriction of the cell reaction to electrochemical reactions at the electrodes, a problem related to reactant solubility and design of the electrodes; and (3) maintenance of unit or known activity of the reactants at the electrodes, a possible problem with the chlorine electrodes because of the high vapor pressures of the molten salts at elevated temperatures. These problems will be discussed in order before turning to a more detailed description of experimental apparatus and technique.

### Mixed Reactions, Melt Purity

Although electrode reaction kinetics is not a primary topic of this work it may be effectively argued that a purely thermodynamic view of the electrode system is inadequate. Such is the case when one confronts the problem of mixed potentials. Consider first a redox reaction at a simple electrode where only one reaction is taking place,

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<sup>2</sup>The term "mixed reactions" means that the potential of the electrode is determined by more than one electrochemical reaction.



At equilibrium the transition of charge carriers across the interface takes place in both directions giving rise to anodic,  $i_+$ , and cathodic,  $i_-$ , current densities and  $i_+ = |i_-| = i_o =$  the exchange current density. Under non-equilibrium conditions the measured current density is

$$i = i_+ - |i_-|$$

and it may be demonstrated that at low current densities, provided certain other conditions are fulfilled, (Kortüm, 1965, p. 466)

$$i = \frac{i_o 2F \eta_t}{RT} \quad (32)$$

where  $\eta_t = \epsilon_i - \epsilon =$  transition overpotential,  $\epsilon_i$  is the electrode potential with respect to a non-current carrying reference when the electrode current density is  $i$  and  $\epsilon$  is the reversible potential of the electrode with respect to the same reference. Interest in this equation centers on the prediction that the degree of polarization or departure of  $\epsilon_i$  from the reversible potential of the electrode,  $\eta_t$ , at a given current density depends on the magnitude of the exchange

current, the polarization being less the greater the magnitude of  $i_o$ .<sup>3</sup>

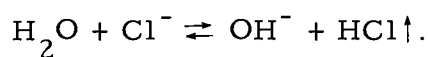
Polarization phenomena at mixed electrodes are more difficult to treat. Kortüm (1965) examines the simple case of two independently occurring reactions associated with exchange currents  $i_{o1}$  and  $i_{o2}$  at the same electrode, with each reaction subject only to transition (activation) polarization. It is predicted that the mixed potential of the electrode with respect to an arbitrary reference electrode will lie between the two single electrode potentials. At the potentiometric null point no current flows in the external circuit; however, net current may still flow across the electrode surface with respect to both of the independent reactions, a common occurrence in metallic corrosion. Kortüm demonstrates for this simple case that when  $i_{o2} \gg i_{o1}$  the measured potential is near the equilibrium value for the reaction of higher exchange current density. Since the exchange current is concentration-dependent, it is apparent that as the concentration of ionic species associated with  $i_{o2}$  becomes less, the effect of the interfering reaction on the measured electrode potential will become greater.

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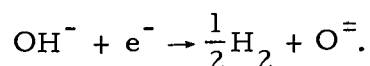
<sup>3</sup>In general, exchange currents at metal electrodes in chloride melts are high, e. g. at a nickel electrode in fused NaCl-KCl  $i_o$  ranges from about one to four amp/cm<sup>2</sup> at concentrations from about  $5 \times 10^{-4}$  to  $5 \times 10^{-3}$  mole fraction (Graves et al., 1966). These numbers may be contrasted with those for the evolution of hydrogen on smooth platinum in 1N HCl where  $i_o = 10^{-3}$  amp/cm<sup>2</sup> (Conway, 1952) which is a high value of  $i_o$  for cationic species in aqueous systems.

The conclusion to be drawn is summarized by Ives and Janz (1961). For an electrode to be well-behaved its exchange current should be large with respect to any net current that it is required to carry in use. If the exchange current falls too low, e. g. by decreasing an ionic concentration in solution, the electrode may no longer be characteristic of the desired reaction, instability may set in and its potential may be largely determined by species considered to be impurities in the melt.

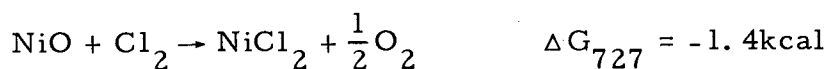
Therefore, it is to be anticipated that the lowest solute range accessible to study in experiments of the type of interest will be determined either by solvent decomposition or by impurities in the melt. Fortunately, a source of NaCl and KCl of better than reagent grade purity was readily available for this work; only reagent grade LiCl was available. It was anticipated that the most serious contaminant to be dealt with would be oxygen or oxygen-containing products of hydrolytic reactions. In particular, Laitinen (1957) has proposed the possibility of melt contamination according to the reaction



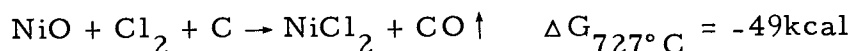
The  $\text{OH}^-$  ion can then interfere with the desired equilibrium at the cathode according to



Prevention of the undesirable hydrolytic reaction has been the subject of several papers. Gardner, Brown, and Janz (1956) have studied the temperature dependence of weight loss in drying the alkali chlorides under high vacuum,  $10^{-6}$  mm Hg. Burkhard and Corbett (1957) have reported on the solubility of water in molten mixtures of LiCl and KCl. Laitinen, Ferguson, and Osteryoung (1957) suggest a method for preventing hydrolysis in LiCl-KCl eutectic which involves several days of drying under moderate vacuum,  $10^{-2}$  mm Hg, followed by fusion under dry HCl and subsequent removal of the HCl from the melt. Maricle and Hume (1960) report equal success with alkali halide mixtures, including those containing LiCl, in certain temperature ranges, by simple chlorination of the melt immediately after fusion of the undried salts. Nissen (1964) preferred chlorination in the presence of carbon, a choice which can be justified on the basis of the thermodynamics of reactions such as



and

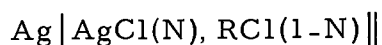


(Kubashewski and Evans, 1956). Various combinations of the above methods have been utilized in the present work as will be described in the Experimental section.



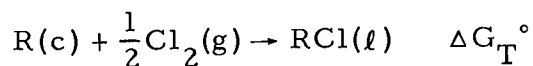
Three ways have been used in this work to evaluate the degree of success in prevention of hydrolysis or removal of hydrolysis products. They were: (a) obedience to the Nernst equation at low solute concentration; (b) the degree of etching of glass cell parts, a qualitative test; and (c) polarographic measurement of decomposition potentials (Laitinen, 1957). Method (a) depends upon the assumption that the activity coefficient,  $\gamma$ , of the solute will become constant at sufficiently low solute concentration. In this concentration range, providing unit activity of reactants is maintained, a plot of  $E$  against  $\log N$  will be linear with slope  $2.303 RT/2F$ . Failure to obtain the proper limiting slope at low solute concentration is taken as evidence of mixed electrode reactions and the presence of undesirable quantities of impurities in the bath.

Satisfactory application of method (c) required the construction and use of a suitable reference electrode. The electrode chosen for this work may be schematically designated as



where the double line indicates a non-porous, ion-conductive bridge. Similar reference electrodes have been studied by several investigators (Bockris, 1959; Flengas and Ingrahm, 1959; Yang and Hudson, 1959). This particular design was developed by Lamb and Labrie (1959).

In the polarographic test three electrodes are used, the reference, a working or counter electrode, and a metallic electrode of small ( $\sim$  area  $< 1 \text{ mm}^2$ ) but constant surface area (micro-electrode). The test is carried out by gradually increasing the magnitude of the applied potential difference between the counter electrode (positive) and the micro-electrode (negative) while monitoring the current,  $I$ , between these electrodes and the potential difference,  $V$ , between the micro-electrode and the non-current carrying reference electrode. The current,  $I$ , is plotted as a function of  $V$ . Depending upon the purity of the electrolyte and the nature of the electrodes,  $I$  gradually increases with increasing  $V$  until the region of the decomposition potential products of a definite electrochemical reaction appear at the electrodes at near unit activity;  $I$  then increases abruptly with increasing  $V$ . For the pure alkali halides the anticipated decomposition potentials may be calculated from the standard change for the formation reaction



and

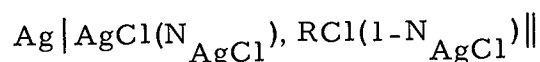
$$E_{\text{decomposition}} \approx - \frac{\Delta G_{\text{T}}^{\circ}}{nF}. \quad (33)$$

Decomposition of the electrolyte at applied voltages lower than

$E_{\text{decomposition}}$  or the observation of high residual currents preceding the decomposition are indicative of the presence of undesirable

quantities of impurities.

In addition to its usefulness in polarographic work the silver reference electrode served other useful purposes. Incorporation of the reference



in the cells



where in each case the solvent, RCl, was the same on both sides of the membrane, allowed measurement of the quantity:

$$\Delta E' = E'_{\text{Ag}} - E_{\text{Ag}}$$

where  $E'_{\text{Ag}}$  and  $E_{\text{Ag}}$  are emf's for the cell.



in the cases  $N_{\text{MCl}_2} \neq 0$  and  $N_{\text{MCl}_2} = 0$ . This information has proved useful in establishing the limits of  $\text{MCl}_2$  concentration over which one may convert potentials measured with the Ag reference electrode to potentials based on the chlorine reference electrode without correcting for junction potentials.

The reference also proved useful in providing a method for continuous monitoring of the chlorine electrode potential during cell

operation.

### Reactant Solubility

In reality, cells without junction are difficult to achieve just as is the reversible cell. Although the cells of interest are described as containing only one solution, in reality there must be small differences in composition of the electrolyte from one electrode to the other. Of prime concern in design and cell feasibility considerations are the solubilities of the reactants M and  $\text{Cl}_2$  in the electrolyte solution. Precise solubility data are not available; however, Greenberg and Sundheim (1958), on the basis of spectral studies indicate a solubility of approximately  $10^{-5}$  mole fraction of  $\text{Cl}_2$  in KCl-LiCl at  $400^\circ\text{C}$ . The halide is believed to be dissolved as the trihalide ion.

No data is available on the solubilities of Co and Ni in alkali halide melts; however, these solubilities are believed to be negligible (Corbett, 1964). The solubility of Ni in  $\text{NiCl}_2$  at  $978^\circ\text{C}$  was found to be appreciable, nine mole % (Johnson, Cubbicciotti and Kelly, 1958). It appears that metal solubility with the possibility of transfer of unreacted metal to the halogen electrode would only be a problem in melts rich in transition metal at high temperature.

The appreciable solubility of chlorine in the alkali halides has been taken into consideration in cell design by connecting the electrode compartments containing M and chlorine electrodes by a tortuous,

capillary path intended to reduce the rate of diffusion of the dissolved chlorine to the metal electrode. It is realized, however, that this problem is an additional limiting factor on the lower level of solute concentration accessible to study with cells without junction which utilize a chlorine electrode.

### Reactant Activity

Maintenance of unit activity of the Co, Ni or Ag reactants has not been considered a serious problem in this work. However, due to the fact that the molten salts used do have appreciable vapor pressures in the temperature range of interest, the problem of deviation of  $\text{Cl}_2$  activity from unity required consideration.

Vapor pressures for the salts used in this work have been determined (Barton and Bloom, 1956; Bloom, Bockris, Richards and Taylor, 1958; Shafer, 1955); values at selected temperatures are given in Table 1. No data are available on vapor pressures of mixtures of the salts.

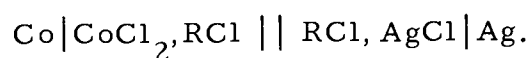
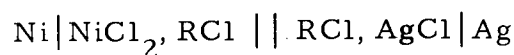
	700° C	800° C	900° C
NaCl	$5.0 \times 10^{-5}$	$4.5 \times 10^{-4}$	$2.7 \times 10^{-3}$
KCl	$1.1 \times 10^{-4}$	$9.1 \times 10^{-4}$	$5.0 \times 10^{-3}$
$\text{CoCl}_2$	$6.5 \times 10^{-3}$	$4.0 \times 10^{-2}$	$1.7 \times 10^{-1}$
$\text{NiCl}_2$	$2.1 \times 10^{-3}$	$3.0 \times 10^{-2}$	$2.7 \times 10^{-1}$
AgCl	$8.4 \times 10^{-3}$	$8.3 \times 10^{-2}$	$5.5 \times 10^{-1}$

Assuming that chlorine activity is equal to the partial pressure of the chlorine gas at one atmosphere total pressure, the Nernst equation may be used to calculate the chlorine pressure decrease necessary to cause a decrease in cell emf of one mv. These values are  $2.5 \times 10^{-2}$ ,  $2.2 \times 10^{-2}$  and  $2.0 \times 10^{-2}$  atm at 700°, 800°, and 900° C respectively. A pressure decrease of approximately 0.1 atm would be required for a 5 mv change in E. One would, therefore, anticipate detectable variations in chlorine activity due to melt vaporization only in melts having high solute concentrations at temperatures near or above 800° C. These considerations have also led us to neglect corrections for fluctuations in atmospheric pressure during cell operation.

A numerical correction of the cell data has not been attempted due to lack of adequate vapor pressure data for the mixtures.

## II. EXPERIMENTAL

Two AgCl formation cells, six cells involving  $\text{NiCl}_2$  as a solute, and four cells in which  $\text{CoCl}_2$  was the solute were tested. The AgCl cells will be referred to as cells A and B, the  $\text{NiCl}_2$  containing cells as cells I through VI, and the  $\text{CoCl}_2$  containing cells as cells VII through X respectively. Cells III through X also contained Ag reference electrodes and, thus, also provided information on the cells



Schematic diagrams of the cell and auxiliary apparatus are shown in Figures 1 and 2. The outer cell envelope consisted of two parts, a closed-end Vycor tube and a Pyrex top. The Vycor tube was 64 mm in diameter, 45 cm long and flanged at the open end; the Pyrex top, also made of 64 mm tubing, had a matching ground flange and tubular openings through which electrodes, a thermocouple, and a sampling tube could be introduced into the cell. When the cell was assembled, the glass flanges were separated by an O ring and clamped together by means of water cooled metal clamps. The various cell parts, which entered through the cell top, were coupled by means of rubber tubing of appropriate sizes to the tubular openings in the Pyrex top. An inner crucible of Vycor, or Ultra Carbon Co. UF-4-S

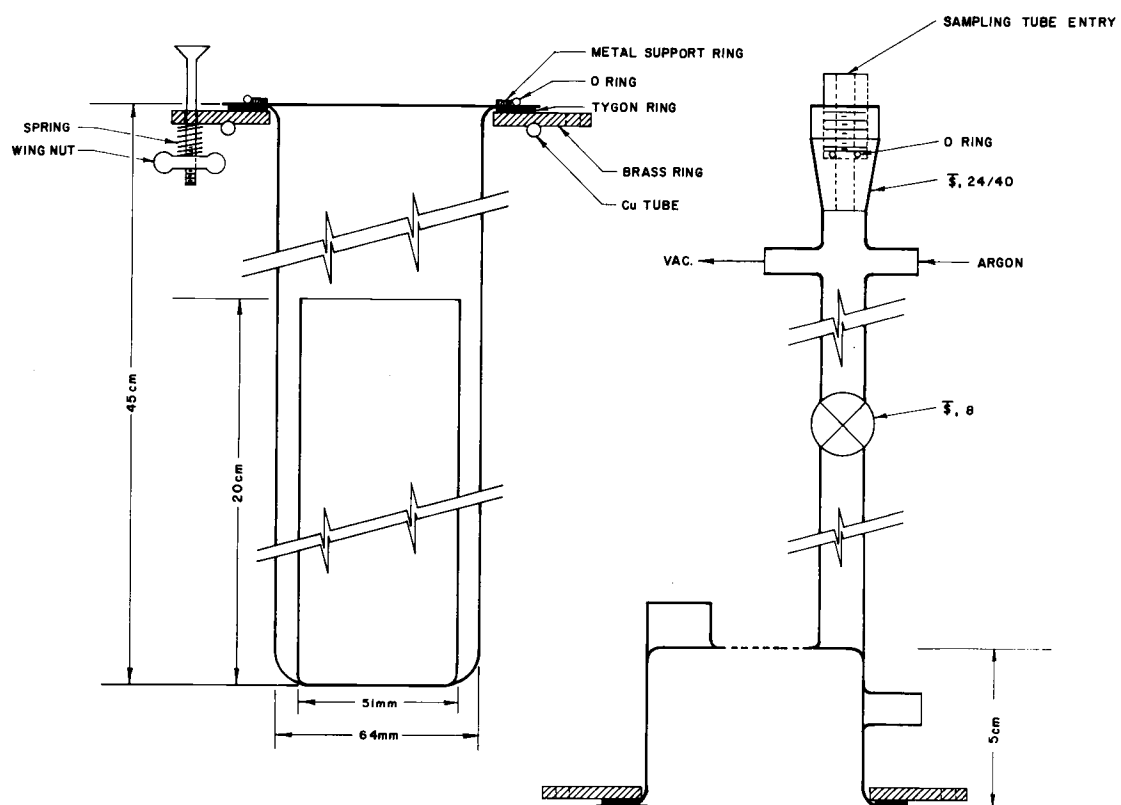


Figure 1. The cell envelope.



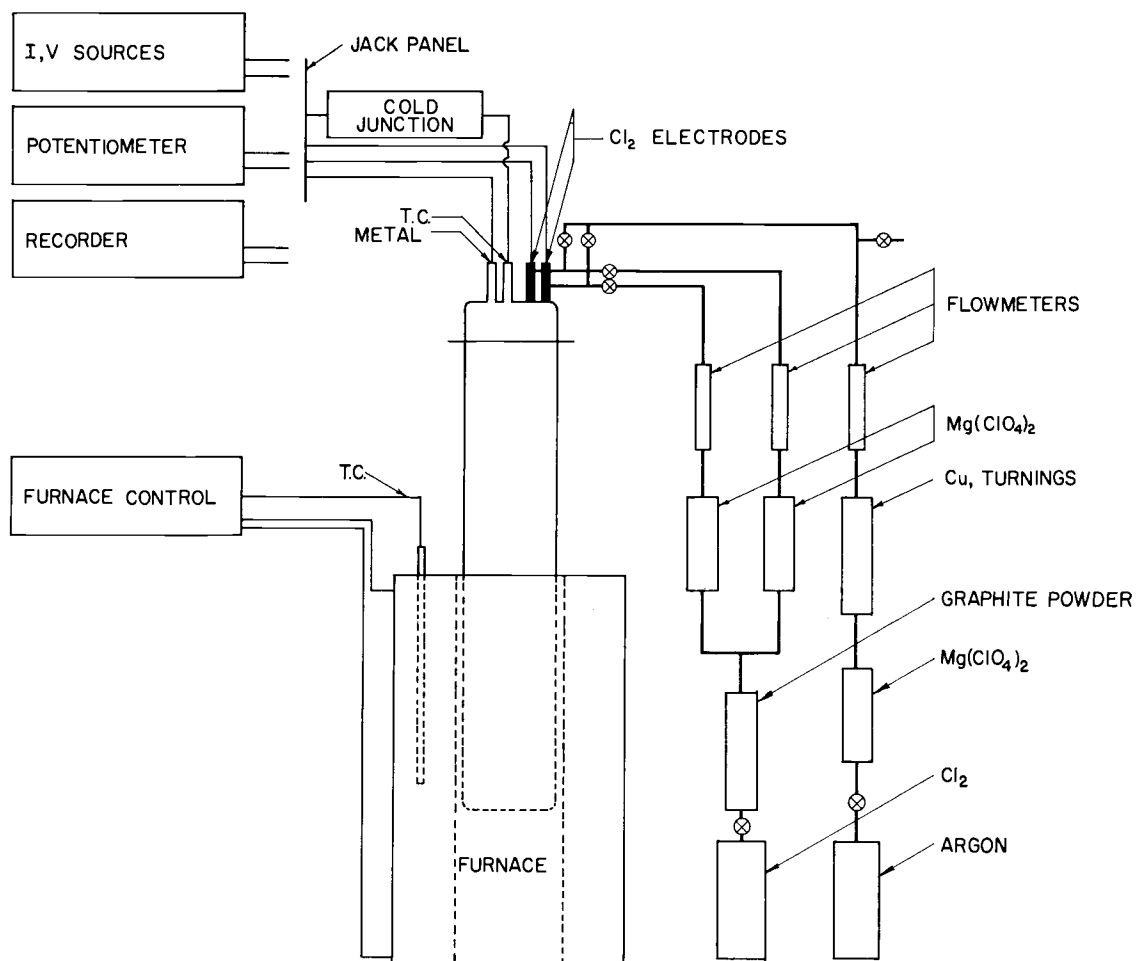


Figure 2. The cell, furnace, and auxiliary apparatus.

graphite in the case of the AgCl formation cells, was used as the melt container.

Each cell tested utilized two chlorine electrodes; the three basic chlorine electrode designs, a, b, and c are illustrated in Figure 3 and the designs utilized in each cell are indicated by subscripts below the carbon electrode symbols in Appendices I and II. The graphite rod was 1/4" diameter Ultra Carbon Co. grade UF-4-S. The porous parts were machined from National Carbon Co., grade 60, porous graphite. The Vycor sheath served to prevent shorting of the electrodes, provided mechanical strength, and defined the path of the Cl<sub>2</sub> into the melt. In addition to serving as an inert electrode material the carbon rods served to preheat the chlorine to bath temperature as the gas passed along the length of the rod into the melt. Correct placement of the chlorine exit holes in the Vycor allowed formation of a three phase junction at the escape pressure of the gas, near atmospheric. Air tightness at the top of the sheath was insured by application of a high melting wax in the liquid state while maintaining a vacuum in the sheath. Pretreatment of the electrodes consisted of dipping in dilute HF, rinsing in tap water, immersion in boiling dilute HCl, rinsing in distilled water, and then heating to 800° C in chlorine for several hours. The electrodes were then placed in an auxiliary container and maintained at approximately 200° C under chlorine until they were transferred to the cell for use.

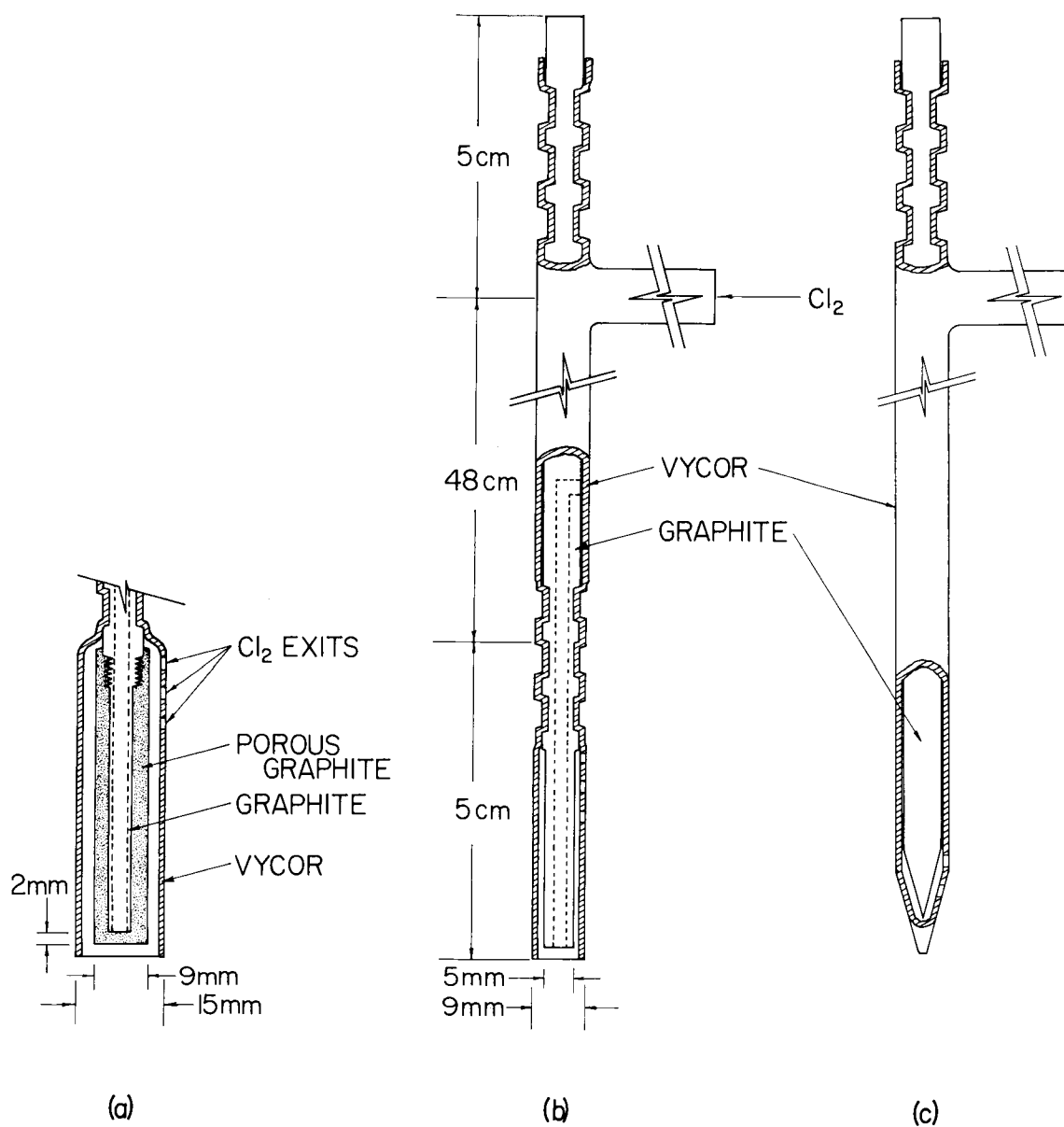


Figure 3. Chlorine electrode designs.

Chlorine, Argon, and HCl gases were Matheson Co. "high purity". The HCl and chlorine gases were passed over  $\text{Mg}(\text{ClO}_4)_2$  or  $\text{P}_2\text{O}_5$  (Granusic) before entering the cell. The argon was passed over  $\text{Mg}(\text{ClO}_4)_2$  or  $\text{P}_2\text{O}_5$  and then over hot Cu,  $500^\circ\text{C}$ ; the Cu was in the form of fine turnings or pellets formed by reduction of copper oxide with  $\text{H}_2$ . The gas delivery system was glass except for several inches of rubber tubing near the cell top. Gas flow was measured by means of Manostat Corp., model M9142C flowmeters in the gas lines. Gases left the cell through sulfuric acid traps, the entry tubes of which were immersed just below the surface of the acid.

Metal electrodes were 0.020" wire obtained from A. D. McKay and described as 99.9 + % pure. The electrodes were cleaned by abrasion with emery paper and wiping with an acetone-dampened cloth. Various designs of Vycor protection tubes for the metal electrodes are shown in Figure 4. All of the designs were tested in the AgCl formation cell; design D was later utilized for all nickel and cobalt electrodes. The capillaries were from 0.1 to 0.5 mm inside diameter and about 1 cm long. The open ended tube, A, was used only in conjunction with a graphite crucible which provided a shallow well into which the lower end of the tube was received (Hamby, 1961). A stream of dry argon was maintained over the melt inside the Ni and Co electrode protection tubes.

The Ag reference electrodes used in this work utilized a 1/2"

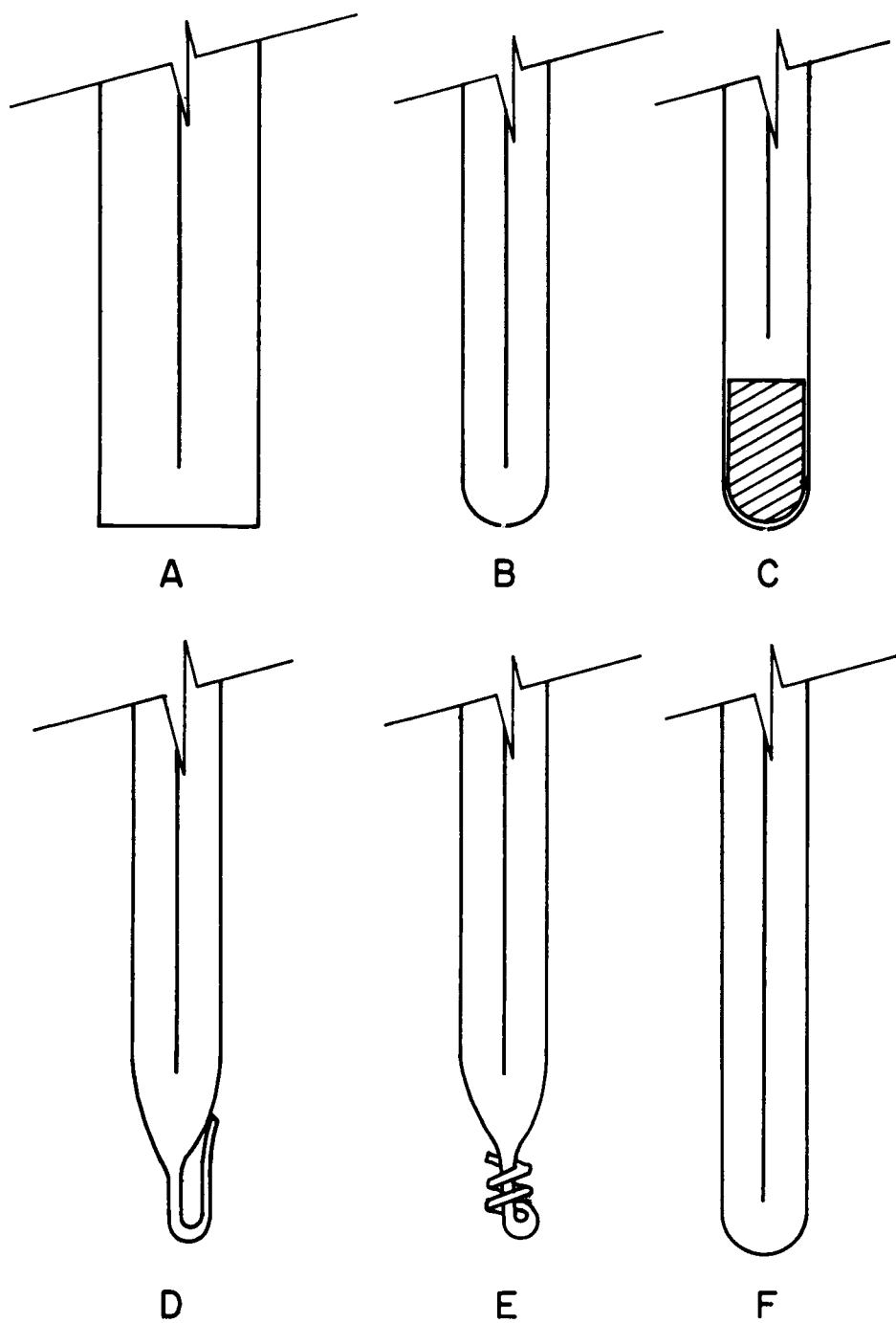


Figure 4. Vycor protection tubes for metal electrodes. Initial tube diameters were 6 mm for designs B through F.

diameter McDanel porcelain tube as a solid electrolyte. Metallic contact to the silver electrode was made by fusion to platinum inside a small-diameter alumina tube; thus, the silver-air interface was eliminated and electrode stability was improved (Littlewood, 1961a). An inert atmosphere over the Ag reference electrodes was not found to be necessary either in the case of the reference electrodes or in the case of the AgCl formation cell.

The salts used in this work were:

AgCl. Mallinckrodt, reagent grade. AgCl was oven dried in air and fused under chlorine in the presence of carbon.

NaCl and KCl. Reagent grade materials were further purified by passage through ion exchange columns (Fredericks, Rosztoczy and Hatchett, 1963; Fredericks, Schuerman and Lewis, 1966). The salts were then vacuum desiccated and oven dried at 120°C in air for many hours. For cells I, II, III and VI the salts were then weighed out, placed in the cell and gradually heated and melted under continuous chlorine flow in the presence of carbon (Maricle and Hume, 1960; Nissen, 1964). For cells VII, VIII and IX the salts were weighed into the cell crucible and then given several days vacuum oven treatment at temperatures up to 200°C and pressures of approximately  $10^{-2}$  mm Hg. The crucible was then transferred to the cell, in air, and the salt again subjected to vacuum of approximately  $10^{-2}$  mm Hg while the salt was slowly brought to near its melting point over a two day period. The salt was melted under HCl and

then chlorinated for several hours. In order to allow polarographic tests of melt purity the cell was then purged with argon and subjected to vacuum treatment for several hours.

LiCl. Reagent grade material was used. Several methods of dehydration were attempted: (a) Cell IV. Aspirator pumping and heating under flowing argon to 400° C was used, followed by fusion under flowing chlorine in the presence of carbon. (b) Cell V. More extensive vacuum pre-treatment was used consisting of approximately 24 hours at pressures from .2 to .7 mm Hg combined with intermittent purging of the cell with dry HCl while slowly bringing the cell temperature to 500° C. The salt was then fused under HCl and chlorinated in the presence of carbon. (c) Cell X. The drying treatment was as described for cells VII, VIII, IX above.

NiCl<sub>2</sub> and CoCl<sub>2</sub>. The reagent grade NiCl<sub>2</sub> · 6H<sub>2</sub>O was given preliminary oven drying in air at 130° C. Reagent grade CoCl<sub>2</sub> · 6H<sub>2</sub>O was initially vacuum oven dried at approximately 10<sup>-2</sup> mm Hg to 200° C. The salts were subsequently dried for at least 4 hours under flowing anhydrous HCl at 400° C. The salts were transferred to weighing bottles in a glove bag under nitrogen, capped, and stored in a desiccator over P<sub>2</sub>O<sub>5</sub> until used.

Transfer to the cell involved brief exposure to the atmosphere.

Electrolytes utilized in the Ag reference electrodes were prepared

from the purified NaCl and KCl and from reagent grade LiCl and AgCl. The salts were weighed out in the desired proportions and fused and chlorinated in the presence of carbon for at least one hour. The melts were drawn into clean, dry, Vycor tubes from which they were removed as the solid and stored under  $\text{CCl}_4$ . Concentrations were calculated from the weights of salts added to the crucible; no additional analysis of the composition was done.

Microelectrodes for polarographic work were of two types:

- (a) 0.018" platinum wire, press sealed into 6 mm Vycor tubing.
- (b) 0.0015" platinum sheet, approximately 1/16" in width, vacuum sealed into 6 mm Vycor tubing. Three-electrode polarograms were taken with a Heath, EUA 19-2 Polarograph.

The furnace was a Marshall Co. test furnace, 16" in length with a 3" diameter throat. Power was supplied to the furnace with a West, Model JSB Control. Cell temperatures were determined by means of a calibrated Cromel-Alumel thermocouple housed in a 6 mm Vycor sheath immersed in the melt. The measuring thermocouple was calibrated in freezing aluminum, supplied by the N. B. S., and by comparison against a Leeds and Northrup Pt, Pt-10% Rh thermocouple, Model 8710-B-K2002 (Roeser and Lonberger, 1958). Temperature measurements were observed to vary as much as 3° due to different positioning of the thermocouple in the bath. Since this is estimated to be greater than the degree of uncertainty involved in the



calibration the uncertainty in temperature is taken to be  $\pm 3^\circ$ .

Emf measurements were made with a Systems Research Corp. differential voltmeter, Model 5501. This instrument was checked periodically against a laboratory standard Eppley cell.

Thermoelectric effects associated with the electrodes in the absence of electrolyte were determined experimentally in situ for each pair of electrodes using powdered graphite as an electrical connection at the hot junction. Thermoelectric potential differences developed by various pairs to Ni-to-graphite or Co-to-graphite electrodes differed by  $\pm 2$  mv.

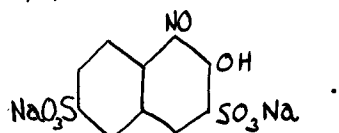
The cell and glassware were cleaned by rinsing in boiling 1 N HCl, and rinsing at least twice with distilled water and dried under flowing chlorine at  $800^\circ\text{C}$  for several hours. The cell was then cooled and solvent (2 moles) added to the crucible. After melt preparation and testing was complete, solute was added and cell emf's were measured as a function of temperature, the usual sequence being intermediate, high, and low temperatures. Linearity and reproducibility of the cell emf as a function of temperature was taken as one indication of reversible behavior. Nickel or cobalt electrodes were left in the melt only long enough for steady potentials to be obtained, usually a few minutes. Equalization of melt concentration inside and outside the metal electrode compartment after solute addition was achieved by purging with dry argon and allowing the compartment to

refill.

At each nominal concentration several melt samples (usually three) were taken by means of an acid washed, flamed, 6 mm Vycor tube. The analytical data were averaged to establish the bath concentration. The analyses were carried out as follows:

Nickel was determined spectrophotometrically at 267.5 m $\mu$  in aqueous solution as the tetracyano complex (Soine, 1957). Aqueous solutions of known concentration of NiCl<sub>2</sub> were used to establish an absorbance curve with slope  $0.203 \times 10^3 \text{ mg}^{-1} \text{ ml}$ . The method of least squares was applied to determine the best relationship between absorbance and concentration for 18 known samples. The standard deviation,  $\sigma$ , from the least squares line was  $\sigma = 4 \times 10^{-3}$  absorbance units. Bath samples were usually diluted to give absorbance values between 0.200 and 0.700. Thus, the limit of error (99% confidence level) of bath concentrations calculated on the basis of one sample is taken to be  $2.6\sigma = 0.010$  absorbance units or approximately  $\pm 3\%$  of bath concentration for intermediate absorbance values.

Cobalt was determined spectrophotometrically at 520 m $\mu$  in aqueous solution as the soluble red complex anion formed by Co<sup>++</sup> and nitroso-R salt (sodium 1-nitroso-2-hydroxynaphthalene-3,6-disulfonate) (Snell and Snell, 1959)



Aqueous solutions of known concentration of  $\text{CoCl}_2$  were used to establish an absorbance curve with slope  $0.225 \times 10^3 \text{ mg}^{-1} \text{ ml}$ . The method of least squares was used to establish this relationship for 10 known samples. The limit of error (99% confidence level) of bath concentrations, based both on the deviations of the original 10 standardizing absorbances from the best least squares line and on the deviations of 10 later absorbance values of samples made up from the original standard solution, is taken to be  $\pm 3\%$  of bath concentration.

Solute additions were made both electrolytically and as the dry powder. A positive pressure of chlorine or inert gas was maintained in the cell at all times and care was taken to open the cell to air for only minimal lengths of time in carrying out changes of electrodes, solute additions, and sampling operations.

The modifications listed below were made in equipment or procedure as the work progressed. For the most part these were aimed at decreasing the possibility of atmospheric contamination of the melt during cell operation.

- (a) Mechanical stirring (Ni cells only) using a teflon bearing at the cell top was discontinued after cell III.
- (b) Provision of the air lock at the top of the cell for sampling was provided after cell III.
- (c) In the initial experiment with KCl the metal electrode compartment was changed after each potential measurement.

Subsequently, this compartment was changed as infrequently as possible.

- (d) The chlorine and HCl were passed over hot, 500° C, powdered graphite beginning with cell IV.
- (e) Hot, 500° C, zirconium sponge was used as a deoxygenating agent for the argon in cells IX and X.
- (f) A problem of sampling, the separation of the salts upon cooling, was partially solved by utilizing the entire sample core in the analysis.

### III. RESULTS

#### The AgCl Formation Cell

The data from cells A and B are tabulated in Appendix I and illustrated in Figures 5, 6, and 7. The cell emf's have been corrected for thermoelectric effects. Experimental results from electrochemical work of other investigators are summarized in Figure 8.

Polarization of chlorine electrodes, Figure 5, as a test of electrode reversibility was carried out by passing current between the chlorine electrode and an auxiliary graphite electrode. Potential differences were measured between the chlorine electrode and a non-current-carrying Ag electrode, design C, Figure 4. Only resistive polarization was evident, and hysteresis effects were absent to within  $\pm 1$  mv. Potential differences between unpolarized chlorine electrodes of different design, a and b, Figure 3, in the same cell were generally less than 1 mv; short term (less than one second) fluctuations were of the order of 0.1 mv. No dependence of chlorine electrode potential on design could be established.

The flow rate of chlorine was varied by factors up to 30 to 1 (approximately 1.5 to 50 ml/min at 70° F and 1 atm. pressure), but the effect upon the emf was always less than 1 mv. Termination of chlorine flow was made apparent within minutes by a decrease in cell emf; however, the cell emf regained its initial values within

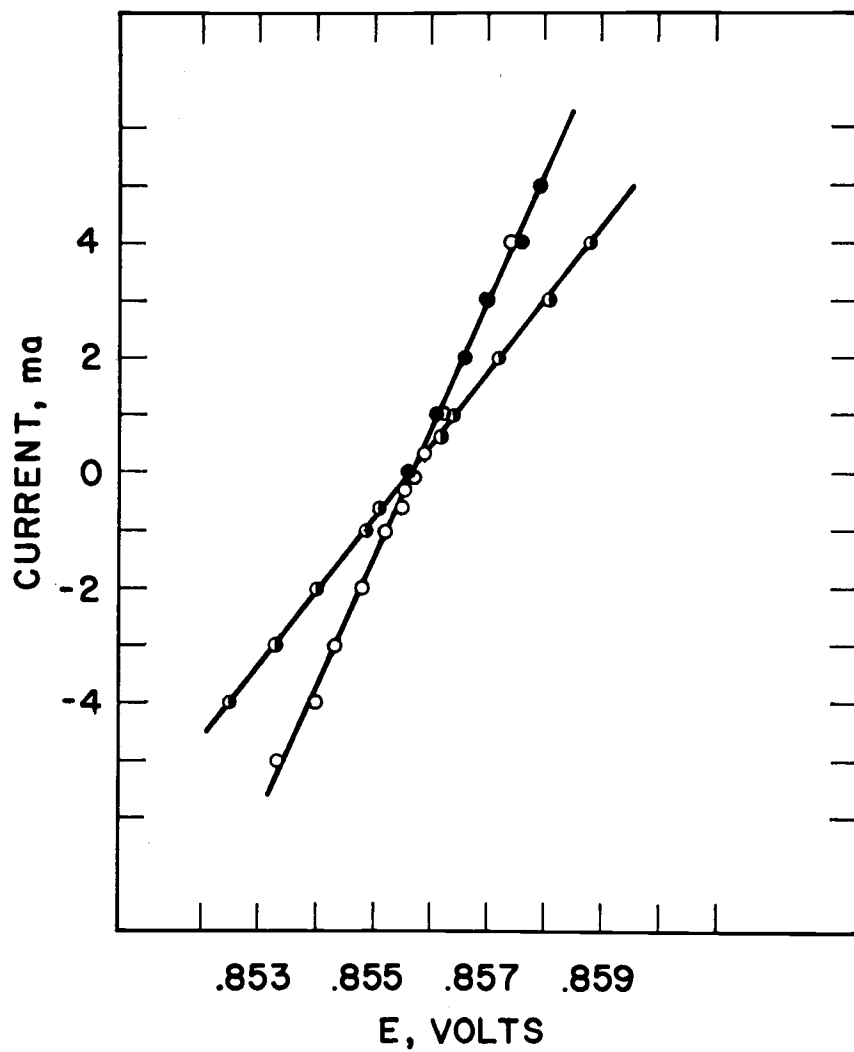


Figure 5. Polarization data for two chlorine electrodes. Porous electrode design: ●, increasing positive current ○, decreasing positive current. Nonporous electrode design: ○, decreasing positive current.

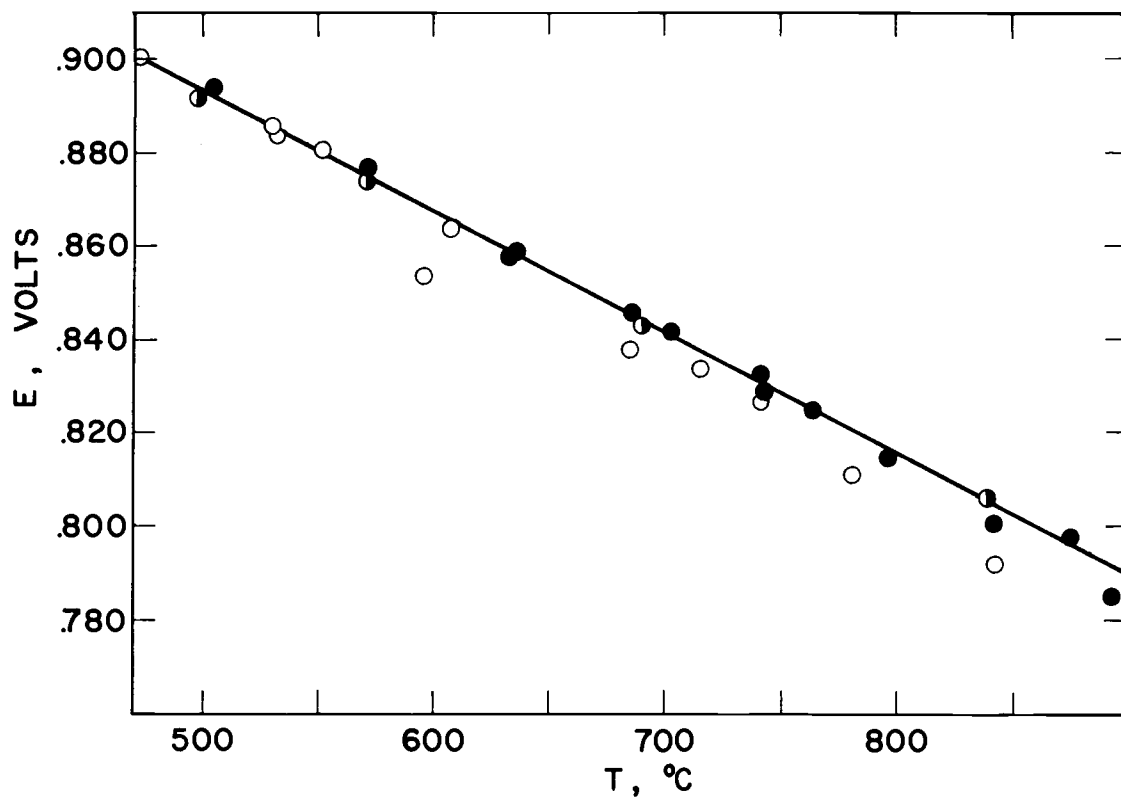


Figure 6. Cell voltage,  $E$ , for AgCl formation cell A; Ag electrode housed in protection tube C, ●, tube B, ◐, tube A, ○. The solid line represents the data of Senderoff and Mellors.

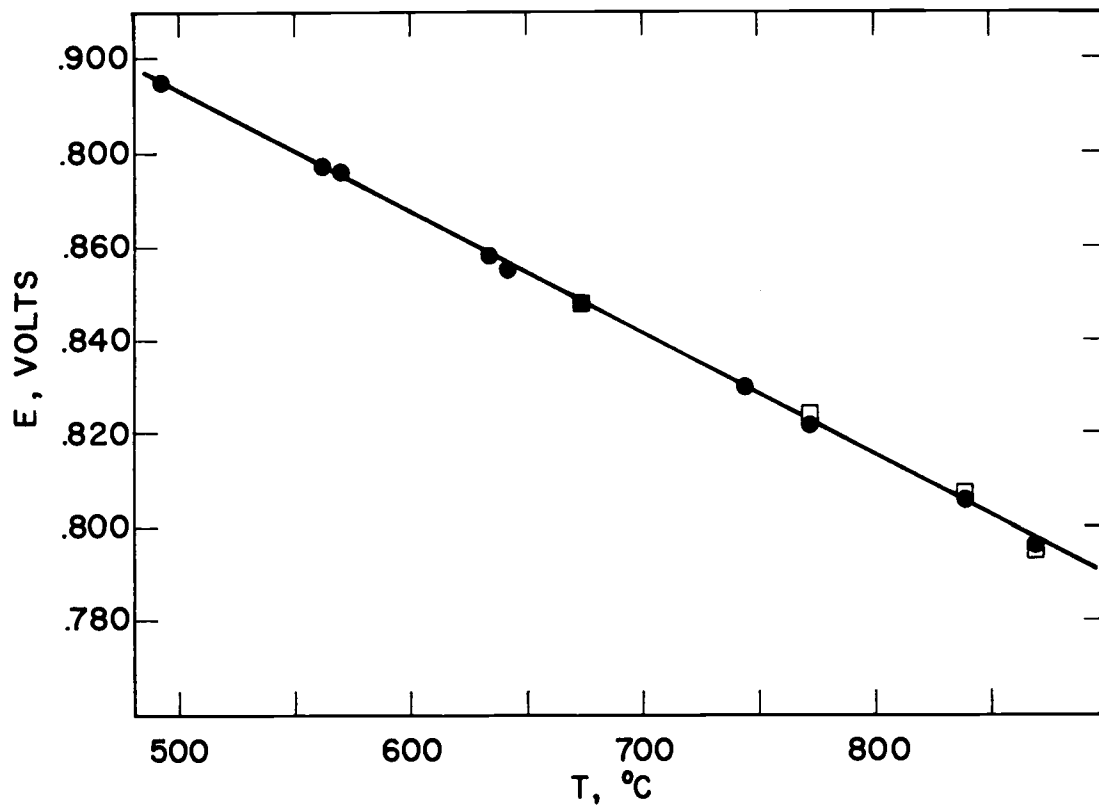


Figure 7. Cell voltage,  $E$ , for AgCl formation cell B; Ag electrode housed in protection tube C, ●, tubes D or E, □. The solid line represents the data of Senderoff and Mellors.



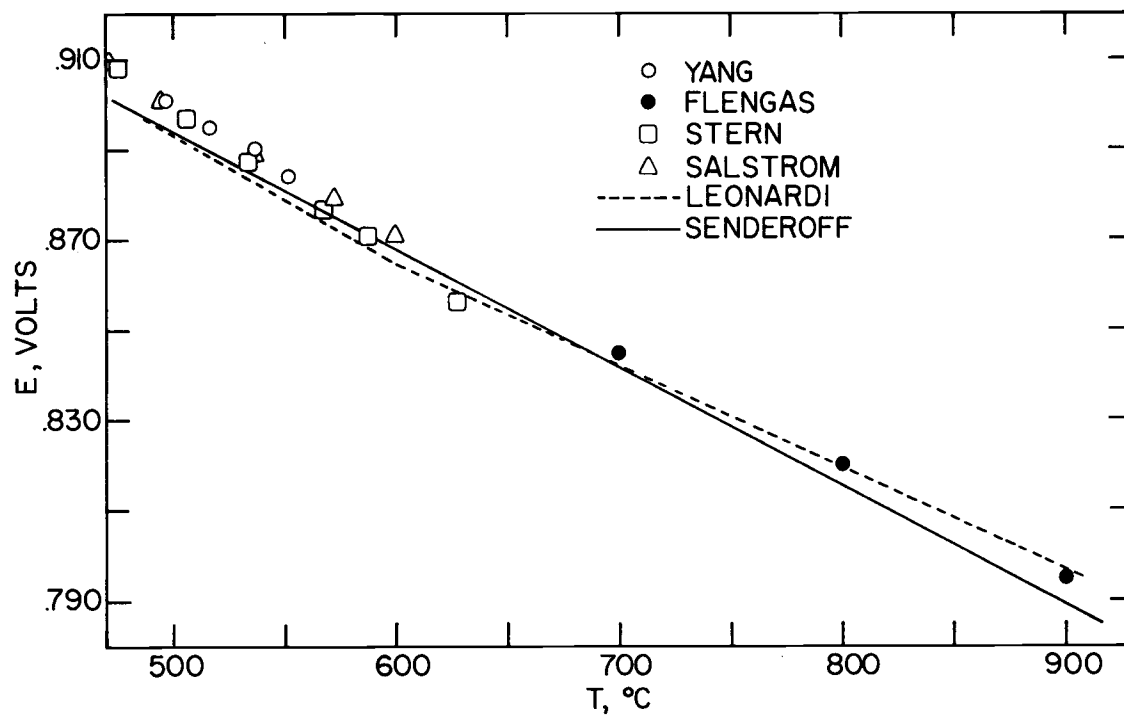


Figure 8. Comparison of data for the AgCl formation cell.

minutes after resumption of chlorine flow. Intermediate chlorine flow rates were adopted as standard.

The effect on cell emf of the degree of shielding of the Ag electrode is illustrated in Figure 6. Cells utilizing Ag electrodes housed in the open well protection tubes A, Figure 4, gave emf's which were scattered, and on the average, less than those observed by Senderoff and Mellors (1958). Short term fluctuations of millivolts were observed between the metal and chlorine electrodes with the magnitude of the fluctuations increasing as the cell temperature was raised. Cells utilizing Ag electrodes housed in constricted or "scavenged", tubes, designs B and C, Figure 4, were found to yield more stable emf's which were in agreement with Senderoff and Mellors' data.

The data in Figure 7 were obtained from a freshly prepared cell, B, utilizing scavenged or capillary, D and E, Figure 4, protection tubes. The agreement with Senderoff and Mellors' data is excellent.

The higher emf values reported for this cell by some investigators as indicated by Figure 8 are difficult to explain. Normal atmospheric fluctuations in pressure (5 mm Hg) or changes in pressure due to differing depths of immersion of the active 3 phase region would not be expected to cause more than 1 mv variation in cell emf. An uncertainty in temperature of about 20° C would be necessary to

produce the observed differences; however, such an uncertainty is not outside the realm of possibility with certain electrode designs.

### Polarographic Tests of Alkali Halide Melt Purity

Considerable difficulty was experienced in obtaining reproducible polarographic decomposition curves in the solvents. In initial experiments two 1/4 inch diameter carbon rods were utilized as electrodes and decomposition curves were taken manually with wet cell power, a voltage divider, and meters for current and voltage measurement. Reproducibility of the current-voltage curves was poor in these initial measurements. In a second series of experiments an Auto-Scan two-electrode polarograph was used with one Pt wire microelectrode, pinch sealed in Vycor tubing, and a 1/4" diameter carbon rod counter and reference electrode. These measurements also proved non-reproducible. The main cause for failure in these experiments was believed to be the failure of the counter electrode to assume a steady, current-independent potential in the melt; however, the possibility of residual  $\text{Cl}_2$ , or HCl in the melt as well as changing microelectrode surface area were also recognized as problems.

The previous difficulties were overcome to some extent by using three-electrode polarography. The  $\text{Ag}|\text{AgCl}, \text{RCl}||$  electrode was used as reference, and 0.0015" thick Pt sheet, approximately 1/16" wide, vacuum sealed in Vycor, was used as a microelectrode. A

transition metal electrode, corresponding to the metal chloride solute to be used later in the cell, was used as a counter electrode. The counter electrode was first housed in a constricted Vycor tube with connection to the bulk of the melt through the constriction (NaCl melt, Figure 9). In later experiments the counter electrode was separated from the bulk of the melt by a Vycor frit of medium porosity (LiCl and 1:1 NaCl-KCl melts, Figure 9). After initial preparative procedures the melts were vacuum treated at least 12 hours at pressures of a few tenths of mm Hg to remove residual HCl and Cl<sub>2</sub>. The cell was then filled with argon, the necessary electrodes inserted, and the polarographs taken.

Under these conditions decomposition curves like those shown in Figure 9 were obtained. Reproducibility was much improved over the earlier work; however, difficulty was still experienced with respect to maintenance of constant microelectrode area. The vacuum seals of Vycor to platinum developed leaks in every case after repeated use.

According to Hamer, Malmberg and Rubin (1956) the decomposition potentials of the alkali halides at 800° C should be as shown:

NaCl	3.2 volts
KCl	3.4
LiCl	3.5 .

It is apparent from Figure 9 that the full decomposition spans for the

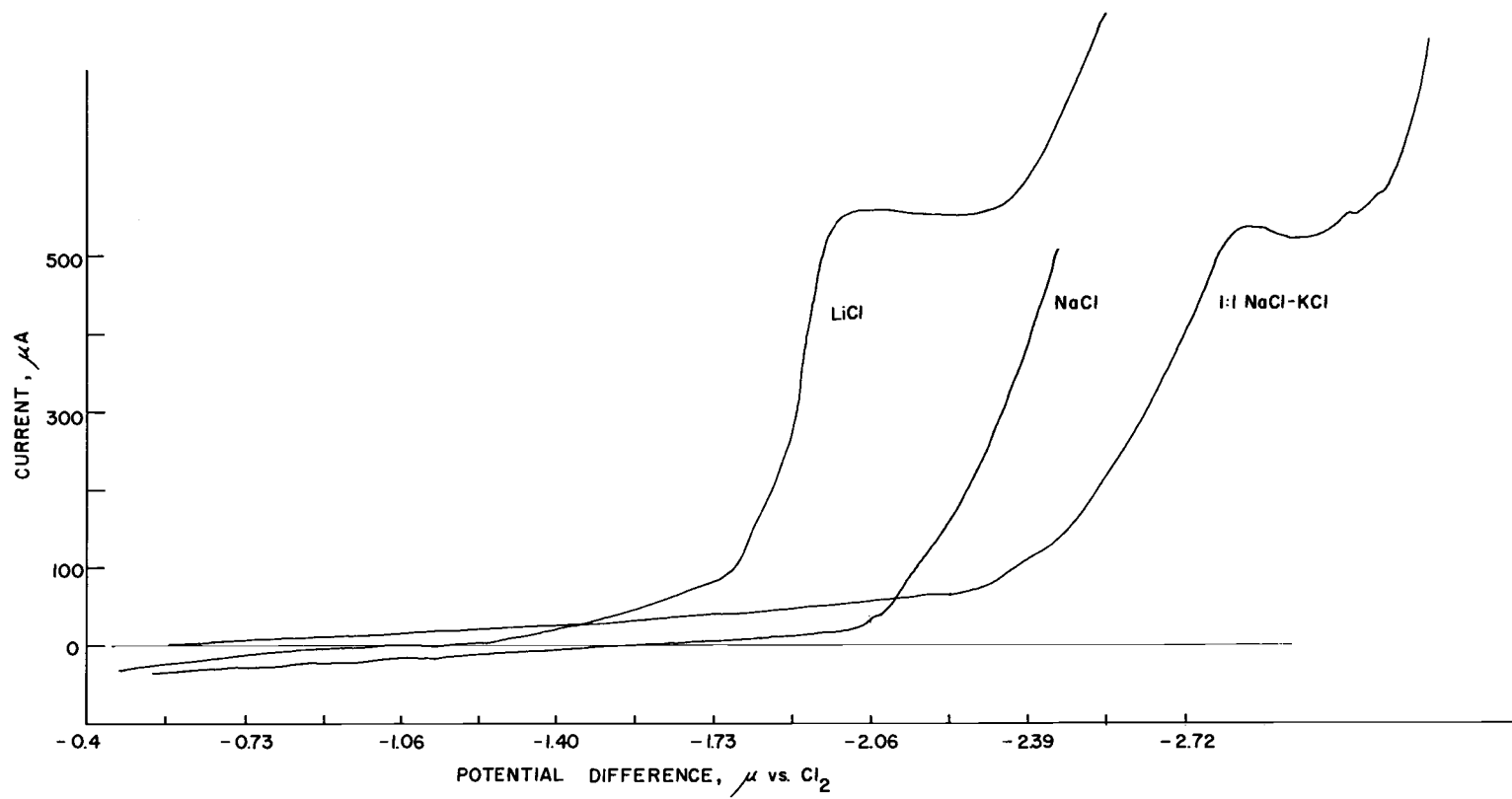
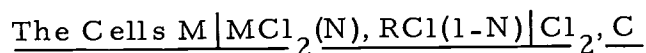


Figure 9. Polarographs taken in the solvents of cells VII, IX, and X, before solute addition.

melts are not being reached. Fortunately, the electrode potentials (with respect to  $\text{Cl}_2$ ) for the metals of interest, Ni and Co, take on sufficiently more positive values at concentrations greater than approximately  $5 \times 10^{-4}$  mole fraction that the competition from the reactions which lead to the decomposition potentials may be neglected.

It is possible that the decomposition potential shown for LiCl results from the presence of metallic impurity in the reagent grade salt. The purity of the NaCl and KCl used in these experiments, as shown by conductivity and spectroscopic measurements on single crystals grown from similarly purified salt (Fredericks, 1966), is such that the decomposition reaction must be associated with the products of hydrolytic reactions or with metallic impurity introduced into the salt during cell operation. In the case of the NaCl melt a concentration of  $1 \times 10^{-6}$  mole fraction  $\text{CoCl}_2$  was found by analysis indicating contamination by the counter electrode. The 1:1 NaCl-KCl and LiCl curves were taken after incorporating the frit into the counter electrode compartment; no initial analysis for Co was made on these melts.



Current reversibility of at least one of the chlorine electrodes used in each cell was checked; curves similar to those shown in Figure 5, indicating millivolt reversibility, resulted in all cases.

Potential differences between chlorine electrodes of different design in the same cell were usually near 1 mv, or less, with short term fluctuations of the order of 0.1 mv. Current reversibility of the metal electrodes was verified in cells II through X at  $MCl_2$  concentrations near  $N = 10^{-2}$ . A typical example of these tests is shown in Figure 10.

The data for these cells are tabulated in Appendix II. Using these data, curves were prepared of cell emf,  $E$ , vs. temperature at each concentration. From these curves, an example of which is shown in Figure 11, the slopes,  $dE/dT$ , were determined and emf's were read at a series of fixed temperatures, 700° C, 800° C, and 900° C, to prepare the graphs shown in Figures 12 and 13. The values of  $dE/dT$  and  $nFdE/dT = \Delta \tilde{s}$  are recorded in Appendix III.

Below  $N = 10^{-2}$  the data of Figures 12 and 13, that is,  $E$  at constant temperatures, may be represented by

$$E = a - b \log N$$

where  $b = 2.303 RT/2F$ . The solid straight lines in these figures were drawn with slopes  $b$  below  $N = 10^{-2}$  and the intercepts  $a$  were chosen to give the best fit with the data points for  $N < 10^{-2}$ .

Table 2 gives the values of the constants  $a$  and the average deviations of the data points from the straight lines in the low concentration range.

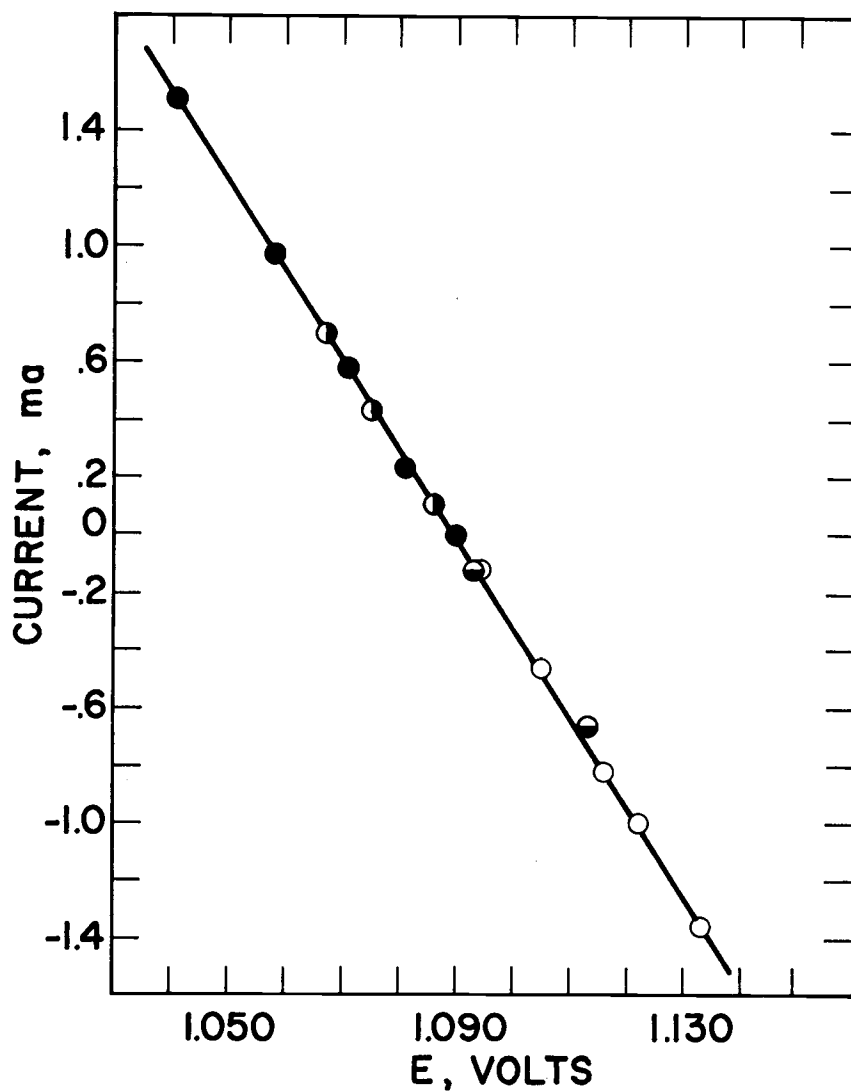


Figure 10. Polarization of a nickel electrode; cell II, NaCl solvent,  $N_{\text{NiCl}_2} = 8.3 \times 10^{-3}$ . Positive current was first increased across the electrode-electrolyte interface, ●, then decreased ●. Negative current was then increased, ○, and subsequently decreased ●.



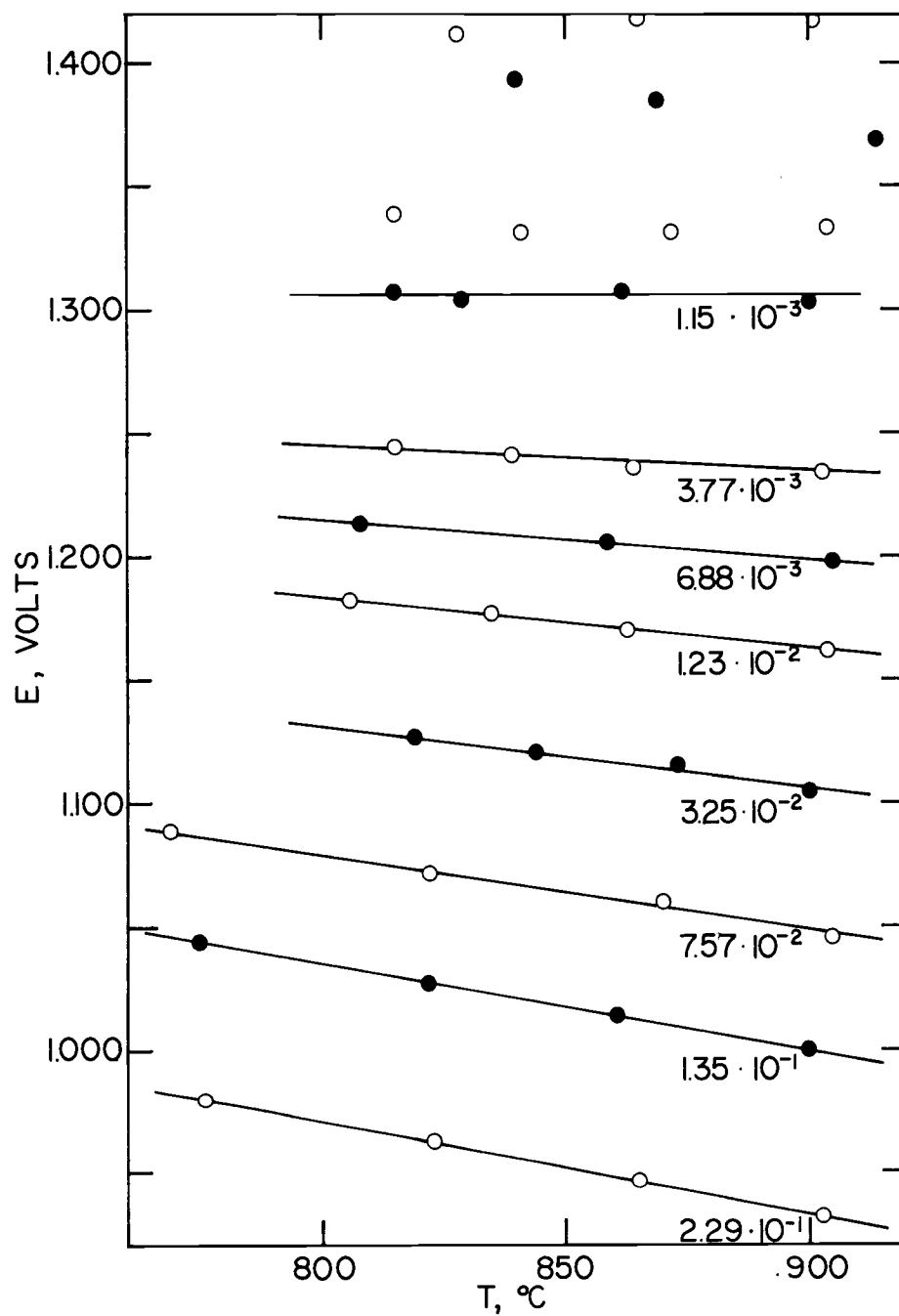


Figure 11. Cell Voltage,  $E$ , versus temperature,  $T$ , for cell I, KCl solvent. Concentrations in mole fraction  $\text{NiCl}_2$  are indicated near the corresponding lines.

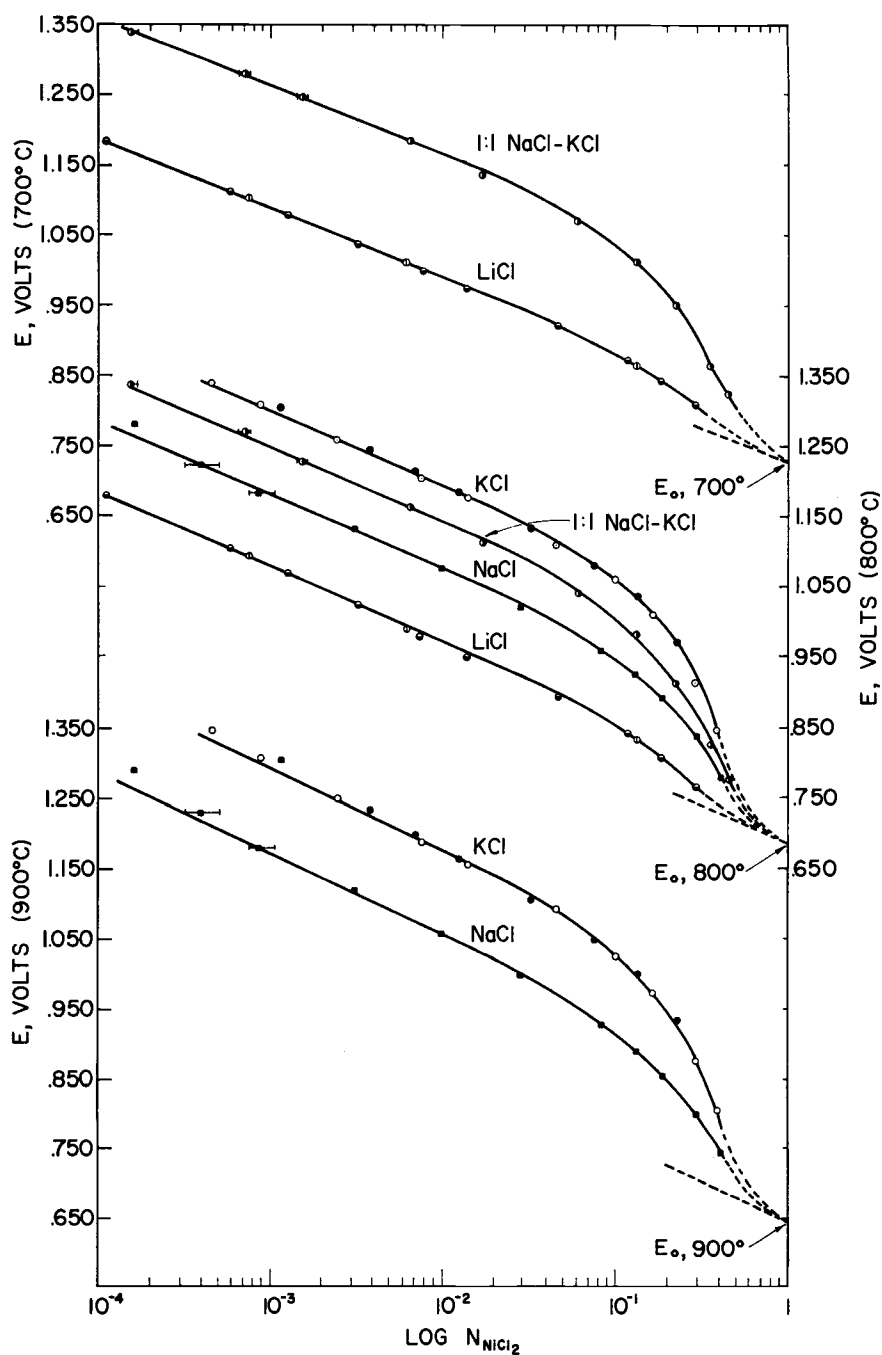


Figure 12. Cell emf,  $E$ , vs.  $\log N_{\text{NiCl}_2}$  at  $700^\circ$ ,  $800^\circ$ , and  $900^\circ$  C.

Cell I, KCl solvent,  $\bullet$ ; cell II, NaCl solvent,  $\blacksquare$ ; cell III, 1:1 NaCl-KCl solvent,  $\odot$ ; cell IV, LiCl solvent,  $\ominus$ ; cell V, LiCl solvent,  $\oplus$ ; cell VI, KCl solvent,  $\circ$ .

Uncertainty in concentration is indicated by extended bars where the magnitude of the uncertainty exceeds the size of the symbol representing the data point.

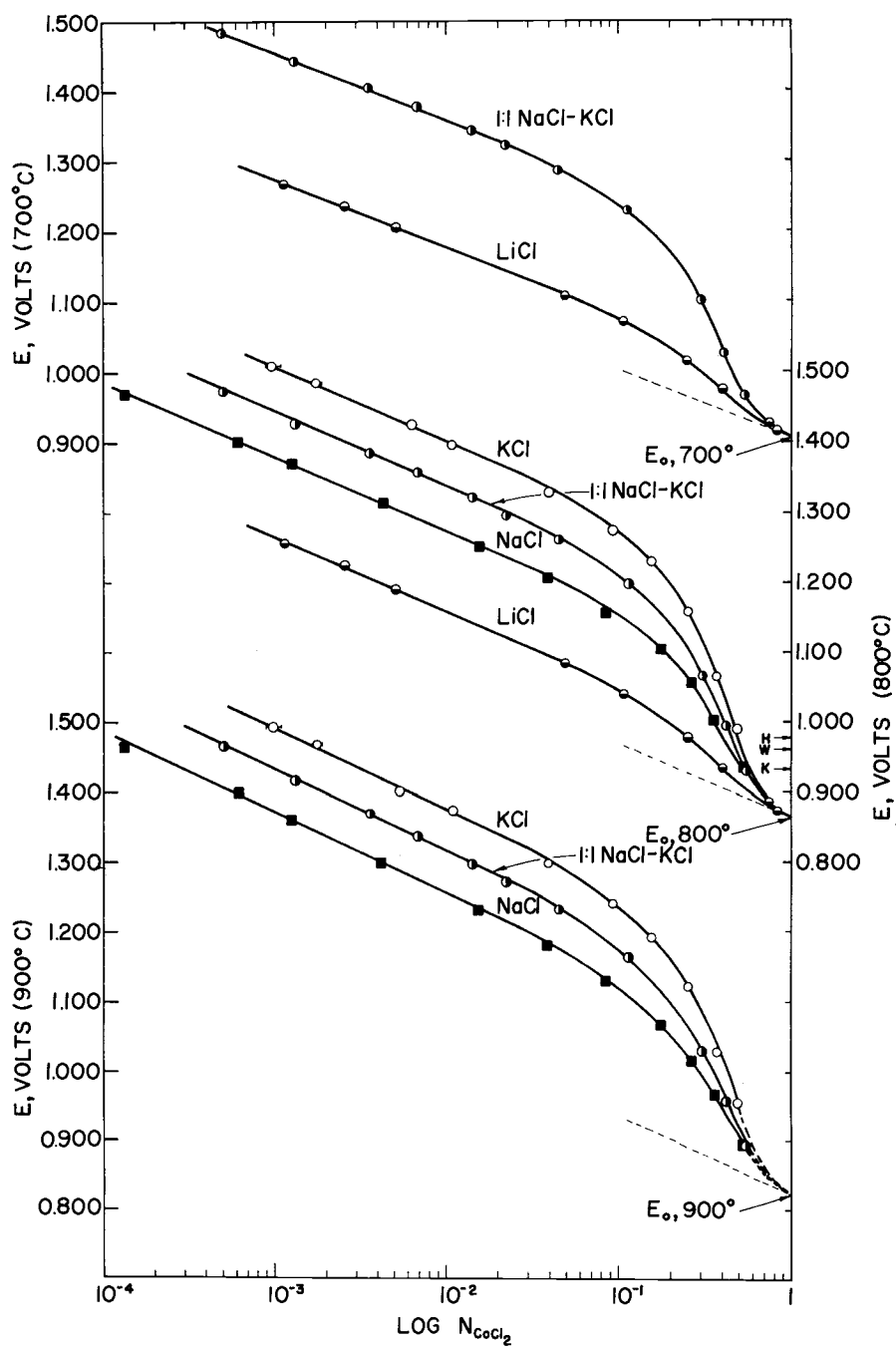


Figure 13, Cell emf,  $E$ , vs.  $\log N_{\text{CoCl}_2}$  at  $700^\circ$ ,  $800^\circ$ ,  $900^\circ\text{C}$ .

Cell VII, KCl solvent,  $\bullet$ ; cell VIII, NaCl solvent,  $\blacksquare$ ; cell IX, 1:1 NaCl-KCl solvent,  $\circ$ ; cell X, LiCl solvent,  $\odot$ . Uncertainty in concentration is indicated by extended bars where the magnitude of the uncertainty exceeds the size of the symbol representing the data point.

Table 2. The constants  $a$ .

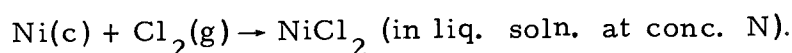
Solute	Solvent	$a$			ave. dev., mv		
		700° C	800°	900°	700°	800°	900°
NiCl <sub>2</sub>	LiCl	.798	.759		2	2	
	NaCl		.864	.824		5	8
	KCl		.982			3	6
	1:1 NaCl-KCl	.973	.930	.946	2	4	
CoCl <sub>2</sub>	LiCl	.985	.946		1	2	
	NaCl		1.061	1.025		2	3
	KCl		1.189	1.143		2	3
	1:1 NaCl-KCl	1.166	1.126	1.085	2	3	3

Attempts were made to obtain cell data at  $N < 10^{-4}$ ; however, stable emf's (i. e., short term fluctuations in  $E$  less than 1 mv) were not achieved in this concentration range. Furthermore, the variation of  $E$  with temperature was usually non-linear, uncertainties in concentration were large, and the values of  $E$  were not in agreement with predictions based on the higher concentration data. These effects are attributed to the appreciable solubility of chlorine in these melts and to the presence of oxygen containing impurities in the cell which seriously effect the metal electrode potential when the exchange current for the desired reaction is low.

For NaCl, KCl, and NaCl-KCl melts, the electrolyte containers and glass cell components were observed to suffer some surface etching during experiments lasting as long as seven days. In the case of LiCl, rapid etching of glass components was noted for melts prepared by all techniques mentioned above. However, in the case of the Ni

cells, the rate of attack was observed to decrease as  $\text{NiCl}_2$  concentration increased. It is possible that the glass-attacking species were removed by precipitation as oxides (Bloom and Hastie; 1965).

The curves of Figure 12 were completed on the basis of the assumed cell reaction



Having chosen the standard and reference states of the solute as the pure liquid at the temperature of the experiment and one atmosphere total pressure, the extrapolated value of the cell emf at  $N = 1$ ,  $E^\circ$ , is related to the standard change  $\Delta\tilde{\mu}^\circ = \sum_i \nu_i \mu_i^\circ$  for the cell reaction through Equations (21) and (22)

$$\Delta\tilde{\mu}^\circ = -nFE^\circ. \quad (33)$$

The value  $E^\circ$  was not directly measured due to the high vapor pressure of the pure chloride,  $\text{NiCl}_2$ . However, values of  $\Delta\tilde{\mu}^\circ$ , can be calculated on the basis of thermal data in the literature. The following equations were derived for  $\text{NiCl}_2$  with the aid of the thermochemical data tabulated by Wicks and Block (1963) and Kubaschewski and Evans (1956)

$$\Delta\tilde{H}^\circ = 6.14 \times 10^4 + 9.35T - 1.05 \times 10^{-3}T^2 - 0.68 \times 10^5 T^{-1} \quad (34)$$

$$\Delta\tilde{\mu}^\circ = 6.14 \times 10^4 + 9.19T - 2.15T \log_{10} T + 1.05 \times 10^{-3}T^2 - 0.34 \times 10^5 T^{-1}. \quad (35)$$

Calculated values of  $\Delta\tilde{\mu}^\circ$ ,  $\Delta\tilde{H}^\circ$  and  $\Delta\tilde{s}^\circ$  for  $\text{NiCl}_2$  at selected temperatures are listed in Table 3.

Table 3. Calculated values of the standard changes for the formation of  $\text{NiCl}_2$ .

	650°C	700°	750°	800°	850°	900°
$\Delta\tilde{H}^\circ$ (kcal)	-53.8	-53.4	-53.0	-52.7	-52.3	-52.0
$\Delta\tilde{\mu}^\circ$ (kcal)	-34.7	-33.6	-32.7	-31.6	-30.7	-29.7
$\Delta\tilde{s}^\circ$ (eu)	-20.7	-20.3	-19.8	-19.7	-19.2	-19.0
$E^\circ$ (v)	0.756	0.727	0.709	0.685	0.675	0.644

The curves of Figure 12 were extrapolated to  $N = 1$ ,  $E^\circ$ , on the basis of the calculated values of  $\Delta\tilde{\mu}^\circ$  at the temperature of the experiment. The calculated values of  $\Delta\tilde{\mu}^\circ$  are, in this case, consistent with the cell data. Values of  $E^\circ$  calculated on the basis of the earlier compilation of Hamer, Malberg and Rubin (1956) lie more than 100 mv higher than those used here and are in conflict with the present cell data.

In case of  $\text{CoCl}_2$  the cell data was not found to be consistent with the thermal data of any of the three sources: Wicks and Block (1963) Kubaschewski and Evans (1956), or Hamer, Malberg, and Rubin (1956). Values of  $E^\circ$  predicted on the basis of their data have been included in Figure 13. In this case, the curves of Figure 13 have been extrapolated to  $N = 1$  on the basis of our experimental data and Raoult's law in order to establish values of  $\Delta\tilde{\mu}^\circ$ . Values of

$\Delta \tilde{s}^\circ$  for use in calculating the mixing functions were established in a similar fashion by plotting  $\Delta \tilde{s}$  vs.  $\log N$  and extrapolating to  $N=1$ .

Emf values have been read from Figures 12 and 13 at selected concentrations and used to calculate the values of the functions given in Tables 4 through 11. Values of  $\bar{S}$ , and, therefore, also  $\bar{H}$  given in the tables are smoothed values based on graphs of  $\Delta \tilde{s}$  as a function of concentration.

#### The Reference Electrodes, $\text{Ag}|\text{AgCl}(N), \text{RC1}(1-N)||$

Properties of the  $\text{Ag}|\text{AgCl}, \text{RC1}||$  reference electrodes incorporated in cells III through X are described in Table 12 and Figure 14.

$E'_{\text{Ag}}$  was found to be independent of the concentration of  $\text{MCl}_2$  in the melt up to concentrations  $N = 10^{-2}$ . Values of  $E'_{\text{Ag}}$  given in the table are average values, corrected for thermoelectric emf's, taken over the duration of the experiments at  $\text{MCl}_2$  concentrations up to  $N = 10^{-2}$ . The maximum deviations from the averages are given.

Values of  $\Delta E' = E'_{\text{Ag}} - E_{\text{Ag}}$  were detectable at higher concentrations; these values are plotted in Figure 14.

Table 4. KCl solvent, cell VI.

$N_{NiCl_2}$	$\overline{E}$ (volts)		$\overline{G}$ (Kcal)		$\overline{E}$ $\overline{G}$ (Kcal)		$\gamma$		$\overline{S}$ (e.u.)	$\overline{H}$ (Kcal)
	800°C	900°C	800°C	900°C	800°C	900°C	800°C	900°C	800°C	800°C
0.00100	1.301	1.292	-28.4	-29.9	-13.7	-13.8	$1.65 \times 10^{-3}$	$2.70 \times 10^{-3}$	+18	-10
0.00300	1.250	1.236	-26.1	-27.3	-13.7	-13.8	$1.65 \times 10^{-3}$	$2.72 \times 10^{-3}$	+14	-11
0.00700	1.212	1.193	-24.3	-25.3	-13.7	-13.8	$1.61 \times 10^{-3}$	$2.75 \times 10^{-3}$	+12	-12
0.0200	1.162	1.140	-22.0	-22.9	-13.7	-13.8	$1.66 \times 10^{-3}$	$2.74 \times 10^{-3}$	+9	-13
0.0500	1.108	1.085	-19.5	-20.3	-13.1	-13.4	$2.14 \times 10^{-3}$	$3.25 \times 10^{-3}$	+7	-13
0.0700	1.087	1.059	-18.5	-19.1	-12.9	-12.9	$2.40 \times 10^{-3}$	$3.89 \times 10^{-3}$	+6	-12
0.100	1.060	1.027	-17.3	-17.7	-12.4	-12.3	$3.01 \times 10^{-3}$	$5.12 \times 10^{-3}$	+5	-13
0.150	1.023	.983	-15.6	-15.6	-11.5	-11.2	$4.49 \times 10^{-3}$	$8.13 \times 10^{-3}$	+3	-12
0.200	.989	.946	-14.0	-13.9	-10.6	-10.2	$7.00 \times 10^{-3}$	$1.27 \times 10^{-2}$	+3	-11
0.250	.957	.910	-12.5	-12.3	-9.6	-9.0	$1.12 \times 10^{-2}$	$2.09 \times 10^{-2}$	+3	-10
0.300	.923	.873	-11.0	-10.6	-8.4	-7.8	$1.94 \times 10^{-2}$	$3.64 \times 10^{-2}$	+2	-9
0.350	.882	.832	-9.1	-8.7	-6.8	-6.2	$4.05 \times 10^{-2}$	$7.00 \times 10^{-2}$	+2	-7
0.400	.838	.792	-7.1	-6.8	-5.1	-4.7	$9.14 \times 10^{-2}$	$1.34 \times 10^{-1}$	+2	-5



Table 5. NaCl solvent, cell II.

N NiCl <sub>2</sub>	$\overline{E}$ (volts)		$\overline{G}$ (Kcal)		$\overline{G}^E$ (Kcal)		$\gamma$		$\overline{S}$ (e.u.)	$\overline{H}$ (Kcal)
	800°C	900°C	800°C	900°C	800°C	900°C	800°C	900°C	800°C	800°C
0.00100	1.182	1.172	-22.9	-24.4	-8.2	-8.3	$2.14 \times 10^{-2}$	$2.88 \times 10^{-2}$	+19	-4
0.00300	1.132	1.117	-20.6	-21.8	-8.2	-8.3	$2.14 \times 10^{-2}$	$2.82 \times 10^{-2}$	+14	-6
0.00700	1.092	1.073	-18.8	-19.8	-8.2	-8.2	$2.14 \times 10^{-2}$	$2.95 \times 10^{-2}$	+12	-6
0.0200	1.043	1.020	-16.5	-17.3	-8.2	-8.2	$2.18 \times 10^{-2}$	$2.95 \times 10^{-2}$	+10	-6
0.0500	0.993	.965	-14.2	-14.8	-7.8	-7.8	$2.56 \times 10^{-2}$	$3.46 \times 10^{-2}$	+ 8	-6
0.0700	0.972	.942	-13.2	-13.8	-7.6	-7.6	$2.88 \times 10^{-2}$	$3.88 \times 10^{-2}$	+ 7	-6
0.100	0.947	.914	-12.1	-12.5	-7.2	-7.1	$3.46 \times 10^{-2}$	$4.80 \times 10^{-2}$	+ 5	-6
0.150	0.912	.878	-10.5	-10.8	-6.4	-6.4	$4.89 \times 10^{-2}$	$6.51 \times 10^{-2}$	+ 4	-6
0.200	0.883	.848	- 9.1	- 9.4	-5.7	-5.7	$6.91 \times 10^{-2}$	$8.90 \times 10^{-2}$	+ 3	-6
0.250	0.857	.822	- 7.9	- 8.2	-5.0	-5.0	$9.79 \times 10^{-2}$	$1.18 \times 10^{-1}$	+ 3	-5
0.300	0.833	.797	- 6.8	- 7.1	-4.3	-4.3	$1.36 \times 10^{-1}$	$1.92 \times 10^{-1}$	+ 3	-4
0.350	0.808	.773	- 5.7	- 6.0	-3.4	-3.5	$2.01 \times 10^{-1}$	$2.23 \times 10^{-1}$	+ 2	-3
0.400	0.783	.748	- 4.5	- 4.8	-2.6	-2.7	$3.01 \times 10^{-1}$	$3.16 \times 10^{-1}$	+ 2	-3

Table 6. NaCl-KCl solvent, cell III.

$N_{NiCl_2}$	$\overline{E}$ (volts)		$\overline{G}$ (Kcal)		$\overline{E}_G$ (Kcal)		$\gamma$		$\overline{S}$ (e.u.)	$\overline{H}$ (Kcal)
	700°C	800°C	700°C	800°C	700°C	800°C	700°C	800°C	700°C	800°C
0.00100	1.263	1.248	-24.7	-26.0	-11.3	-11.2	$2.92 \times 10^{-3}$	$5.16 \times 10^{-3}$	+18	-7
0.00300	1.217	1.198	-22.5	-23.7	-11.3	-11.3	$2.90 \times 10^{-3}$	$5.10 \times 10^{-3}$	+13	-10
0.00700	1.181	1.158	-20.9	-21.8	-11.3	-11.2	$2.93 \times 10^{-3}$	$5.16 \times 10^{-3}$	+11	-11
0.0200	1.134	1.110	-18.7	-19.6	-11.2	-11.2	$3.15 \times 10^{-3}$	$5.14 \times 10^{-3}$	+8	-11
0.0500	1.086	1.058	-16.5	-17.2	-10.7	-10.8	$3.95 \times 10^{-3}$	$6.33 \times 10^{-3}$	+7	-10
0.0700	1.064	1.034	-15.5	-16.1	-10.3	-10.4	$4.79 \times 10^{-3}$	$7.54 \times 10^{-3}$	+6	-10
0.100	1.037	1.004	-14.2	-14.7	-9.8	-9.8	$6.35 \times 10^{-3}$	$1.01 \times 10^{-2}$	+5	-10
0.150	1.000	.962	-12.5	-12.8	-8.9	-8.7	$1.03 \times 10^{-2}$	$1.67 \times 10^{-2}$	+4	-9
0.200	.968	.927	-11.0	-11.2	-7.9	-7.7	$1.65 \times 10^{-2}$	$2.68 \times 10^{-2}$	+3	-8
0.250	.933	.894	-9.4	-9.6	-6.8	-6.7	$3.02 \times 10^{-2}$	$4.39 \times 10^{-2}$	+2	-8
0.300	.902	.865	-8.0	-8.3	-5.7	-5.7	$5.32 \times 10^{-2}$	$6.85 \times 10^{-2}$	+2	-7
0.350	.868	.835	-6.4	-6.9	-4.4	-4.7	$1.04 \times 10^{-1}$	$1.12 \times 10^{-1}$	+2	-5
0.400	.847	.808	-5.5	-5.7	-3.7	-3.7	$1.48 \times 10^{-1}$	$1.75 \times 10^{-1}$	+0	-6

Table 7. LiCl solvent, cell IV.

$N_{\text{NiCl}_2}$	$\overline{E}$ (volts)		$\overline{G}$ (Kcal)		$\overline{G}^E$ (Kcal)		$\gamma$		$\overline{S}$ (e.u.)	$\overline{H}$ (Kcal)
	700°C	800°C	700°C	800°C	700°C	800°C	700°C	800°C	800°C	800°C
0.00100	1.088	1.078	-16.6	-18.1	-3.2	-3.4	.189	.204	+17	-0
0.00300	1.043	1.028	-14.5	-15.8	-3.3	-3.4	.184	.201	+14	-1
0.00700	1.007	.988	-12.8	-14.0	-3.3	-3.4	.186	.204	+11	-3
0.0200	.963	.940	-10.8	-11.8	-3.3	-3.4	.186	.201	+ 8	-4
0.0500	.920	.895	- 8.8	- 9.7	-3.0	-3.3	.207	.214	+ 6	-3
0.0700	.902	.876	- 8.0	- 8.8	-2.9	-3.1	.228	.231	+ 5	-3
0.100	.883	.853	- 7.1	- 7.7	-2.7	-2.8	.251	.266	+ 5	-3
0.150	.857	.823	- 5.9	- 6.4	-2.3	-2.3	.313	.339	+ 4	-2
0.200	.838	.800	- 5.1	- 5.3	-1.9	-1.9	.366	.417	+ 3	-2
0.250	.822	.780	- 4.3	- 4.4	-1.6	-1.4	.430	.516	+ 2	-2
0.300	.806	.763	- 3.6	- 3.6	-1.2	-1.0	.525	.621	+ 0	-3

Table 8. KCl solvent, cell VII.

$N_{\text{CoCl}_2}$	$\bar{E}$ (volts)		$\bar{G}$ (Kcal)		$\bar{G}^E$ (Kcal)		$\gamma$		$\bar{S}$ (e.u.)	$\bar{H}$ (Kcal)
	800°C	900°C	800°C	900°C	800°C	900°C	800°C	900°C	800°C	800°C
0.001	1.507	1.491	-29.7	-30.9	-15.0	-14.8	$9.01 \times 10^{-4}$	$1.78 \times 10^{-3}$	11	18
0.003	1.457	1.435	-27.4	-28.3	-15.0	-14.7	$8.92 \times 10^{-4}$	$1.80 \times 10^{-3}$	9	18
0.007	1.418	1.393	-25.6	-26.3	-15.0	-14.8	$8.92 \times 10^{-4}$	$1.78 \times 10^{-3}$	7	18
0.0200	1.370	1.339	-23.3	-23.9	-15.0	-14.7	$8.78 \times 10^{-4}$	$1.81 \times 10^{-3}$	5	18
0.0500	1.323	1.288	-21.2	-21.5	-14.8	-14.5	$9.72 \times 10^{-4}$	$1.98 \times 10^{-3}$	3	18
0.0700	1.299	1.263	-20.1	-20.3	-14.4	-14.1	$1.16 \times 10^{-3}$	$2.33 \times 10^{-3}$	2	18
0.100	1.272	1.235	-18.8	-19.0	-13.9	-13.7	$1.46 \times 10^{-3}$	$2.83 \times 10^{-3}$	2	17
0.150	1.234	1.196	-17.1	-17.3	-13.0	-12.8	$2.23 \times 10^{-3}$	$4.08 \times 10^{-3}$	1	16
0.200	1.197	1.160	-15.4	-15.6	-11.9	-11.8	$3.72 \times 10^{-3}$	$6.26 \times 10^{-3}$	1	14
0.250	1.160	1.125	-13.7	-14.0	-10.7	-10.8	$6.62 \times 10^{-3}$	$1.00 \times 10^{-2}$	1	13
0.300	1.120	1.090	-11.8	-12.4	-9.3	-9.6	$1.31 \times 10^{-2}$	$1.66 \times 10^{-2}$	1	11
0.350	1.081	1.056	-9.0	-10.8	-6.8	-8.3	$4.18 \times 10^{-2}$	$2.80 \times 10^{-2}$	1	9
0.400	1.044	1.023	-8.3	-9.3	-6.4	-7.1	$5.10 \times 10^{-2}$	$4.71 \times 10^{-2}$	0	9
0.500	0.973	0.947	-5.0	-5.8	-3.5	-4.1	$1.94 \times 10^{-1}$	$1.84 \times 10^{-1}$	0	5
0.700	0.891	0.862	-1.2	-1.8	-.4	-1.0	$8.17 \times 10^{-1}$	$6.65 \times 10^{-1}$	0	1
0.900	0.868	0.831	-0.2	-.4	0	-0.1	1	$9.6 \times 10^{-1}$	0	0
1.00	0.864	0.822	0	0	0	0	1	1	0	0

Table 9. NaCl solvent, cell VIII.

$N_{\text{CoCl}_2}$	$E$ (volts)		$\bar{G}$ (Kcal)		$\bar{G}^E$ (Kcal)		$Y$		$\bar{S}$ (e.u.)	$\bar{H}$ (Kcal)
	800°C	900°C	800°C	900°C	800°C	900°C	800°C	900°C	800°C	900°C
0.00100	1.379	1.372	-23.8	-25.4	-9.0	-9.3	$1.44 \times 10^{-2}$	$1.88 \times 10^{-2}$	14	9
0.00300	1.329	1.316	-21.5	-22.8	-9.1	-9.3	$1.42 \times 10^{-2}$	$1.89 \times 10^{-2}$	12	8
0.00700	1.290	1.273	-19.7	-20.8	-9.1	-9.2	$1.42 \times 10^{-2}$	$1.91 \times 10^{-2}$	10	9
0.0200	1.242	1.221	-17.4	-18.4	-9.1	-9.3	$1.40 \times 10^{-2}$	$1.97 \times 10^{-2}$	8	9
0.0500	1.198	1.169	-15.4	-16.0	-9.0	-9.0	$1.46 \times 10^{-2}$	$2.08 \times 10^{-2}$	6	9
0.0700	1.178	1.147	-14.5	-15.0	-8.8	-8.8	$1.59 \times 10^{-2}$	$2.31 \times 10^{-2}$	5	9
0.100	1.153	1.120	-13.3	-13.8	-8.4	-8.4	$1.92 \times 10^{-2}$	$2.74 \times 10^{-2}$	5	8
0.150	1.120	1.083	-11.8	-12.0	-7.8	-7.6	$2.62 \times 10^{-2}$	$3.81 \times 10^{-2}$	4	8
0.200	1.091	1.052	-10.5	-10.6	-7.0	-6.9	$3.69 \times 10^{-2}$	$5.28 \times 10^{-2}$	3	7
0.250	1.063	1.023	-9.2	-9.3	-6.2	-6.0	$5.38 \times 10^{-2}$	$7.51 \times 10^{-2}$	3	6
0.300	1.032	0.977	-7.7	-8.1	-5.2	-5.3	$8.81 \times 10^{-2}$	$1.05 \times 10^{-1}$	2	6
0.350	1.002	0.972	-6.4	-6.9	-4.1	-4.5	$1.45 \times 10^{-1}$	$1.47 \times 10^{-1}$	2	4
0.400	0.977	0.950	-5.2	-5.9	-3.3	-3.8	$2.17 \times 10^{-1}$	$1.99 \times 10^{-1}$	2	3
0.500	0.940	0.909	-3.5	-4.0	-2.0	-2.3	$3.97 \times 10^{-1}$	$3.66 \times 10^{-1}$	1	3
0.700	0.890	0.852	-1.2	-1.4	-0.4	-.5	$8.50 \times 10^{-1}$	$8.11 \times 10^{-1}$	1	0
0.900	0.868	0.830	-.2	-0.4	0	-.1	1.00	$9.71 \times 10^{-1}$	0	0
1.00	0.864	0.822	0	0	0	0	1.00	1.00	0	0

Table 10. 1:1 NaCl-KCl solvent, cell IX.

$N_{CoCl_2}$	E (volts)			$\bar{G}$ (Kcal)			$\bar{G}^E$			$\gamma$			$\bar{S}$ (e.u.)	$\bar{H}$ (Kcal)
	700°C	800°C	900°C	700°C	800°C	900°C	700°C	800°C	900°C	700°C	800°C	900°C	800°C	800°C
0.00100	1.454	1.446	1.433	25.2	26.8	28.2	11.9	12.1	12.1	$2.16 \times 10^{-3}$	$3.39 \times 10^{-3}$	$5.62 \times 10^{-3}$	12	14
0.00300	1.407	1.394	1.377	23.1	24.4	25.6	11.8	12.1	12.1	$2.21 \times 10^{-3}$	$3.48 \times 10^{-3}$	$5.67 \times 10^{-3}$	10	14
0.00700	1.373	1.355	1.335	21.5	22.6	23.7	11.9	12.1	12.1	$2.19 \times 10^{-3}$	$3.48 \times 10^{-3}$	$5.60 \times 10^{-3}$	9	13
0.0200	1.328	1.307	1.282	19.4	20.4	21.2	11.9	12.1	12.1	$2.23 \times 10^{-3}$	$3.44 \times 10^{-3}$	$5.58 \times 10^{-3}$	6	14
0.0500	1.283	1.258	1.227	17.3	18.2	18.7	11.9	11.8	11.7	$2.55 \times 10^{-3}$	$3.97 \times 10^{-3}$	$6.63 \times 10^{-3}$	4	14
0.0700	1.262	1.235	1.202	16.4	17.1	17.5	11.2	11.5	11.3	$3.01 \times 10^{-3}$	$4.66 \times 10^{-3}$	$7.78 \times 10^{-3}$	4	13
0.100	1.238	1.208	1.172	15.3	15.9	16.1	10.8	11.0	10.7	$3.73 \times 10^{-3}$	$5.87 \times 10^{-3}$	$9.87 \times 10^{-3}$	3	13
0.150	1.202	1.172	1.132	13.6	14.2	14.3	9.9	10.2	9.9	$5.87 \times 10^{-3}$	$8.55 \times 10^{-3}$	$1.45 \times 10^{-2}$	2	12
0.200	1.169	1.138	1.097	12.1	12.6	12.7	9.0	9.2	9.1	$9.70 \times 10^{-3}$	$1.34 \times 10^{-2}$	$2.01 \times 10^{-2}$	2	11
0.250	1.137	1.105	1.065	10.6	11.1	11.2	7.9	8.2	8.0	$1.66 \times 10^{-2}$	$2.18 \times 10^{-2}$	$3.26 \times 10^{-2}$	1	10
0.300	1.102	1.070	1.033	9.0	9.5	9.7	6.7	6.9	6.9	$3.21 \times 10^{-2}$	$3.86 \times 10^{-2}$	$5.14 \times 10^{-2}$	1	9
0.350	1.068	1.037	1.044	7.4	8.0	8.4	5.4	5.7	5.9	$6.13 \times 10^{-2}$	$6.78 \times 10^{-2}$	$7.83 \times 10^{-2}$	1	7
0.400	1.031	1.007	0.977	5.7	6.6	7.2	4.0	4.6	5.0	$1.30 \times 10^{-1}$	$1.14 \times 10^{-1}$	$1.14 \times 10^{-1}$	1	6
0.500	.979	.948	0.922	3.3	3.9	4.6	1.9	2.3	2.9	$3.68 \times 10^{-1}$	$3.34 \times 10^{-1}$	$2.84 \times 10^{-1}$	1	3
0.700	.930	.890	0.857	1.1	1.2	1.6	0.3	0.4	0.7	$8.45 \times 10^{-1}$	$8.34 \times 10^{-1}$	$7.36 \times 10^{-1}$	0	1
0.900	.911	.868	0.830	0.2	.2	.4	.0	.0	0.1	1	1	$9.71 \times 10^{-1}$	0	0
1.00	.907	.864	0.822	.0	.0	.0	.0	.0	.0	1	1	1	0	0

Table 11. LiCl solvent, cell X.

$N_{\text{CoCl}_2}$	$\bar{E}$ (volts)		$\bar{G}$ (Kcal)		$\bar{G}^E$ (Kcal)		$\bar{Y}$		$\bar{S}$ (e.u.)	$\bar{H}$ (Kcal)
	700°C	800°C	700°C	800°C	700°C	800°C	700°C	800°C	800°C	800°C
0.00100	1.274	1.265	-16.9	-18.5	3.6	3.8	.158	.170	13	5
0.00300	1.227	1.213	-14.8	-16.1	3.5	3.7	.162	.175	11	4
0.00700	1.192	1.173	-13.2	-14.3	3.6	3.7	.160	.178	9	5
0.0200	1.148	1.125	-11.1	-12.0	3.6	3.7	.160	.175	7	5
0.0500	1.109	1.083	-9.3	-10.1	3.5	3.7	.161	.175	5	5
0.0700	1.093	1.065	-8.6	-9.3	3.4	3.6	.169	.184	5	4
0.100	1.075	1.044	-7.8	-8.3	3.3	3.4	.182	.203	4	4
0.150	1.052	1.017	-6.7	-7.1	3.0	3.0	.210	.244	3	4
0.200	1.032	.997	-5.8	-6.1	2.7	2.3	.253	.334	2	4
0.250	1.015	.978	-5.0	-5.3	2.3	2.0	.305	.386	2	3
0.300	.999	.962	-4.2	-4.5	1.9	1.7	.374	.455	2	3
0.350	.986	.947	-3.6	-3.8	1.6	1.4	.435	.519	1	3
0.400	.974	.933	-3.1	-3.2	1.3	1.1	.507	.586	1	2
0.500	.952	.912	-2.1	-2.2	0.7	.6	.698	.772	1	1
0.700	.926	.886	-0.9	-1.0	0.2	.1	.927	.970	0	1
0.900	.911	.868	-0.2	-0.2	0	0	1	1	0	0
1.00	.907	.864	0	0	0	0	1	1	0	0

Table 12. The Ag|AgCl, RCl || reference electrodes.

Cell	$N_{\text{AgCl}}$	Solvent	$E'_{\text{Ag}}$ (volts)	
			700°	800°
III	$6.6 \times 10^{-2}$	1:1 NaCl-KCl	$1.063 \pm 6$ mv	$1.063 \pm 6$ mv
IV	$7.3 \times 10^{-2}$	LiCl	$0.983 \pm 2$ mv	$0.980 \pm 2$ mv
VI	$5.5 \times 10^{-2}$	KCl		$1.136 \pm 4$ mv
VII	$5.5 \times 10^{-2}$	KCl		$1.131 \pm 4$ mv
VIII	$6.0 \times 10^{-2}$	NaCl		$1.030 \pm 2$ mv
IX	$6.6 \times 10^{-2}$	1:1 NaCl-KCl	$1.074 \pm 2$ mv	$1.074 \pm 2$ mv
X	$7.3 \times 10^{-2}$	LiCl	$0.975 \pm 2$ mv	$0.969 \pm 2$ mv

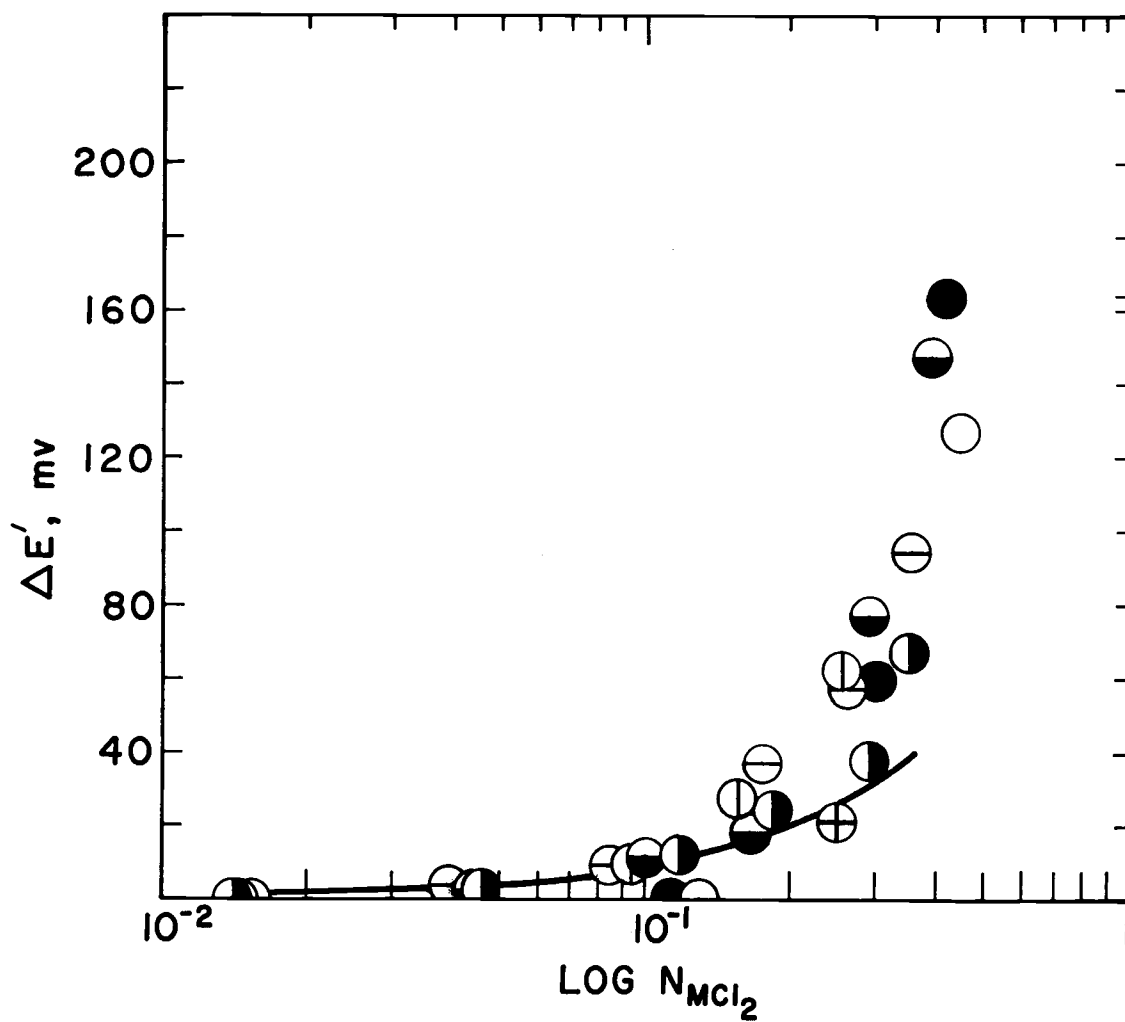


Figure 14. Values of  $\Delta E' = E'_{Ag} - E_{Ag}$  vs.  $\log N_{MCl_2}$ ,  $800^\circ C$ .

Cell	Solute	Solvent	Symbol
III	NiCl <sub>2</sub>	1:1 NaCl-KCl	○
IV	"	LiCl	●
VI	"	KCl	●
VII	CoCl <sub>2</sub>	KCl	⊙
VIII	"	NaCl	⊖
IX	"	1:1 NaCl-KCl	●
X	"	LiCl	⊕

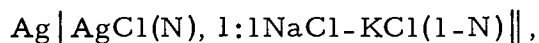


#### IV. DISCUSSION OF RESULTS

##### Comparisons with Results of Other Investigators

##### Nickel Electrodes

Various aspects of the behavior of nickel electrodes in fused media have been studied previously (Flengas and Ingrahm, 1957b, 1959; Maricle and Hume, 1964; Littlewood, 1961b; Hamby, 1961; Walker and Danley, 1957; Stromatt, 1966; Laitinen and Liu, 1958). Equilibrium electrode potentials in 1:1 NaCl-KCl have been measured by Flengas and Ingrahm (1957b) and their data may be compared with the present results. They used the reference electrode



where the double line represents an asbestos fiber, to measure the potential of the nickel electrode as a function of  $\text{NiCl}_2$  concentration up to  $N_{\text{NiCl}_2} = 6.2 \times 10^{-2}$  at  $705^\circ\text{C}$  in 1:1 NaCl-KCl. In an independent experiment the potential of their reference electrode was compared with that of the chlorine electrode in the same solvent. Thus, neglecting the possibility of junction potentials, potential differences between nickel and chlorine electrodes may be estimated from Flengas and Ingrahm's data. Corrections for thermoelectric effects were included in a later publication (Flengas and Ingrahm, 1959);

however, the polarity of the stated correction for a Ni, Ni-Ag, Pt combination is opposite that expected on the basis of the tabulated thermal emf's of various elements relative to platinum (American Institute of Physics Handbook, 1957, p. 4-8). Flengas and Ingrahm's 705° data without thermoelectric corrections have been included in Figure 15. It is believed that proper correction for thermoelectric effects would bring their data into good agreement with the present data at concentrations near  $10^{-2}$  mole fraction.

Stromatt (1966) has carried out a rather extensive but unpublished study of solvent effects on nickel and cobalt electrodes at fixed solute concentration. Measurements of nickel electrode potentials with respect to a chlorine electrode were taken at or near 0.1 molal and normalized to 0.1 molal at 670° C. The summarized results of his study are shown in Figure 16. Solvent composition was varied over wide ranges for the mixtures NaCl-KCl, LiCl-KCl, and LiCl-NaCl; however, measurements were not carried out utilizing the single alkali metal chlorides as solvents. Comparison of Stromatt's data with the present data require, in the case of 1:1 NaCl-KCl, both a temperature and a thermoelectric adjustment of data. Temperature coefficients of emf from the present study and Handbook thermoelectric values were used to make the necessary corrections. The comparison is shown in Figure 15 and the agreement is considered good.

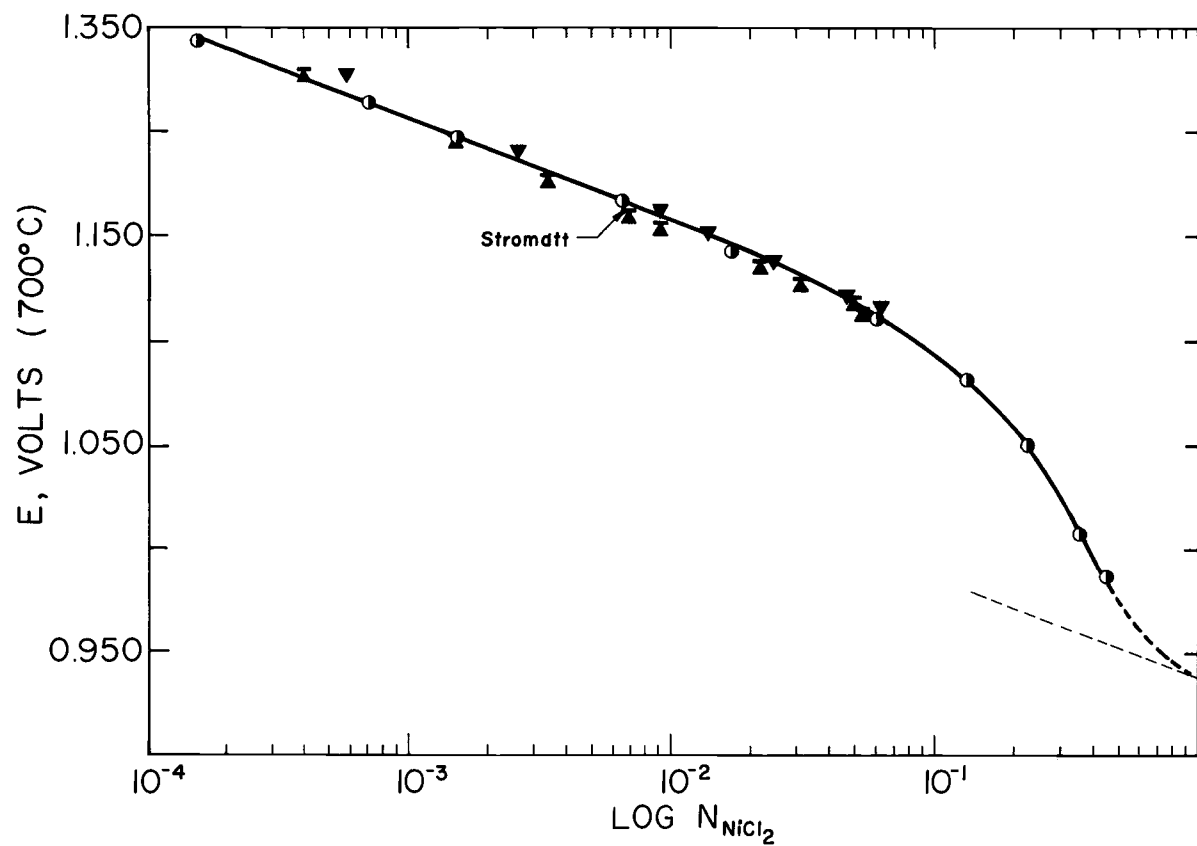


Figure 15. Cell emf, E, vs.  $\log N_{\text{NiCl}_2}$ ; solvent 1:1 NaCl-KCl. Cell III, 700°C, ●; data of Hamby (1961), 700°C, ▲; data of Flengas (1959b) 705°C, ▼; data point from Stromatt (1966) indicated by arrow.

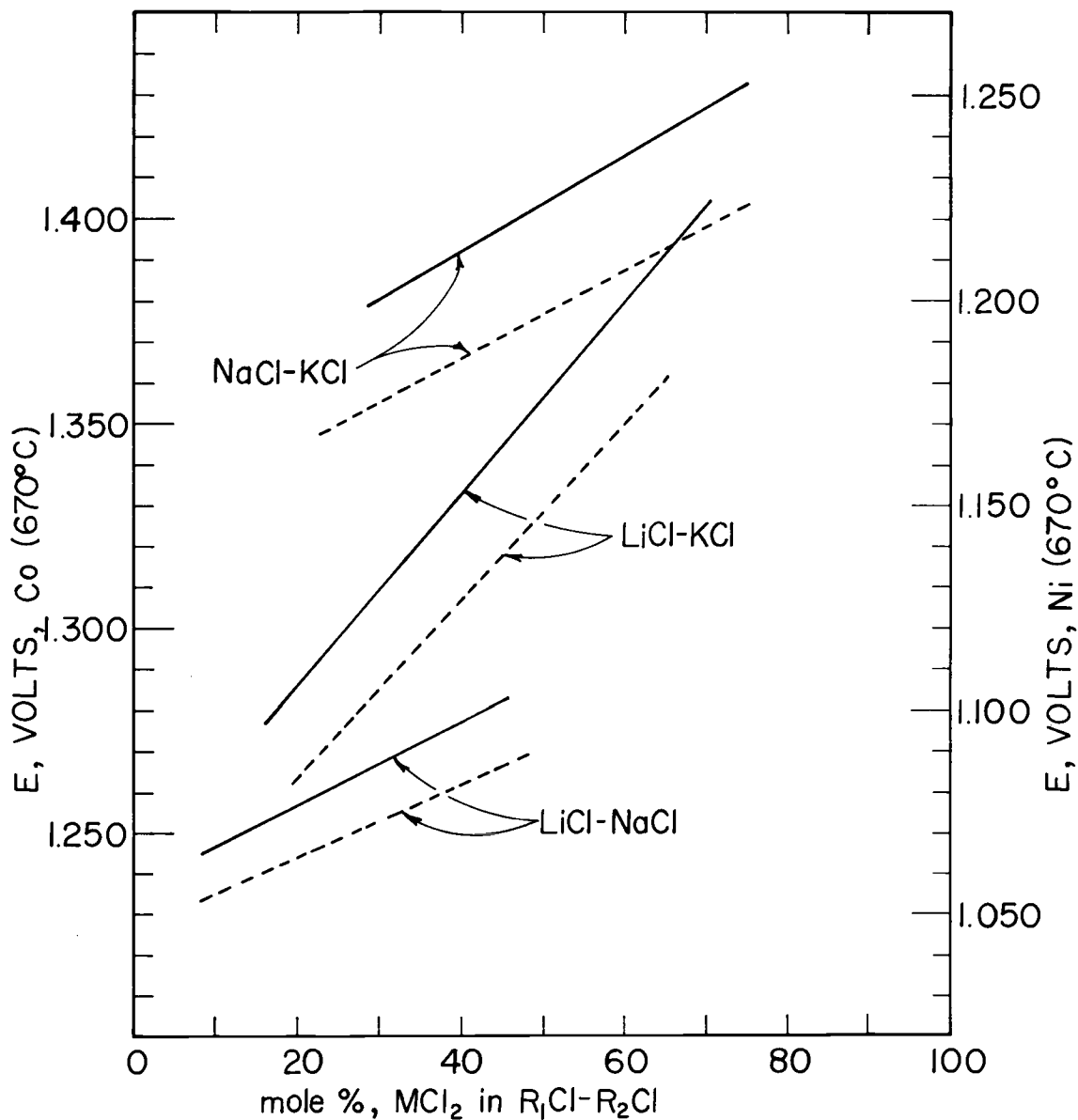
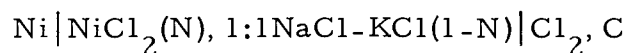


Figure 16. Summarized results of unpublished work of Stromatt (1966). Cell emf,  $E$ , vs. solvent composition. The solid lines refer to the solute  $CoCl_2$ , the dotted lines to the solute  $NiCl_2$ . Solvent composition becomes rich in the larger alkali metal cation in going from left to right across the abscissa.

The present author determined emf's for the cell



in an earlier study (Hamby, 1961). The experimental arrangement differed in several respects, principally, however, in the use of less effective shielding<sup>4</sup> of the metal electrode from the chlorine electrode. The results of this earlier work are compared with the present results in Figure 15. The earlier emf values tend to fall lower at any given concentration, a result that can be explained by concentration polarization at the nickel electrode due to the accessibility of the electrode to dissolved chlorine. Temperature coefficients of emf from this earlier study are in reasonable agreement with the present results.

Flengas and Ingrahm (1957) observed a non-Nernstian slope, 0.107, as opposed to an expected 0.097, in their work with the nickel electrode. Similar effects have been reported by Maricle and Hume (1964) in polarographic work and a tendency toward high emf values at low concentrations was observed in the present work. This tendency might be attributed to the existence of a mixed potential at the nickel electrode arising from the presence of oxygen containing impurities in the cell. Attention is called to the difference in the data for cells I

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<sup>4</sup>A graphite crucible was used with protection tube A, Figure 4.

and VI, Figure 12, both involving KCl solvent. Changes in experimental procedures<sup>5</sup> decreased the possibility of oxygen contamination of the cell and resulted in decreased values of cell emf at low NiCl<sub>2</sub> concentration.

### Cobalt Electrodes

The equilibrium cobalt electrode has been studied in fused media by Flengas and Ingram (1957a, 1959), Laitinen and Liu (1958), Stromatt (1966), Trzebiatowski and Kiswa (1961), and Hamby (1961). The data of Flengas and Ingrahm for 1:1 NaCl-KCl at 710°C, based on the same reference electrode as used in their Ni study, are compared with our results in Figure 17. The same comments apply here with respect to polarity of thermoelectric corrections as were made in the nickel section; the uncorrected data have been plotted. Thermoelectric corrections, which were reported to be approximately 4 mv at 700°C would leave the two sets of data in good agreement.

Stromatt's (1966) work may be compared in this case for 1:1 NaCl-KCl solvent with adjustments for temperature and thermoelectric effects as previously mentioned for the case of nickel. The comparison point is shown in Figure 17 and the two sets of data are found to be in good agreement.

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<sup>5</sup>Changes in procedure are listed in the Experimental section.

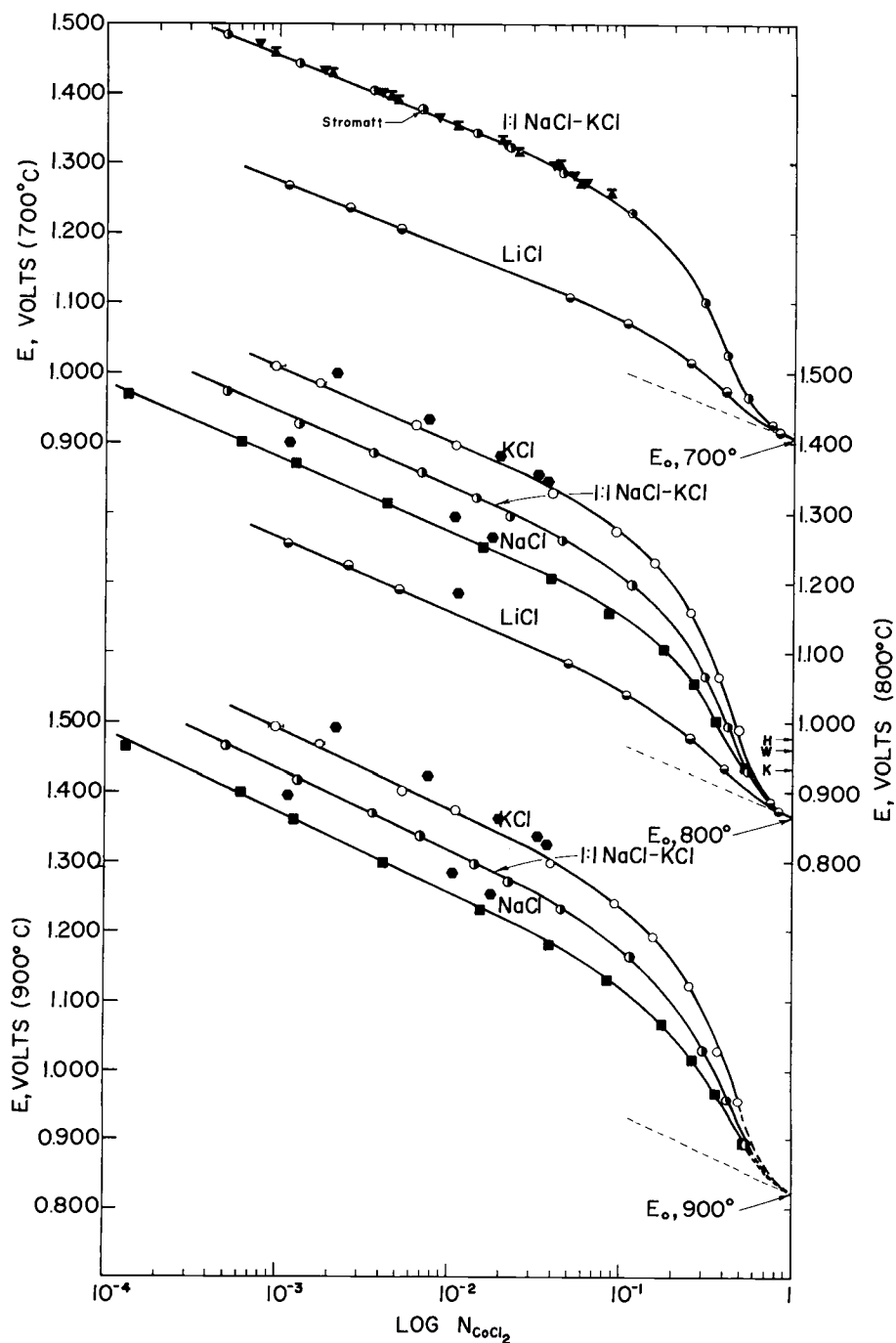
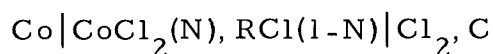


Figure 17. Cell emf,  $E$ , vs.  $\log N_{\text{CoCl}_2}$ . Data from the present study are included as in Figure 13. Also included are: The data of Hamby (1961), 700°C,  $\blacktriangle$ ; Flengas (1959a), 710°C,  $\blacktriangledown$ ; Stromatt (1966), indicated by arrow; Trzebiatowski (1961) 800° and 900° C, KCl, NaCl and LiCl,  $\blacklozenge$ .

Trzebiatowski and Kiszka (1961) have studied the cells



where RCl is KCl, NaCl or LiCl. Five concentrations were tested in the case of KCl, three for NaCl and only two for LiCl. Temperature coefficients of emf were determined for these concentrations so that both cell emf and  $dE/dT$  values may be compared with the present work. The comparison of emf values is shown in Figure 17 and appears poor; however, these authors make no mention in their article of correction for thermoelectric effects which are in this case between 20 and 30 mv. Correction for thermoelectric effects would improve the agreement between the two sets of data; however, it must also be noted that the slopes  $dE/d \log N$  deviate rather strongly from theoretical values indicating mixed electrode reactions. Values of  $dE/dT$  are compared in Table 13. Again the comparison is poor, the two sets of data disagreeing by almost a factor of two.

Our earlier data (Hamby, 1961) for the cobalt electrode in 1:1 NaCl-KCl is shown in Figure 17. Experimental arrangements differed as previously mentioned for the nickel electrodes. Agreement in this case is good. Temperature coefficients from the earlier study are in reasonable agreement with the present data; they were, however, taken over a shorter temperature span.



Table 13. Comparison of  $dE/dT$ ,  $\text{CoCl}_2$ .

Solvent	$N_{\text{CoCl}_2}$	Trezebiatowski $dE/dT$ (volts/degree)	This study $dE/dT$ (volts/degree)
KCl	$2.18 \times 10^{-3}$	$-0.85 \times 10^{-4}$	$-1.9 \times 10^{-4}$
	$7.5 \times 10^{-3}$	$-1.31 \times 10^{-4}$	$-2.5 \times 10^{-4}$
	$1.92 \times 10^{-2}$	$-1.92 \times 10^{-4}$	$-2.8 \times 10^{-4}$
	$3.23 \times 10^{-2}$	$-2.02 \times 10^{-4}$	$-3.1 \times 10^{-4}$
	$3.70 \times 10^{-2}$	$-2.15 \times 10^{-4}$	$-4.7 \times 10^{-4}$
NaCl	$1.15 \times 10^{-3}$	$-0.40 \times 10^{-4}$	$-0.91 \times 10^{-4}$
	$1.05 \times 10^{-2}$	$-1.16 \times 10^{-4}$	$-1.8 \times 10^{-4}$
	$1.75 \times 10^{-2}$	$-1.34 \times 10^{-4}$	$-2.1 \times 10^{-4}$
LiCl	$1.10 \times 10^{-2}$	$-1.34 \times 10^{-4}$	$-2.1 \times 10^{-4}$

The rather large discrepancy between the several values of the quantity  $\tilde{\Delta}\mu^\circ$  quoted in the literature, and between the literature values and the values determined by extrapolation in the present study as shown in Figure 13 and Table 14, require further comment. A check of the literature references cited by the authors listed in Table 14 indicates that the quantity  $\Delta H^\circ_{298} = -77.8 \text{ Kcal}$  used by all was taken from Rossini's (1952) compilation. Kubaschewski gives  $\pm 4 \text{ Kcal}$  as the uncertainty in this quantity. The disagreement in  $\tilde{\Delta}\mu^\circ$  among these authors at higher temperatures must be sought in the values of heat capacities and heats of fusion used in their calculations. These quantities have not been explicitly indicated in two out of the three cases; however, various tabulations of the pertinent heat capacities

claim one to two percent uncertainty. It is of interest to note a very wide discrepancy in literature values of the heat of fusion for  $\text{CoCl}_2$ ; these range from 7.4 Kcal/mole to 14.1 Kcal/mole.

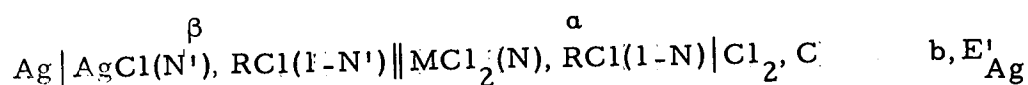
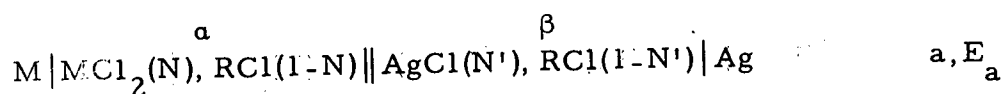
Table 14.  $-\Delta\tilde{\mu}_T^\circ$  (Kcal),  $\text{Co}(c) + \text{Cl}_2(g) \rightarrow \text{CoCl}_2(l)$ .

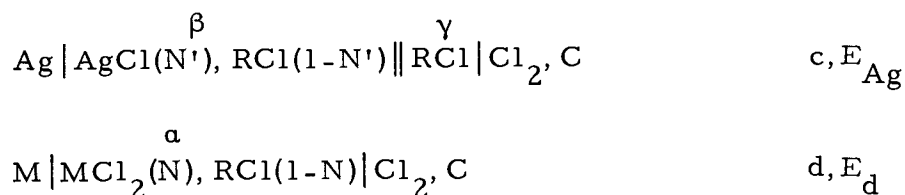
	Hamer (1956)	Kubaschewski (1956)	Wicks (1963)	This study
700° C		45.	46.	41.8
800° C	45.0	43.	44.	40.0
900° C		41.	42.	38.0
1000° C	41.5	38.	39.	

The information listed above leads us to suspect that Rossini's listed value of  $\Delta H_{298}^\circ$  is too negative by three to four Kcal. This suspicion is supported by lower temperature (400° to 450° C) electrochemical work of Egan (1965) who reports values of  $\Delta\tilde{\mu}^\circ$  approximately two to three kcal/mole less negative than the values of Wicks and Block.

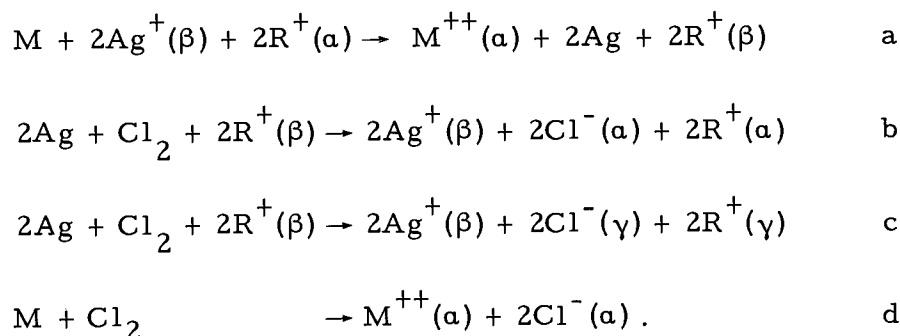
The Reference Electrodes,  $\text{Ag}|\text{AgCl}(N), \text{RCl}(1-N)||$

Given the following cells





designated a, b, c, and d, with corresponding emf's  $E_a$ ,  $E'_{\text{Ag}}$ ,  $E_{\text{Ag}}$ , and  $E_d$ , and various liquid phases designated  $\alpha$ ,  $\beta$ , and  $\gamma$ ; we wish to consider the error involved in calculating the emf for a cell without junction containing the chlorine electrode, d, from that of a cell in which the chlorine electrode is replaced by the  $\text{Ag}|\text{AgCl}, \text{RCl}|$  reference, a. The junctions in cells a, b, and c are ion-conductive membranes of the type used in this work and it is assumed that charge is transported through the membranes only by alkali metal cations (Labrie, 1959; Yang and Hudson, 1959). We assume that the membrane-containing cells may be treated according to the equilibrium thermodynamics outlined in Chapter I, a point which is recognized to be controversial (Janz, 1961). Detailed consideration of the reactions at all of the phase boundaries in each of the cells indicates that the cell reactions should be written as follows:



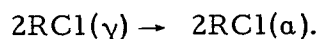
If we add reactions a and b we obtain immediately reaction d and we would expect

$$\Delta\tilde{\mu}_d = -2FE_d = -2F(E_a + E'_{Ag}). \quad (36)$$

In some cases, however, for instance  $M = Fe$ , it would be impossible to determine either  $E_d$  or  $E'_{Ag}$  directly, due to the oxidation of ferrous to ferric iron.  $E_a$  and  $E_{Ag}$  would be determinable but

$$\Delta\tilde{\mu}_{a+c} = -2F(E_a + E_{Ag}) \neq \Delta\tilde{\mu}_d. \quad (37)$$

It is of interest to consider the magnitude,  $-nF\Delta E'$ , and the source of the error involved if one does assume  $\Delta\tilde{\mu}_d = \Delta\tilde{\mu}_{a+c}$ . The source of the error can be identified by subtracting the sum of reactions a and c from reaction d yielding



The magnitude of  $\Delta E'$  is given by

$$\Delta\tilde{\mu}_d - \Delta\tilde{\mu}_{a+c} = -2F(E'_{Ag} - E_{Ag}) = -2F\Delta E'. \quad (38)$$

Applying the Nernst equation to the overall reaction, d-a-c, we obtain

$$\Delta E' = -\frac{RT}{F} \ln \frac{a_{\text{RCl}}^{\alpha}}{a_{\text{RCl}}^{\gamma}} = -\frac{RT}{F} \ln a_{\text{RCl}}^{\alpha}, \quad (39)$$

having used  $a_{\text{RCl}}^{\gamma} = 1$  according to our choice of reference states for liquids.

In the present study we have measured  $E'_{\text{Ag}}$  and  $E_{\text{Ag}}$  for the cases  $M = \text{Ni}$  and  $M = \text{Co}$  and found  $\Delta E'$  to be experimentally undetectable up to  $N_{\text{MCl}_2} < 10^{-2}$ . Assuming Raoult's law behavior of RCl at this concentration, which is justified on the basis of Henry's law behavior of the solute at this concentration, (Wall, 1965)<sup>6</sup> Equation (39) would predict  $\Delta E < 1 \text{ mv}$  which is in agreement with the experimental result.

If these results are taken to be generally valid for divalent solutes,  $\text{MCl}_2$ , the  $\text{Ag}|\text{AgCl}, \text{MCl}_2||$  reference may be reliably used in place of the chlorine electrode to study, at low concentrations, solutes subject to oxidation such as  $\text{FeCl}_2$ .

#### The Variation of $\bar{G}^E$ with Solvent

One measure of solute deviation from ideal behavior is the magnitude of the excess partial molar free energy,  $\bar{G}^E$ . According to

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<sup>6</sup>Henry's law behavior of the solute at low concentration, that is, constancy of the solute activity coefficient, is indicated by obedience of the Nernst equation (see Figures 12 and 13).

Equations (27) and (31)

$$\bar{G}^E = -nFE - RT \ln N - \Delta\tilde{\mu}^\circ, \quad (40)$$

and it is obvious that the magnitude of  $\bar{G}^E$  is dependent on the choice of standard states and on the particular components chosen to describe the system through both the third and fourth terms in Equation (40).<sup>7</sup> The order of variation of the magnitude of  $\bar{G}^E$  with solvent at fixed solute concentration is, however, independent of these quantities. The order observed in this study was



which follows the order established in numerous previous studies which include the solutes  $\text{PbCl}_2$ ,  $\text{CdCl}_2$ ,  $\text{ZnCl}_2$ ,  $\text{MgCl}_2$ ,  $\text{CeCl}_3$ ,  $\text{FeCl}_2$ , and  $\text{BeCl}_2$  in the alkali chlorides (Blander, 1964). This order of variation with solvent is commonly explained on the basis of a competition for anions between solute and solvent cations. The solvent cation of largest charge to size ratio,  $\text{Li}^+$ , is considered to be the most effective competitor for chloride ions, and its presence results in the smallest degree of bonding between the solute cations and solvent anions.

There is good evidence (Gruen and McBeth, 1959, 1963;

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<sup>7</sup> An alternative choice of components might have been  $\text{RCl}$  and  $\text{R}_2\text{MCl}_4$ .

Hornyak, 1957; Smith and Boston, 1965, Boston and Smith, 1958; Øye and Gruen, 1965; Angel and Gruen, 1966; Brynestad, Boston, and Smith, 1967; Brynestad and Smith, 1967) that both nickel and cobalt exist as chloro-complexes in the alkali chloride melts; this is likely a major cause of non-ideal behavior with respect to  $\bar{G}^E$  as well as the heat and the entropy of mixing. We will return to this point later in connection with the entropy of mixing.

### The Entropy of Mixing

In Figure 18 and 19 the variation of the partial molar entropy of mixing of  $MCl_2$ ,  $\bar{S}$ , is shown as a function of  $\log N_{MCl_2}$  for the two solutes and four solvents studied. If the solutions of  $MCl_2$  in the alkali halides were ideal according to Raoult's law we could assert that  $\bar{S}$  would follow the equation

$$\bar{S} = \left[ \frac{\partial \Delta S_{\text{mix}}}{\partial N_{MCl_2}} \right]_{T,P, n_{RCl}} = -R \ln N_{MCl_2} \quad (41)$$

where  $\Delta S_{\text{mix}}$  is the ideal entropy of mixing. The ideal curves are shown as solid lines in Figures 18 and 19. The deviations from ideality are not severe, probably lying within the experimental error ( $\pm 2$  eu for  $\Delta \bar{s}$ ) in the cases  $NiCl_2$  in LiCl and 1:1 NaCl-KCl, and  $CoCl_2$  in all four solvents.

It has been interesting to compare the experimental values of

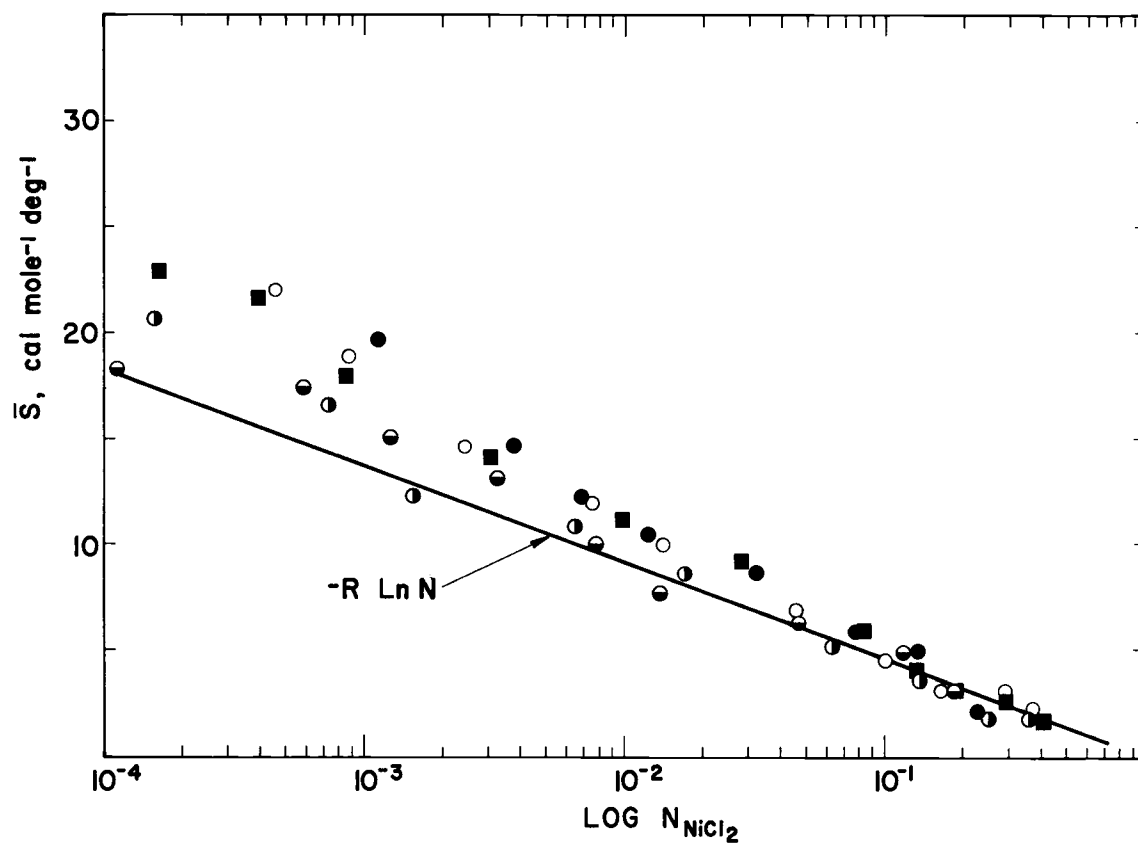


Figure 18. Partial molar entropy of mixing for  $NiCl_2$ ,  $\bar{S}$ , as a function of  $\log N_{NiCl_2}$ , compared with the values predicted on the basis of the Temkin model. Symbols are related to cells and solvents as in Figure 12.



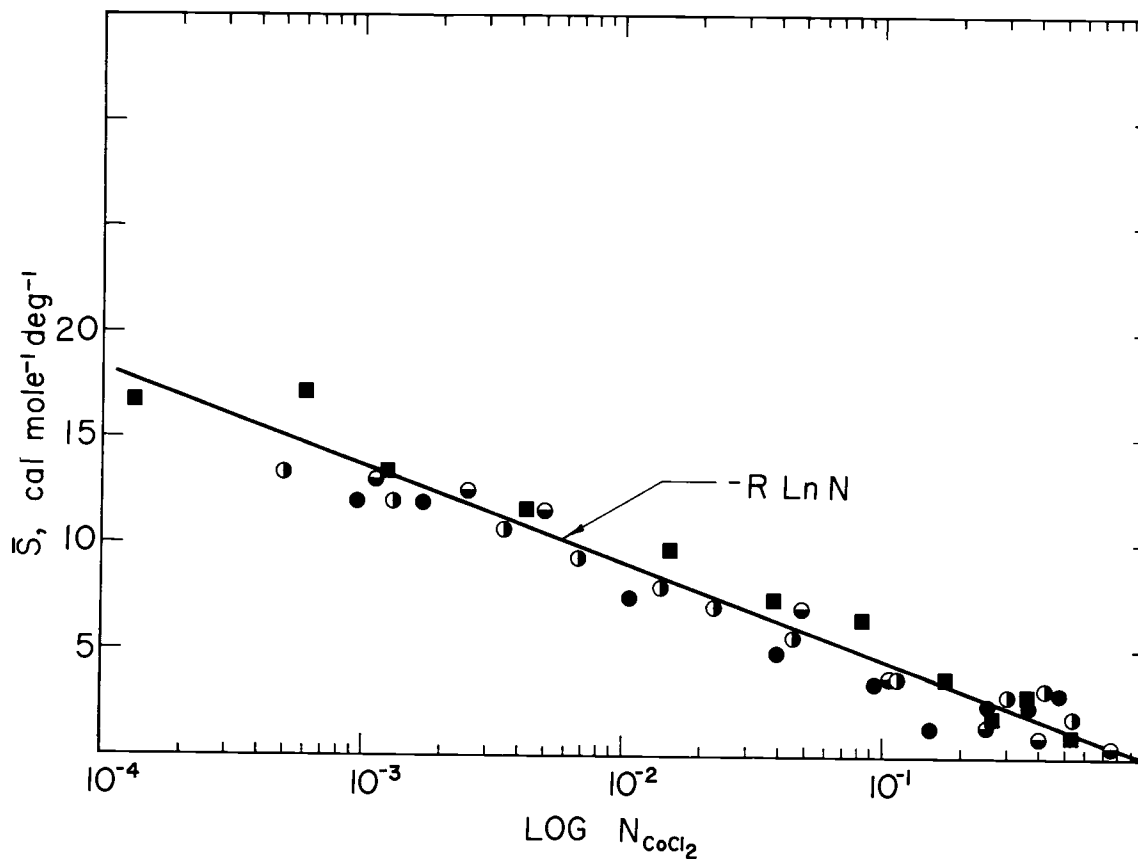


Figure 19. Partial molar entropy of mixing for  $\text{CoCl}_2$ ,  $\bar{S}$ , as a function of  $\log N_{\text{CoCl}_2}$ , compared with the values predicted on the basis of the Temkin model. Symbols are related to cells and solvents as in Figure 13.

$\bar{S}$  with several values of the configurational entropy of mixing calculated on the basis of some simple lattice models of the liquids. Justification of the use of lattice models for ionic liquids has been discussed by Førlund (1957) who argues effectively on the basis of energy considerations that cations will preferentially have anions as nearest neighbors and vice versa. Although the long range order of ionic crystals is destroyed by melting, the neutron and X-ray scattering experiments of Levy (1964) have shown that ionic liquids do contain ordered regions which range over several atom distances and average numbers of nearest and next nearest neighbors may be determined.

Several causes for non-ideal mixing suggest themselves and merit comment. First there is the excess entropy of mixing, which may be present even in the case of perfect random mixing, which derives from the temperature coefficients of the intermolecular interaction energies. This is usually small, and in any case can only be found empirically (Lewis and Randall, 1961, p. 285). In the absence of specific chemical interactions, e. g. , complex formation, incorporation of cation vacancies, to balance the excess charge of the  $\text{Ni}^{2+}$  ion and maintain a pseudo-lattice structure, may or may not lead to non-ideality, depending upon the assumptions under which the vacancies are incorporated into the lattice. In addition, the degree of departure from ideality depends upon the degree of association between  $\text{Ni}^{2+}$  and the vacancy. The formation of a complex can also lead to a deviation

from (41) as shown below; in addition, vacancy incorporation may also occur together with complex formation, with the possibility of vacancy association, so that the functional dependence of  $\bar{S}$  on  $N_{\text{NiCl}_2}$  may be extremely complicated even if simple models are used for the statistical calculation of the configurational entropy.

In order to be more definite in the following discussion we will first consider the solute  $\text{NiCl}_2$  in the various solvents.

Lattice models for the mixing of liquid  $\text{NiCl}_2$  with a liquid alkali halide (in which the formation of halo-complexes is not considered) have been reviewed (Blander, 1964; Førland, 1957, 1961, 1964), and lead to the following results:

$$(a) \text{ Temkin Model: } \bar{S} = -R \ln N \quad (42)$$

$$(b) \text{ Vacancy Model: } \bar{S} = -2R \ln N' \quad (43)$$

(c) Associated Vacancy Model:

$$\bar{S} = -R[-N'_s + \ln N' - (N'_s)^2/Z \ln 2], \quad (44)$$

where

$$N = N_{\text{NiCl}_2} = n_{\text{Ni}} / (n_{\text{Ni}} + n_s), \quad N' = 2n_{\text{Ni}} / (2n_{\text{Ni}} + n_s), \quad N'_s = 1 - N',$$

with  $n_{\text{Ni}}$  and  $n_s$  representing the number of moles of  $\text{NiCl}_2$  and the number of moles of alkali halide respectively, and  $Z$  is the number of nearest cation sites surrounding a cation site. We take  $Z \approx 12$  for molten alkali halides (Lumsden, 1966, p. 177; Levy,

1964).

In each of these cases the assumption has been made that only one anion,  $\text{Cl}^-$ , exists in solution; thus, its mole fraction is unity and there is no anion contribution to the partial molar configurational entropy. The Temkin entropy is calculated from the number of ways one can distribute a given number of distinguishable sites among a certain number of cations; no provision is made for charge compensation in the case of mixing mono and divalent cations. The entropy of the Temkin model is that of an ideal mixture. Vacancy model (b) allows for charge compensation by requiring that one vacant cation site be created per divalent cation. No association between vacancies and divalent cations is assumed, however, this particular model, (b), is obtained only by incorporating cation vacancies into the initial  $\text{NiCl}_2$  lattice. The associated vacancy model assumes complete association of divalent cations and vacancies.

In Figure 20, the observed values of  $\bar{S}$ , plotted against  $\log N'_{\text{NiCl}_2}$ , are compared with the predictions of models (b) and (c). The data are clearly inconsistent with the vacancy model, but agree about as well with the associated vacancy model as with the Temkin model. This is not surprising, as the slope of  $\bar{S}$  calculated for the associated vacancy case vs.  $\ln N'$ , is, except at  $N' > 0.2$ , virtually indistinguishable from that of  $\bar{S}$  calculated for the ideal case vs.  $\ln N$ .

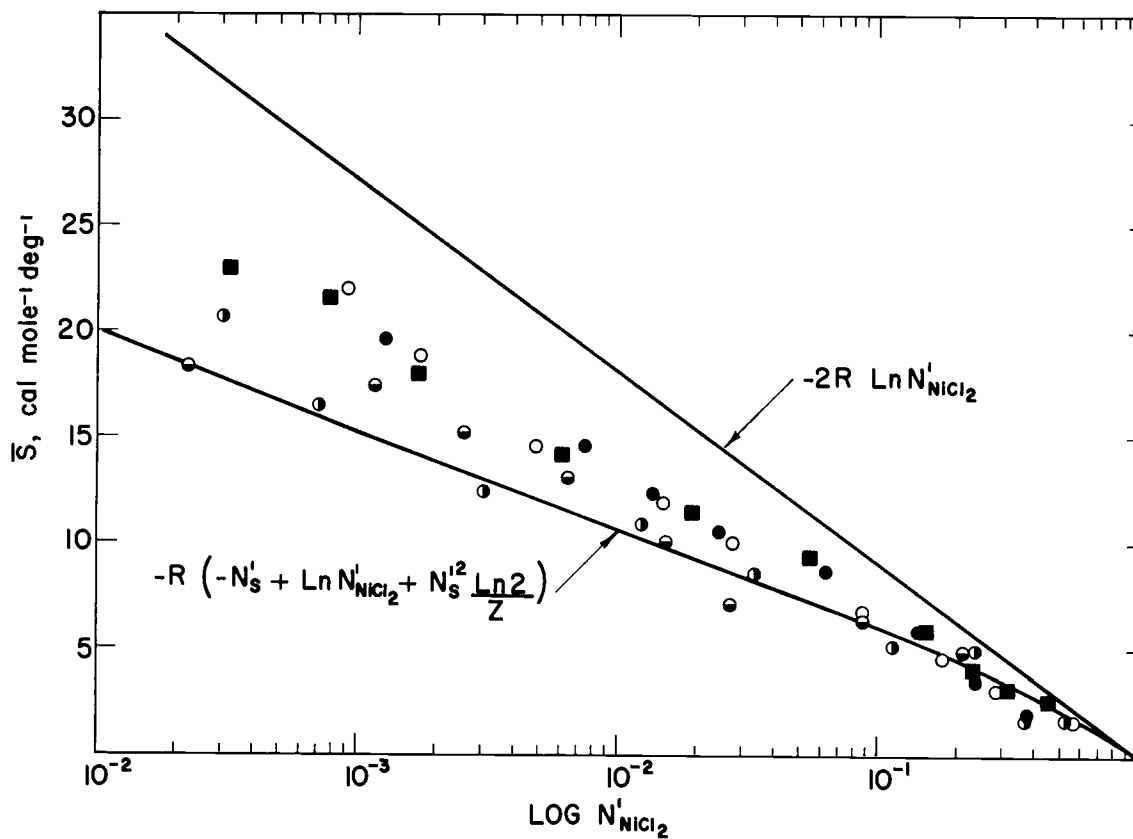


Figure 20. Partial molar entropy of mixing for  $\text{NiCl}_2$ ,  $\bar{S}$ , as a function of  $\text{log } N'_{\text{NiCl}_2}$ , compared with values predicted on the basis of the vacancy and associated vacancy models. Symbols are related to cells and solvents as in Figure 12.

Further consideration of non-associated vacancy models can lead to results quite different from (b). For instance one might reasonably assume on the basis of molar volume data (Bloom and Bockris, 1964), that large numbers of both anion and cation vacancies,  $xn_s$  moles, are present in  $n_s$  moles of liquid RCl.<sup>8</sup> Random mixing of the ions and vacancies of this solvent with  $n_{Ni}$  moles of liquid NiCl<sub>2</sub> which contain  $yn_{Ni}$  moles of vacancies can be shown to yield

$$(d) \quad \bar{S} = -R \ln N + f(x, y) \quad (45)$$

under the condition  $n_{Ni} \ll n_s$  where

$$f(x, y) = \text{constant}$$

and

$$f(x, y) = 0 \quad \text{if} \quad x = y.$$

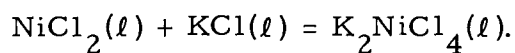
We turn next to the effect of complex formation. The absorption spectrum of NiCl<sub>2</sub>-KCl solutions bears a close resemblance to that of crystalline Cs<sub>2</sub>ZnCl<sub>4</sub> in which Cs<sub>2</sub>NiCl<sub>4</sub> is isomorphically substituted (Gruen and McBeth, 1959), which is good evidence that tetrahedral NiCl<sub>4</sub><sup>2-</sup> complexes exist in KCl solutions. The same species is also found in RbCl and CsCl (Smith and Boston, 1965). The coordination

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<sup>8</sup>Consideration of data on the change in molar volume on fusion for the alkali halides has led to an estimate that about every 6th position is vacant in the liquid (Førland, 1957). See also Bloom's (1967) comments on free volume.

geometry is evidently considerably altered in NaCl and LiCl (Gruen, 1959; Smith, 1965; Brynestad, Boston, and Smith, 1967). In LiCl, for example, an octahedral form appears to exist in equilibrium with the tetrahedral form (Brynestad, 1967a). A pronounced distortion also occurs in KCl solutions to which a third electrolyte such as  $\text{ZnCl}_2$  is added (Angell and Gruen, 1966). One may assume that a high concentration of  $\text{NiCl}_2$  itself would have an effect similar to addition of  $\text{ZnCl}_2$  upon the coordination geometry of  $\text{NiCl}_4^{2-}$ . For simplicity, we consider only the tetrahedral case, applicable strictly only to  $\text{NiCl}_2$  in KCl among the solvents we report on here. Further, we anticipate that, at high  $\text{NiCl}_2$  concentration, even in KCl the assumption of tetrahedral coordination about nickel may be subject to later modification; however, here we will assume the tetrahedral complex to be the only nickel species present at all compositions having  $N_{\text{NiCl}_2} < 1/3$ , that is, the composition corresponding to  $\text{K}_2\text{NiCl}_4$ .

Let us consider the mixing to occur in two steps. The first is the formation of the complex liquid salt according to




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<sup>9</sup>This assumption can obviously be invalidated by dissociation of the complex salt. Dissociation will not be treated here but see Flood and Urnes (1955), Niel and Clark (1965) and Braunstein (1968).

The second step consists of mixing the complex liquid salt with an excess of KCl to give the desired solution. Let the entropy change for the complex salt formation be  $\Delta S'$ . The partial molar entropy of  $K_2NiCl_4$  for mixing  $K_2NiCl_4$  with KCl will then be given by

$$\begin{aligned}\bar{S}_{K_2NiCl_4} &= \left[ \partial \Delta S_{\text{mix}} / \partial n_{K_2NiCl_4} \right]_{T, p, n^\circ_{KCl}} \\ &= nF \left( \frac{\partial E}{\partial T} \right)_P - \Delta S^\circ - \Delta S' = \bar{S} - \Delta S'\end{aligned}\quad (46)$$

where  $n^\circ_{KCl}$  is the number of moles of KCl in excess of that consumed in forming the complex salt. For pure liquid  $K_2NiCl_4$  (that is, at  $N_{NiCl_2} = 1/3$ )  $\bar{S}_{K_2NiCl_4}$  is zero, and  $\Delta S'$  is just the value of  $\bar{S}$  at  $N_{NiCl_2} = 1/3$ . According to Figure 18,  $\Delta S'$  is about 2 cal/mole deg. This is not far from the value for ideal mixing of  $NiCl_2$  and KCl; this may be largely fortuitous, as  $\Delta S'$  certainly must be composed of significant contributions from vibrational frequency changes as the complex ion is formed from  $NiCl_2$ .

For the second step, that is, mixing of  $K_2NiCl_4$  with more KCl, we may again obtain certain results based upon ideal mixing or upon pseudo-lattice models of the kind already discussed.

For model-independent ideal mixing,  $\bar{S}_{K_2NiCl_4}$  is given by

$$\bar{S}_{K_2NiCl_4} = -R \ln N_1, \quad (47)$$



where  $N_1$ , the mole fraction of  $K_2NiCl_4$ , is given by

$$N_1 = n_{Ni} / (n_s - n_{Ni}) = N / (1 - 2N). \quad (48)$$

Note that  $N_1$  can exceed unity; if so, however, assuming complete complexing, the solution is then a mixture of  $K_2NiCl_4$  and  $NiCl_2$ . The experimental quantity  $\bar{S}$  is then, according to the assumption of ideal mixing of  $K_2NiCl_4$  with  $KCl$ , given by

$$(e) \quad \bar{S} = \Delta S' - R \ln N_1. \quad (49)$$

In Figure 21 the observed values of  $\bar{S}$  for  $NiCl_2$  in  $KCl$  are presented as a function of  $\ln N_1$ , together with the ideal-mixing curve, (e), drawn so as to pass through  $\Delta S' = 2.00$  e. u. at  $N_1 = 1.00$ .

Next we consider some pseudo-lattice models for the mixing of  $K_2NiCl_4$  with  $KCl$ , as follows:

(f) The  $NiCl_4^{2-}$  ion occupies the position of one  $K^+$  ion and four surrounding  $Cl^-$  ions on the  $KCl$  pseudo-lattice. The excess charge of nickel is not compensated by vacancies. This model is the Temkin model for the assumed species. The partial molar entropy of mixing,  $K_2NiCl_4$ , is

$$\bar{S}_{K_2NiCl_4} = -R \ln N_1 (N_1 + 1)^2 + R \ln (2N_1 + 1)^3 - R \ln \frac{27}{4}. \quad (50)$$

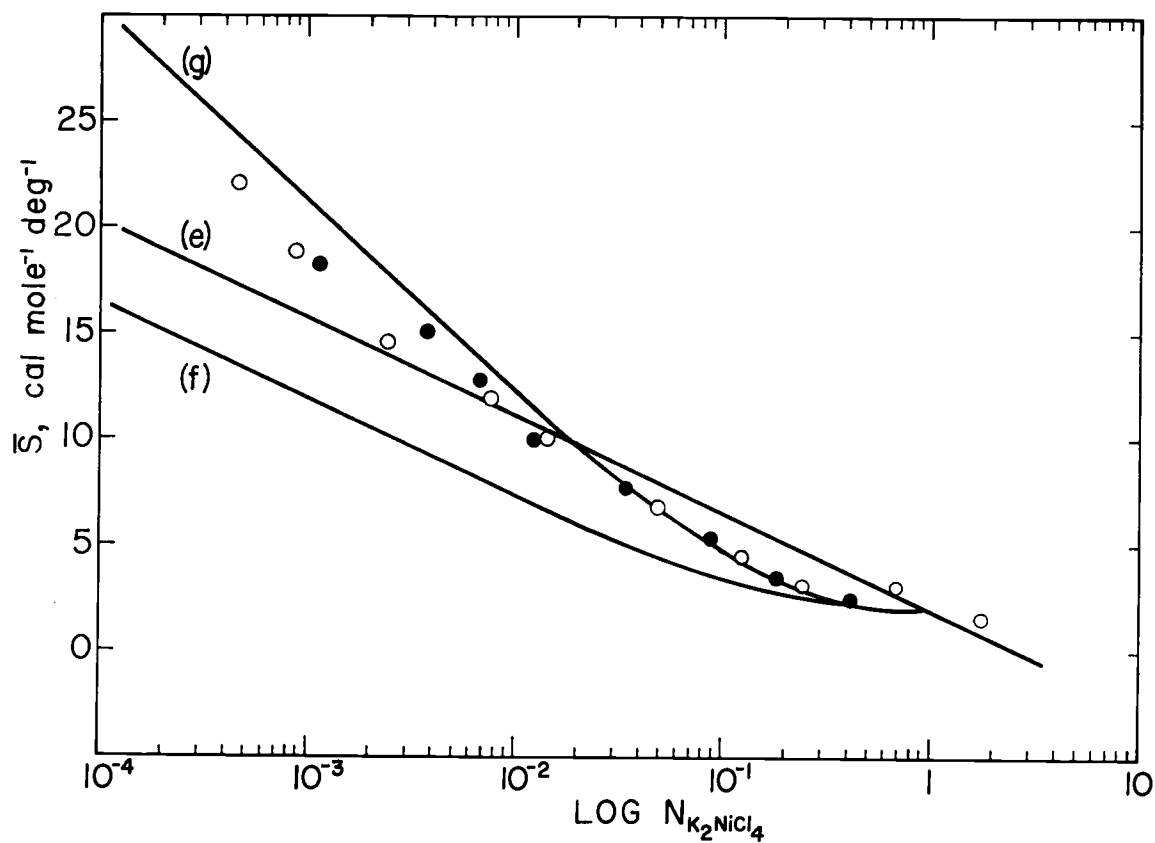


Figure 21. Partial molar entropy of mixing for  $\text{NiCl}_2$  in  $\text{KCl}$  as a function of  $\log N_{\text{K}_2\text{NiCl}_4}$ , compared with predictions based on ideal mixing of  $\text{K}_2\text{NiCl}_4$  with  $\text{KCl}$  (curve e) and models (f) and (g) as indicated (see text). See Figure 12 for symbols.

This model, which reduces to  $\bar{S}_{K_2NiCl_4} = -R \ln N - R \ln 27/4$  as  $N_1 \rightarrow 0$ , has some questionable features in addition to the artificiality of assigning lattice positions to ions in the liquid state. The coordination number of  $K^+$  in fused KCl is about four (Levy, 1964) and it may be inferred from the isotropic properties of the liquid that the coordination is tetrahedral, but the Cl-Cl distance in the solvent is probably larger than that in the complex (Gruen, 1959; Levy and Danford, 1964) so that the fit of the complex upon the pseudo-lattice is not very close.

(g) The  $NiCl_4^{2-}$  is accommodated as in (f), but one vacancy is created on the positive-ion sublattice for each  $NiCl_4^{2-}$  ion by incorporation of the necessary vacancies in the initial  $K_2NiCl_4$  lattice. In this case  $\bar{S}_{K_2NiCl_4}$  is given by

$$\bar{S}_{K_2NiCl_4} = -2R \ln \frac{8N_1(N_1+1)}{(3N_1+1)^2}.$$

(h) If vacancy free  $K_2NiCl_4$  is accommodated as in (f), but the solvent contains anion and cation vacancies,  $xn_s$ , initially; then one obtains at  $N_1 \ll x$

$$\bar{S}_{K_2NiCl_4} = -R \ln N + f(x)$$

where  $f(x) = \text{constant}$  which takes on values less than the experimental

uncertainty for reasonable values of  $x$ . A similar result in which  $\bar{S}_{\text{K}_2\text{NiCl}_4} \rightarrow -R \ln N + \text{constant}$  as  $N_1 \rightarrow 0$  is anticipated for the case in which anion and cation vacancies are initially present at high concentration in both components.

On Figure 21 are also shown curves for  $\bar{S}$  corresponding to the predictions based on models (f) and (g) with  $\Delta S' = 2.00$  e. u. The observed values for KCl are most nearly in accord with model (g); it is noteworthy, however, that most of the experimental points fall within experimental error of model (h) which is felt to be the physically most reasonable model.

Although the number of plausible models which may be tested is large (including, for example, those in which complex ions are distributed on the anion sublattice either with or without vacancy-compensation and those in which solute cation nearest neighbor positions are excluded from solute cation occupancy on the basis of repulsive energy considerations) the examples above suffice to allow us to state some conclusions.

First, the entropy-of-mixing data, the uncertainty of which we estimate to be about  $\pm 2$  e. u., is insufficiently accurate, and the calculated entropies insufficiently sensitive to variations in the model, to permit one to select unambiguously the most representative model for each of these solutions.

Second, the Temkin (a) or ideal model for mixing  $\text{NiCl}_2$  with the

alkali halides (as well as the associated vacancy model (c)) is satisfactory for LiCl, and NaCl-KCl but less so for KCl and NaCl, while the vacancy model (b) is unsatisfactory for any of the solutions. Vacancy model (d) would be equally as satisfactory as (a) or (c) for LiCl and NaCl-KCl and is more soundly based on physical reality.

Third, the entropy of mixing in KCl is reasonably consistent with the predictions based upon models in which tetrahedral  $\text{NiCl}_4^{2-}$  complex ions and positive-ion vacancies are distributed on the cation pseudo-lattice.

In the case of the solute  $\text{CoCl}_2$  spectroscopic evidence similar to that quoted for  $\text{NiCl}_2$  in KCl (Gruen and McBeth, 1963) indicates that  $\text{CoCl}_2$  is present as tetrahedrally coordinated  $\text{CoCl}_4^-$ , at least at low concentrations, in all the four solvents studied. It would, therefore, be appropriate to compare the quantity  $\bar{S}$  for  $\text{CoCl}_2$  with the predictions of models (e) through (h). This comparison is made in Figure 22. The data are consistent with the physically most plausible model, (h), which involves complexing and mixing of the vacancy rich pure components.

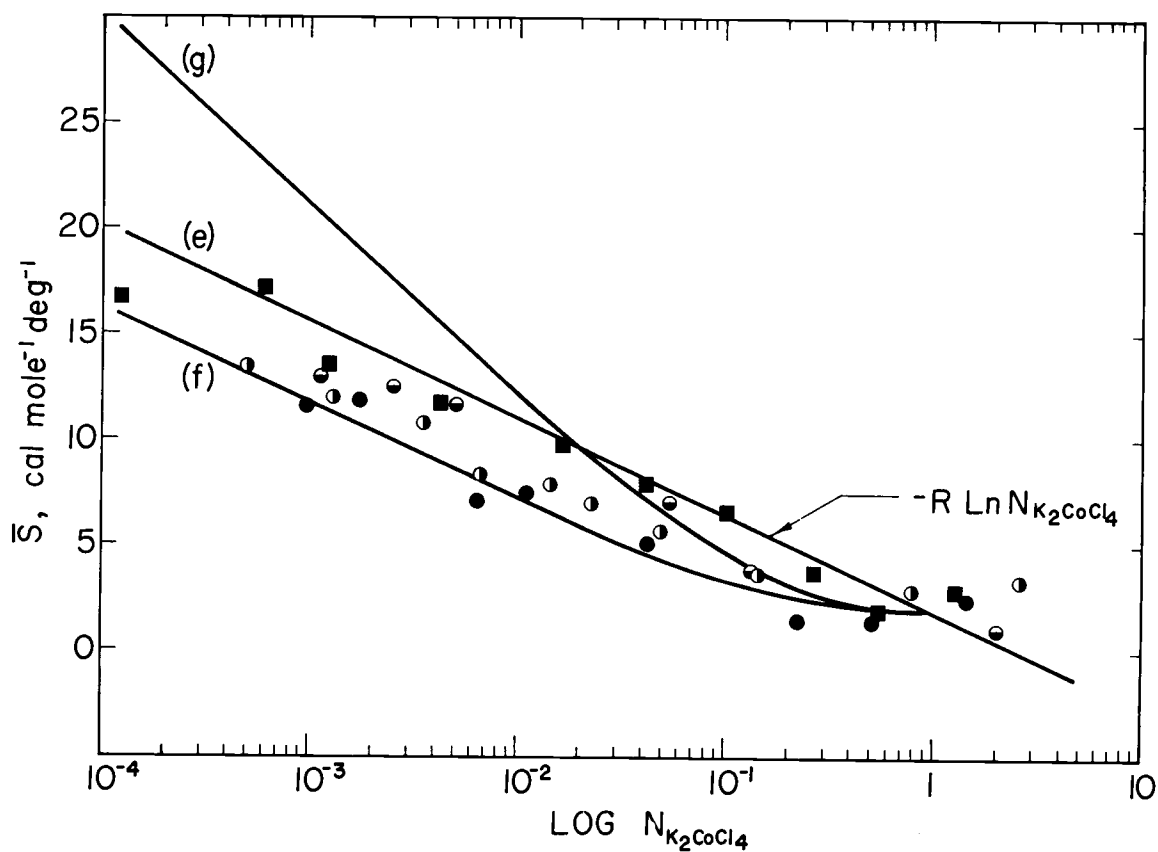


Figure 22. Partial molar entropy of mixing for  $\text{CoCl}_2$  in  $\text{KCl}$ ,  $\text{NaCl}$ , 1:1  $\text{NaCl-KCl}$ , and  $\text{LiCl}$  as a function of  $\log N_{\text{K}_2\text{CoCl}_4}$ , compared with predictions based on ideal mixing (curve e) and models (f) and (g) as indicated (see text). See Figure 13 for symbols.

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## APPENDICES



## APPENDIX I

## Summary of Data for the AgCl Formation Cells

$\text{Ag}/\text{AgCl}/\text{Cl}_2, \text{C}_{a, b}$ ; cell emf's have been corrected for thermal emf's.

List of electrode designations:

1.  $\text{C}_{a, b}$ , the cell contained two chlorine electrodes, one type a and one type b (Figure 3).
2.  $\text{Ag}_A, \text{Ag}_B, \text{Ag}_C, \text{Ag}_D$ , silver electrodes of types A, B, C, and D, Figure 4, respectively.
3.  ${}^{-}\text{Ag}_A - \text{C}_a^{+}$ , designates emf measured between chlorine electrode, design a, and silver electrode, design A.  
Measured polarity is indicated by superscripts.

Cell A

$T^{\circ}\text{C}$	$-\text{Ag}_A-\text{C}_a^+$	$-\text{Ag}_A-\text{C}_b^+$		
474	0.901	0.901		
532	.884	.881		
595	.854	.852		
685	.838	.838		
781	.811	.809		
882	.743	.741		
530	.886	.886		
607	.864	.864		
715	.834	.828		
	<u><math>\text{Ag}_A</math></u>	<u><math>\text{Ag}_B</math></u>	<u><math>\text{Ag}_A</math></u>	<u><math>\text{Ag}_B</math></u>
842		.801		.801
498	.892	.892		
571	.874	.874	.873	.872
690	.843	<u><math>\text{Ag}_C</math></u>		<u><math>\text{Ag}_C</math></u>
552	.881	.891		
741	.827	.833	.827	.834
632		.858		
686		.846		
742		.829		
796		.815		
842		.801		
892		.785		
505		.894		
571		.877		
636		.859		
703	<u><math>\text{Ag}_B</math></u>	.842		
764		.825		
839	.806	.806		
874	.798	.798		

Cell B

$T^{\circ}\text{C}$	$-\text{Ag}_C-\text{C}_a^+$	$-\text{Ag}_D-\text{C}_a^+$
572	.876	
674	.848	.848
772	.822	.824
869	.796	.795
634	.858	
492	.895	
562	.877	
642	.855	
744	.830	
839	.806	.807
503	.894	.895
607	.866	.867
495		.894
790	.818	.818
493	.897	.897
697	.842	.842
494	.899	.897
600	.867	.868
781	.817	.817
847	.800	.800
495	.896	
547	.881	

APPENDIX II

Summary of Data for Cells I through X

Cell I. Ni/NiCl<sub>2</sub>, KCl/Cl<sub>2</sub>, C<sub>a, b</sub>

T °C	E(volts)	N(ave.)	N'(ave.)	N <sub>1</sub> (ave.)
828	1.411	2.2 x10 <sup>-4</sup>	4.4 x10 <sup>-4</sup>	2.2 x10 <sup>-4</sup>
865	1.418	"	"	"
901	1.417	"	"	"
840	1.393	3. x10 <sup>-4</sup>	6. x10 <sup>-4</sup>	3. x10 <sup>-4</sup>
864	1.385	"	"	"
914	1.369	"	"	"
815	1.368	4.6 x10 <sup>-4</sup>	9.2 x10 <sup>-4</sup>	4.6 x10 <sup>-4</sup>
872	1.361	"	"	"
841	1.361	"	"	"
904	1.363	"	"	"
805	1.307	1.15x10 <sup>-3</sup>	2.30x10 <sup>-3</sup>	1.15x10 <sup>-3</sup>
829	1.304	"	"	"
862	1.307	"	"	"
900	1.303	"	"	"
805	1.244	3.77x10 <sup>-3</sup>	7.5 x10 <sup>-3</sup>	3.8 x10 <sup>-3</sup>
829	1.241	"	"	"
864	1.236	"	"	"
903	1.234	"	"	"
808	1.213	6.9 x10 <sup>-3</sup>	1.37x10 <sup>-2</sup>	7.0 x10 <sup>-3</sup>
859	1.206	"	"	"
905	1.198	"	"	"
806	1.182	1.23x10 <sup>-2</sup>	2.43x10 <sup>-2</sup>	1.26x10 <sup>-2</sup>
835	1.177	"	"	"
863	1.170	"	"	"
904	1.162	"	"	"
819	1.127	3.25x10 <sup>-2</sup>	6.3 x10 <sup>-2</sup>	3.44x10 <sup>-2</sup>
844	1.121	"	"	"
873	1.115	"	"	"
906	1.105	"	"	"
822	1.072	7.6 x10 <sup>-2</sup>	1.41x10 <sup>-1</sup>	8.9 x10 <sup>-2</sup>
769	1.089	"	"	"
870	1.060	"	"	"
905	1.046	"	"	"
775	1.044	1.35x10 <sup>-1</sup>	2.38x10 <sup>-1</sup>	1.85x10 <sup>-1</sup>
822	1.027	"	"	"
861	1.014	"	"	"
900	1.000	"	"	"
776	0.980	2.29x10 <sup>-1</sup>	3.73x10 <sup>-1</sup>	4.2 x10 <sup>-1</sup>
823	0.962	"	"	"
865	0.946	"	"	"
903	0.932	"	"	"

Cell II. Ni/NiCl<sub>2</sub>, NaCl/Cl<sub>2</sub>, C<sub>a, b</sub>

T <sup>o</sup> C	E(volts)	N(ave.)	N'(ave.)	N <sub>1</sub> (ave.)
857	1.288	1.62x10 <sup>-4</sup>	3.24x10 <sup>-4</sup>	1.62x10 <sup>-4</sup>
819	1.284	"	"	"
873	1.232	4. x10 <sup>-4</sup>	8. x10 <sup>-4</sup>	4. x10 <sup>-4</sup>
903	1.228	"	"	"
814	1.227	"	"	"
866	1.181	8. x10 <sup>-4</sup>	1.6 x10 <sup>-3</sup>	8. x10 <sup>-4</sup>
904	1.180	"	"	"
818	1.183	"	"	"
859	1.124	3.09x10 <sup>-3</sup>	6.2 x10 <sup>-3</sup>	3.09x10 <sup>-3</sup>
895	1.121	"	"	"
815	1.130	"	"	"
860	1.065	9.8 x10 <sup>-3</sup>	1.94x10 <sup>-2</sup>	1.00x10 <sup>-2</sup>
904	1.058	"	"	"
809	1.074	"	"	"
859	1.007	2.81x10 <sup>-2</sup>	5.5 x10 <sup>-2</sup>	2.98x10 <sup>-2</sup>
907	0.996	"	"	"
804	1.019	"	"	"
859	0.940	8.3 x10 <sup>-2</sup>	1.53x10 <sup>-1</sup>	1.00x10 <sup>-1</sup>
908	0.926	"	"	"
816	0.953	"	"	"
864	0.903	1.31x10 <sup>-1</sup>	2.32x10 <sup>-1</sup>	1.78x10 <sup>-1</sup>
910	0.890	"	"	"
813	0.920	"	"	"
860	0.869	1.88x10 <sup>-1</sup>	3.16x10 <sup>-1</sup>	3.01x10 <sup>-1</sup>
902	0.854	"	"	"
806	0.888	"	"	"
861	0.813	2.95x10 <sup>-1</sup>	4.6 x10 <sup>-1</sup>	7.2 x10 <sup>-1</sup>
910	0.796	"	"	"
810	0.833	"	"	"
861	0.752	4.1 x10 <sup>-1</sup>	5.8 x10 <sup>-1</sup>	2.28
915	0.737	"	"	"
824	0.770	"	"	"

Cell III. Ni/NiCl<sub>2</sub>, 1:1 NaCl, KCl/Cl<sub>2</sub>, C<sub>a, b</sub>

T °C	E(volts)	N(ave. )	N'(ave. )	N <sub>1</sub> (ave. )
702	1.373	7. x10 <sup>-5</sup>	1.4 x10 <sup>-4</sup>	7. x10 <sup>-5</sup>
745	1.368	"	"	"
795	1.367	"	"	"
699	1.338	1.56x10 <sup>-4</sup>	3.12x10 <sup>-4</sup>	1.56x10 <sup>-4</sup>
740	1.338	"	"	"
788	1.340	"	"	"
700	1.279	7.2 x10 <sup>-4</sup>	1.44x10 <sup>-3</sup>	7.2 x10 <sup>-4</sup>
783	1.273	"	"	"
694	1.271	"	"	"
736	1.269	"	"	"
692	1.247	1.52x10 <sup>-3</sup>	3.04x10 <sup>-3</sup>	1.52x10 <sup>-3</sup>
784	1.232	"	"	"
734	1.240	"	"	"
737	1.177	6.4 x10 <sup>-3</sup>	1.27x10 <sup>-3</sup>	6.5 x10 <sup>-3</sup>
775	1.168	"	"	"
671	1.188	"	"	"
744	1.126	1.70x10 <sup>-2</sup>	3.34x10 <sup>-2</sup>	1.76x10 <sup>-2</sup>
798	1.114	"	"	"
699	1.138	"	"	"
694	1.073	6.1 x10 <sup>-2</sup>	1.15x10 <sup>-1</sup>	7.0 x10 <sup>-2</sup>
757	1.054	"	"	"
802	1.040	"	"	"
739	1.001	1.32x10 <sup>-1</sup>	2.33x10 <sup>-1</sup>	1.79x10 <sup>-1</sup>
802	0.981	"	"	"
745	0.934	2.25x10 <sup>-1</sup>	3.67x10 <sup>-1</sup>	4.09x10 <sup>-1</sup>
673	0.962	"	"	"
655	0.883	3.6 x10 <sup>-1</sup>	5.3 x10 <sup>-1</sup>	1.29
698	0.866	"	"	"
786	0.783	4.6 x10 <sup>-1</sup>	6.3 x10 <sup>-1</sup>	5.18
741	0.805	"	"	"
674	0.846	"	"	"

Cell IV. Ni/NiCl<sub>2</sub>, LiCl/Cl<sub>2</sub>, C<sub>a, b</sub>

T °C	E (volts)	N (ave.)	N' (ave.)	N <sub>1</sub> (ave.)
674	1.185	1.12x10 <sup>-4</sup>	2.24x10 <sup>-4</sup>	1.12x10 <sup>-4</sup>
721	1.184	"	"	"
775	1.182	"	"	"
679	1.113	5.8 x10 <sup>-4</sup>	1.16x10 <sup>-4</sup>	5.8 x10 <sup>-4</sup>
723	1.107	"	"	"
768	1.107	"	"	"
817	1.107	"	"	"
732	1.080	1.27x10 <sup>-3</sup>	2.54x10 <sup>-3</sup>	1.27x10 <sup>-3</sup>
804	1.069	"	"	"
706	1.076	"	"	"
660	1.083	"	"	"
732	1.034	3.2 x10 <sup>-3</sup>	6.4 x10 <sup>-3</sup>	3.2 x10 <sup>-3</sup>
768	1.028	"	"	"
806	1.024	"	"	"
663	1.044	"	"	"
717	0.996	7.7 x10 <sup>-3</sup>	1.53x10 <sup>-2</sup>	7.8 x10 <sup>-3</sup>
763	0.986	"	"	"
803	0.979	"	"	"
666	1.007	"	"	"
727	0.967	1.38x10 <sup>-2</sup>	2.72x10 <sup>-2</sup>	1.42x10 <sup>-2</sup>
805	0.949	"	"	"
667	0.984	"	"	"
716	0.918	4.6 x10 <sup>-2</sup>	8.8 x10 <sup>-2</sup>	5.1 x10 <sup>-2</sup>
762	0.904	"	"	"
805	0.892	"	"	"
670	0.931	"	"	"
749	0.856	1.18x10 <sup>-1</sup>	2.11x10 <sup>-1</sup>	1.54x10 <sup>-2</sup>
807	0.839	"	"	"
664	0.885	"	"	"
768	0.819	1.8 x10 <sup>-1</sup>	3.05x10 <sup>-1</sup>	2.8 x10 <sup>-1</sup>
809	0.804	"	"	"
673	0.852	"	"	"
713	0.839	"	"	"
820	0.757	2.9 x10 <sup>-1</sup>	4.5 x10 <sup>-1</sup>	6.9 x10 <sup>-1</sup>
767	0.780	"	"	"



Cell V. Ni/NiCl<sub>2</sub>, LiCl/Cl<sub>2</sub>, C<sub>a, b</sub>

T °C	E (volts)	N(ave.)	N'(ave.)	N <sub>1</sub> (ave.)
847	1.167	9.7 x10 <sup>-5</sup>	1.94x10 <sup>-4</sup>	9.7 x10 <sup>-5</sup>
827	1.206	"	"	"
761	1.195	"	"	"
648	1.190	"	"	"
686	1.104	7.6 x10 <sup>-4</sup>	1.52x10 <sup>-4</sup>	7.6 x10 <sup>-4</sup>
636	1.110	"	"	"
778	1.096	"	"	"
644	1.027	6.1 x10 <sup>-3</sup>	1.21x10 <sup>-2</sup>	6.2 x10 <sup>-3</sup>
719	1.008	"	"	"
805	.988	"	"	"
786	.836	1.32x10 <sup>-1</sup>	2.33x10 <sup>-2</sup>	1.79x10 <sup>-1</sup>
729	.856	"	"	"
649	.886	"	"	"

Cell VI. Ni/NiCl<sub>2</sub>, KCl/Cl<sub>2</sub>, C<sub>a, b</sub>

T <sup>o</sup> C	E (volts)	N (ave.)	N' (ave.)	N <sub>1</sub> <sup>-</sup> (ave.)
832	1.345	4.6 x10 <sup>-4</sup>	9.2 x10 <sup>-4</sup>	4.6 x10 <sup>-4</sup>
881	1.346	"	"	"
785	1.342	"	"	"
835	1.310	8.8 x10 <sup>-4</sup>	1.76x10 <sup>-3</sup>	8.8 x10 <sup>-4</sup>
878	1.308	"	"	"
792	1.310	"	"	"
802	1.259	2.42x10 <sup>-3</sup>	4.8 x10 <sup>-3</sup>	2.43x10 <sup>-3</sup>
885	1.250	"	"	"
820	1.257	"	"	"
834	1.198	7.5 x10 <sup>-3</sup>	1.48x10 <sup>-2</sup>	7.6 x10 <sup>-3</sup>
893	1.188	"	"	"
785	1.206	"	"	"
828	1.169	1.40x10 <sup>-2</sup>	2.76x10 <sup>-2</sup>	1.44x10 <sup>-2</sup>
893	1.155	"	"	"
794	1.176	"	"	"
800	1.108	4.5 x10 <sup>-2</sup>	8.7 x10 <sup>-2</sup>	5.0 x10 <sup>-2</sup>
888	1.084	"	"	"
830	1.099	"	"	"
833	1.047	1.00x10 <sup>-1</sup>	1.82x10 <sup>-1</sup>	1.25x10 <sup>-1</sup>
784	1.064	"	"	"
888	1.030	"	"	"
885	0.978	1.65x10 <sup>-1</sup>	2.83x10 <sup>-1</sup>	2.46x10 <sup>-1</sup>
828	1.000	"	"	"
792	1.011	"	"	"
816	0.923	2.90x10 <sup>-1</sup>	4.5 x10 <sup>-1</sup>	6.9 x10 <sup>-1</sup>
885	0.884	"	"	"
770	0.923	"	"	"
831	0.828	3.9 x10 <sup>-1</sup>	5.6 x10 <sup>-1</sup>	1.77
881	0.813	"	"	"
781	0.852	"	"	"

Cell VII.  $\text{Co/CoCl}_2, \text{KCl/Cl}_2, C_{a,b}$ 

$T^\circ\text{C}$	E(volts)	N(ave.)	$N^f$ (ave.)	$N_1$ (ave.)
853	1.500	$9.7 \times 10^{-4}$	$1.94 \times 10^{-3}$	$9.7 \times 10^{-4}$
898	1.494	"	"	"
805	1.507	"	"	"
814	1.483	$1.75 \times 10^{-3}$	$3.49 \times 10^{-3}$	$1.76 \times 10^{-3}$
846	1.478	"	"	"
902	1.469	"	"	"
815	1.423	$6.3 \times 10^{-3}$	$1.25 \times 10^{-2}$	$6.4 \times 10^{-3}$
840	1.415	"	"	"
899	1.401	"	"	"
860	1.384	$1.09 \times 10^{-2}$	$2.16 \times 10^{-2}$	$1.11 \times 10^{-2}$
903	1.372	"	"	"
811	1.393	"	"	"
861	1.310	$3.94 \times 10^{-2}$	$7.6 \times 10^{-2}$	$4.28 \times 10^{-2}$
908	1.279	"	"	"
805	1.327	"	"	"
834	1.266	$9.3 \times 10^{-2}$	$1.70 \times 10^{-1}$	$1.14 \times 10^{-1}$
902	1.240	"	"	"
799	1.274	"	"	"
839	1.215	$1.55 \times 10^{-1}$	$2.68 \times 10^{-1}$	$2.25 \times 10^{-1}$
900	1.192	"	"	"
794	1.231	"	"	"
805	1.158	$2.52 \times 10^{-1}$	$4.0 \times 10^{-1}$	$5.08 \times 10^{-1}$
900	1.121	"	"	"
843	1.144	"	"	"
842	1.049	$3.7 \times 10^{-1}$	$5.40 \times 10^{-1}$	1.42
898	1.030	"	"	"
792	1.068	"	"	"
746	1.082	"	"	"
701	1.099	"	"	"
850	0.972	$4.8 \times 10^{-1}$	$6.5 \times 10^{-1}$	12.
784	0.994	"	"	"
699	1.022	"	"	"
601	1.055	"	"	"

Cell VIII. Co/CoCl<sub>2</sub>, NaCl/Cl<sub>2</sub>, C<sub>a, c</sub>

T <sup>o</sup> C	E(volts)	N(ave.)	N'(ave.)	N' <sub>1</sub> (ave.)
823	1.468	1.34x10 <sup>-4</sup>	2.68x10 <sup>-4</sup>	1.34x10 <sup>-4</sup>
862	1.466	"	"	"
889	1.462	"	"	"
845	1.463	"	"	"
850	1.400	6.1 x10 <sup>-4</sup>	1.22x10 <sup>-4</sup>	6.1 x10 <sup>-4</sup>
898	1.398	"	"	"
816	1.401	"	"	"
862	1.364	1.26x10 <sup>-3</sup>	2.52x10 <sup>-3</sup>	1.26x10 <sup>-3</sup>
896	1.361	"	"	"
810	1.370	"	"	"
828	1.309	4.3 x10 <sup>-3</sup>	8.6 x10 <sup>-3</sup>	4.3 x10 <sup>-3</sup>
895	1.299	"	"	"
843	1.306	"	"	"
843	1.242	1.54x10 <sup>-2</sup>	3.03x10 <sup>-2</sup>	1.59x10 <sup>-3</sup>
898	1.231	"	"	"
804	1.249	"	"	"
843	1.193	3.89x10 <sup>-2</sup>	7.5 x10 <sup>-2</sup>	4.2 x10 <sup>-3</sup>
809	1.201	"	"	"
903	1.179	"	"	"
847	1.142	8.4 x10 <sup>-2</sup>	1.55x10 <sup>-1</sup>	1.01x10 <sup>-1</sup>
906	1.129	"	"	"
796	1.156	"	"	"
863	1.079	1.76x10 <sup>-1</sup>	2.99x10 <sup>-1</sup>	2.72x10 <sup>-1</sup>
898	1.068	"	"	"
791	1.103	"	"	"
848	1.032	2.62x10 <sup>-1</sup>	4.15x10 <sup>-1</sup>	5.5 x10 <sup>-1</sup>
895	1.019	"	"	"
780	1.060	"	"	"
817	1.047	"	"	"
815	0.994	3.6 x10 <sup>-1</sup>	5.29x10 <sup>-1</sup>	1.29
892	0.971	"	"	"
756	1.017	"	"	"
796	1.003	"	"	"
883	0.888	5.3 x10 <sup>-1</sup>	6.9 x10 <sup>-1</sup>	-9.
826	0.924	"	"	"
763	0.951	"	"	"
705	0.970	"	"	"

Cell IX. Co/CoCl<sub>2</sub>, 1:1 NaCl-KCl/Cl<sub>2</sub>, C<sub>a, c</sub>

T °C	E (volts)	N(ave.)	N <sup>r</sup> (ave.)	N <sub>1</sub> (ave.)
714	1.483	5.0 x10 <sup>-4</sup>	1.00x10 <sup>-4</sup>	5 x10 <sup>-4</sup>
808	1.474	"	"	"
888	1.462	"	"	"
676	1.485	"	"	"
741	1.440	1.31x10 <sup>-3</sup>	2.62x10 <sup>-3</sup>	1.31x10 <sup>-3</sup>
816	1.427	"	"	"
881	1.417	"	"	"
682	1.446	"	"	"
827	1.383	3.56x10 <sup>-3</sup>	7.1 x10 <sup>-3</sup>	3.59x10 <sup>-3</sup>
882	1.373	"	"	"
733	1.398	"	"	"
747	1.368	6.8 x10 <sup>-3</sup>	1.35x10 <sup>-3</sup>	6.9 x10 <sup>-3</sup>
671	1.384	"	"	"
843	1.349	"	"	"
892	1.339	"	"	"
669	1.351	1.41x10 <sup>-2</sup>	2.78x10 <sup>-2</sup>	1.45x10 <sup>-2</sup>
745	1.333	"	"	"
834	1.314	"	"	"
827	1.291	2.23x10 <sup>-2</sup>	4.4 x10 <sup>-2</sup>	2.33x10 <sup>-2</sup>
897	1.273	"	"	"
732	1.314	"	"	"
744	1.275	4.5 x10 <sup>-2</sup>	8.6 x10 <sup>-2</sup>	4.9 x10 <sup>-2</sup>
818	1.255	"	"	"
904	1.231	"	"	"
665	1.297	"	"	"
739	1.217	1.13x10 <sup>-1</sup>	2.03x10 <sup>-2</sup>	1.46x10 <sup>-1</sup>
824	1.189	"	"	"
676	1.237	"	"	"
861	1.044	3.07x10 <sup>-1</sup>	4.7 x10 <sup>-1</sup>	8.0 x10 <sup>-1</sup>
770	1.076	"	"	"
673	1.113	"	"	"
713	1.022	4.2 x10 <sup>-1</sup>	5.9 x10 <sup>-1</sup>	2.63
807	0.992	"	"	"
892	0.963	"	"	"
793	0.932	5.4 x10 <sup>-1</sup>	7.0 x10 <sup>-1</sup>	-6.7
704	0.964	"	"	"
652	0.983	"	"	"

Cell X. Co/CoCl<sub>2</sub>, LiCl/Cl<sub>2</sub>, C<sub>a, c</sub>

T °C	E (volts)	N (ave.)	N' (ave.)	N <sub>1</sub> (ave.)
654	1.273	1.13x10 <sup>-3</sup>	2.26x10 <sup>-3</sup>	1.13x10 <sup>-3</sup>
728	1.262	"	"	"
810	1.253	"	"	"
791	1.221	2.57x10 <sup>-3</sup>	5.1 x10 <sup>-3</sup>	2.58x10 <sup>-3</sup>
714	1.230	"	"	"
652	1.240	"	"	"
765	1.195	5.1 x10 <sup>-3</sup>	1.01x10 <sup>-2</sup>	5.1 x10 <sup>-3</sup>
647	1.213	"	"	"
696	1.204	"	"	"
697	1.107	4.9 x10 <sup>-2</sup>	9.3 x10 <sup>-2</sup>	5.4 x10 <sup>-2</sup>
759	1.091	"	"	"
644	1.120	"	"	"
816	1.031	1.07x10 <sup>-1</sup>	1.93x10 <sup>-1</sup>	1.36x10 <sup>-1</sup>
746	1.052	"	"	"
647	1.081	"	"	"
803	0.974	2.5 x10 <sup>-1</sup>	4.0 x10 <sup>-1</sup>	5.0 x10 <sup>-1</sup>
648	1.030	"	"	"
708	1.011	"	"	"
709	0.960	4.0 x10 <sup>-1</sup>	5.7 x10 <sup>-1</sup>	2.0
807	0.933	"	"	"
653	0.990	"	"	"
709	0.969	"	"	"
799	0.885	7.5 x10 <sup>-1</sup>	8.6 x10 <sup>-1</sup>	-1.5
723	0.917	"	"	"
669	0.938	"	"	"
727	0.903	8.3 x10 <sup>-1</sup>	9.1 x10 <sup>-1</sup>	-1.26
796	0.866	"	"	"
730	0.899	"	"	"
780	0.867	"	"	"
826	0.862	"	"	"

## APPENDIX III

Summary of  $dE/dT$  Data

Cell	N	$\frac{dE}{dT} \times 10^4$	$nF \frac{dE}{dT} = \Delta \tilde{s}$
I	$1.15 \times 10^{-3}$	-0.3	- 1
"	$3.77 \times 10^{-3}$	-1.0	- 4.6
"	$6.9 \times 10^{-3}$	-1.5	- 6.9
"	$1.23 \times 10^{-2}$	-2.1	- 9.7
"	$2.35 \times 10^{-2}$	-2.5	-12
"	$7.6 \times 10^{-2}$	-3.1	-14
"	$1.35 \times 10^{-1}$	-3.5	-16
"	$2.29 \times 10^{-1}$	-3.7	-17
II	$1.62 \times 10^{-4}$	0.7	- 3
"	$4 \times 10^{-4}$	0.4	- 2
"	$8 \times 10^{-4}$	-0.4	- 2
"	$3.09 \times 10^{-3}$	-1.2	- 5.5
"	$9.8 \times 10^{-3}$	-1.8	- 8.3
"	$2.8 \times 10^{-2}$	-2.2	-10
"	$8.3 \times 10^{-2}$	-3.0	-14
"	$1.31 \times 10^{-1}$	-3.4	-16
"	$1.88 \times 10^{-1}$	-3.6	-17
"	$2.95 \times 10^{-1}$	-3.7	-17
"	$4.1 \times 10^{-1}$	-3.7	-17
III	$7 \times 10^{-5}$	-0.6	- 2.8
"	$1.56 \times 10^{-4}$	0.2	.9
"	$1.52 \times 10^{-3}$	-1.6	- 7.4
"	$6.4 \times 10^{-3}$	-1.9	- 8.8
"	$1.70 \times 10^{-2}$	-2.4	-11
"	$6.1 \times 10^{-2}$	-3.1	-14
"	$1.32 \times 10^{-1}$	-3.2	-15
"	$2.25 \times 10^{-1}$	-3.9	-18
"	$3.6 \times 10^{-1}$	-3.9	-18
"	$4.6 \times 10^{-1}$	-4.8	-22
IV	$1.12 \times 10^{-4}$	- .3	- 1
"	$5.84 \times 10^{-4}$	- .5	- 2.3
"	$1.27 \times 10^{-3}$	-1.0	- 4.6
"	$3.22 \times 10^{-3}$	-1.4	- 6.5
"	$7.73 \times 10^{-3}$	-2.1	- 9.7
"	$1.38 \times 10^{-2}$	-2.6	-12
"	$4.67 \times 10^{-2}$	-2.9	-13
"	$1.18 \times 10^{-1}$	-3.2	-15
"	$1.84 \times 10^{-1}$	-3.6	-17
"	$2.94 \times 10^{-1}$	-4.3 <sup>2</sup>	-20
V	$7.6 \times 10^{-4}$	- .9	- 4
"	$6.1 \times 10^{-3}$	-2.3	-11
"	$1.32 \times 10^{-1}$	-3.4	-16



Cell	N	$\frac{dE}{dT} \times 10^4$	$nF \frac{dE}{dT} = \Delta \tilde{s}$
VI	$4.6 \times 10^{-4}$	.5	2
"	$8.8 \times 10^{-4}$	-.2	- 0.9
"	$2.42 \times 10^{-3}$	-1.0	- 4.6
"	$7.5 \times 10^{-3}$	-1.7	- 7.8
"	$1.40 \times 10^{-2}$	-2.1	- 9.7
"	$4.5 \times 10^{-2}$	-2.7	-12
"	$1.00 \times 10^{-1}$	-3.3	-15
"	$1.65 \times 10^{-1}$	-3.6	-17
"	$2.90 \times 10^{-1}$	-3.4	-16
"	$3.9 \times 10^{-1}$	-3.9	-18
VII	$9.7 \times 10^{-4}$	-1.5	- 6.9
"	$1.75 \times 10^{-3}$	-1.6	- 7.4
"	$6.3 \times 10^{-3}$	-2.5	-12
"	$1.09 \times 10^{-2}$	-2.4	-11
"	$3.94 \times 10^{-2}$	-2.9	-13
"	$9.3 \times 10^{-2}$	-3.2	-15
"	$1.55 \times 10^{-1}$	-3.7	-17
"	$2.52 \times 10^{-1}$	-3.5	-16
"	$3.7 \times 10^{-1}$	-3.5	-16
"	$4.8 \times 10^{-1}$	-3.4	-16
VIII	$1.34 \times 10^{-4}$	-.4	- 2
"	$6.1 \times 10^{-4}$	-.3	- 1
"	$1.26 \times 10^{-3}$	-1.1	- 5.1
"	$4.3 \times 10^{-3}$	-1.5	- 6.9
"	$1.54 \times 10^{-2}$	-1.9	- 8.8
"	$3.89 \times 10^{-2}$	-2.3	-11
"	$8.4 \times 10^{-2}$	-2.6	-12
"	$1.76 \times 10^{-1}$	-3.2	-15
"	$2.62 \times 10^{-1}$	-3.6	-17
"	$3.6 \times 10^{-1}$	-3.4	-16
"	$5.3 \times 10^{-1}$	-3.8	-18
IX	$5.0 \times 10^{-4}$	-1.1	- 5.1
"	$1.31 \times 10^{-3}$	-1.4	- 6.5
"	$3.56 \times 10^{-3}$	-1.7	- 7.8
"	$6.8 \times 10^{-3}$	-2.0	- 9.2
"	$1.41 \times 10^{-2}$	-2.3	-11
"	$2.23 \times 10^{-2}$	-2.5	-12
"	$4.5 \times 10^{-2}$	-2.8	-13
"	$1.13 \times 10^{-1}$	-3.2	-15
"	$3.07 \times 10^{-1}$	-3.4	-17
"	$4.2 \times 10^{-1}$	-3.3	-15
"	$5.4 \times 10^{-1}$	-3.6	-17

Cell	N	$\frac{dE}{dT} \times 10^4$	$nF \frac{dE}{dT} = \Delta \tilde{s}$
X	$1.13 \times 10^{-3}$	-1.2	- 5.5
"	$2.57 \times 10^{-3}$	-1.3	- 6.0
"	$5.1 \times 10^{-3}$	-1.5	- 6.9
"	$4.9 \times 10^{-2}$	-2.5	-12
"	$1.07 \times 10^{-1}$	-3.2	-15
"	$2.5 \times 10^{-1}$	-3.7	-17
"	$4.0 \times 10^{-1}$	-3.8	-18
"	$7.5 \times 10^{-1}$	-3.9	-18
"	$8.3 \times 10^{-1}$	-4.3	-20

APPENDIX IV

Summary of E vs. N Data

Cell	700°C	E(volts) 800°C	900°C	N(ave.)
I		1.307	1.304	$1.15 \times 10^{-3}$
"		1.244	1.234	$3.77 \times 10^{-3}$
"		1.214	1.199	$6.9 \times 10^{-3}$
"		1.184	1.163	$1.23 \times 10^{-2}$
"		1.132	1.107	$3.25 \times 10^{-2}$
"		1.079	1.048	$7.6 \times 10^{-1}$
"		1.035	1.000	$1.35 \times 10^{-1}$
"		0.971	0.934	$2.29 \times 10^{-1}$
II		1.282	1.290	$1.62 \times 10^{-4}$
"		1.226	1.230	$4 \times 10^{-4}$
"		1.183	1.180	$8 \times 10^{-4}$
"		1.132	1.120	$3.09 \times 10^{-3}$
"		1.076	1.058	$9.8 \times 10^{-2}$
"		1.020	0.998	$2.81 \times 10^{-2}$
"		.958	.928	$8.3 \times 10^{-1}$
"		.924	.890	$1.31 \times 10^{-1}$
"		.890	.854	$1.88 \times 10^{-1}$
"		.837	.799	$2.95 \times 10^{-1}$
"		.778	.742	$4.1 \times 10^{-1}$
III	1.338	1.340		$1.56 \times 10^{-4}$
"	1.279	1.272		$7.2 \times 10^{-4}$
"	1.246	1.229		$1.52 \times 10^{-3}$
"	1.183	1.164		$6.4 \times 10^{-3}$
"	1.137	1.113		$1.70 \times 10^{-2}$
"	1.071	1.040		$6.1 \times 10^{-2}$
"	1.013	.982		$1.32 \times 10^{-1}$
"	.951	.912		$2.25 \times 10^{-1}$
"	.865	.826		$3.6 \times 10^{-1}$
"	.825	.776		$4.6 \times 10^{-1}$
IV	1.184	1.181		$1.12 \times 10^{-4}$
"	1.112	1.106		$5.8 \times 10^{-4}$
"	1.079	1.070		$1.27 \times 10^{-3}$
"	1.038	1.025		$3.2 \times 10^{-3}$
"	1.000	.979		$7.7 \times 10^{-3}$
"	.975	.949		$1.38 \times 10^{-2}$
"	.922	.893		$4.6 \times 10^{-2}$
"	.873	.841		$1.18 \times 10^{-1}$
"	.843	.807		$1.8 \times 10^{-1}$
"	.809	.756		$2.9 \times 10^{-1}$
V	1.105	1.094		$7.6 \times 10^{-4}$
"	1.025	.989		$6.1 \times 10^{-3}$
"	.866	.832		$1.32 \times 10^{-1}$

Cell	700°C	E (volts) 800°C	900°C	N( ave. )
VI		1.342	1.347	$4.6 \times 10^{-4}$
"		1.310	1.307	$8.8 \times 10^{-4}$
"		1.259	1.249	$2.42 \times 10^{-3}$
"		1.204	1.187	$7.5 \times 10^{-3}$
"		1.175	1.154	$1.40 \times 10^{-2}$
"		1.109	1.092	$4.5 \times 10^{-2}$
"		1.059	1.026	$1.00 \times 10^{-1}$
"		1.009	.973	$1.65 \times 10^{-1}$
"		.912	.877	$2.90 \times 10^{-1}$
"		.845	.805	$3.9 \times 10^{-1}$
VII		1.508	1.493	$9.7 \times 10^{-4}$
"		1.485	1.469	$1.75 \times 10^{-3}$
"		1.426	1.401	$6.3 \times 10^{-3}$
"		1.397	1.373	$1.09 \times 10^{-2}$
"		1.328	1.299	$3.94 \times 10^{-2}$
"		1.279	1.241	$9.3 \times 10^{-2}$
"		1.229	1.192	$1.55 \times 10^{-1}$
"		1.159	1.121	$2.52 \times 10^{-1}$
"		1.064	1.029	$3.7 \times 10^{-1}$
"		.989	.955	$4.8 \times 10^{-1}$
VIII		1.468	1.464	$1.34 \times 10^{-4}$
"		1.401	1.398	$6.1 \times 10^{-4}$
"		1.371	1.360	$1.26 \times 10^{-3}$
"		1.313	1.298	$4.3 \times 10^{-3}$
"		1.250	1.231	$1.54 \times 10^{-2}$
"		1.203	1.180	$3.89 \times 10^{-2}$
"		1.155	1.130	$8.4 \times 10^{-2}$
"		1.104	1.068	$1.76 \times 10^{-1}$
"		1.053	1.017	$2.62 \times 10^{-1}$
"		1.002	.968	$3.6 \times 10^{-1}$
"		.934	.896	$5.3 \times 10^{-1}$
IX	1.483	1.472	1.466	$5.0 \times 10^{-4}$
"	1.443	1.428	1.415	$1.31 \times 10^{-3}$
"	1.403	1.386	1.370	$3.56 \times 10^{-3}$
"	1.378	1.358	1.338	$6.8 \times 10^{-3}$
"	1.343	1.321	1.298	$1.41 \times 10^{-2}$
"	1.322	1.297	1.272	$2.23 \times 10^{-2}$
"	1.287	1.260	1.232	$4.5 \times 10^{-2}$
"	1.229	1.198	1.165	$1.13 \times 10^{-1}$
"	1.103	1.066	1.030	$3.07 \times 10^{-1}$
"	1.026	.994	.960	$4.2 \times 10^{-1}$
"	.966	.930	.894	$5.4 \times 10^{-1}$

Cell	700°C	E(volts) 800°C	900°C	N(ave.)
X	1.268	1.255		$1.13 \times 10^{-3}$
"	1.235	1.223		$2.57 \times 10^{-3}$
"	1.206	1.190		$5.1 \times 10^{-3}$
"	1.108	1.082		$4.9 \times 10^{-2}$
"	1.071	1.039		$1.07 \times 10^{-1}$
"	1.014	.977		$2.5 \times 10^{-1}$
"	.974	.936		$4.0 \times 10^{-1}$
"	.926	.886		$7.5 \times 10^{-1}$
"	.915	.872		$8.3 \times 10^{-1}$