

ELECTRODE POTENTIALS OF NICKEL AND COBALT  
IN A FUSED ELECTROLYTE

by

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A THESIS

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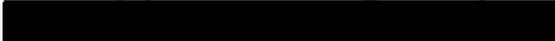
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# ELECTRODE POTENTIALS OF NICKEL AND COBALT IN A FUSED ELECTROLYTE

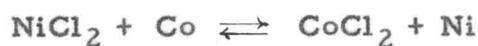
## I. INTRODUCTION

" Fused salt systems are becoming increasingly important in modern technology. Mantel lists 12 elements which are currently being produced by fused salt electrolysis (37, p. 481); fused salts are being used in atomic power development (2, p. 160); many proposed fuel cells and high temperature voltaic cells use fused electrolytes (50, p. 15); attention has been drawn to possibilities for extractive metallurgy (29, p. 243-245) and refractory metal plating from fused baths (47, p. 161-170). Fused oxide systems are being studied because of their close association with glass manufacture and slags in metallurgical processes (2, p. 219). Therefore, apart from the intrinsic scientific interest of fused salt systems, the rapid development of fused salt technology has led to increased efforts by scientists to obtain more basic knowledge concerning these systems."

The literature of fused salts has become sufficiently extensive that review articles have been written covering several specialized topics within the larger area of fused salt research. Some of the topics which have been recently reviewed are electrode processes (24, p. 90-106), conductance, transport numbers, and cryoscopy (27, p. 461-508), structure, physical properties of melts, and

methods of studying fused systems (2, p. 160-262). A group at the University of Illinois has studied polarography and associated techniques in fused salts. The thesis of R. A. Osteryoung of this group contains a history of fused salt work and an extensive bibliography (39, p. 2-11, 91-98). Subsequently completed theses by W. S. Ferguson and C. H. Liu of the same group provide a more specialized bibliography with coverage to 1957 (12, p. 61-62; 34, p. 66-70). Vapor pressures of salts and the solubilities of metals in their molten salts (7, p. 1-19) are two areas of current interest which have not been thoroughly reviewed. A comprehensive bibliography on the physical and chemical properties of fused salts, compiled by G. J. Janz, is available from ASTIA (26).

The primary purpose of this research was to obtain practical equilibrium constants for the reaction



in a solvent composed of equimolar portions of potassium chloride and sodium chloride. This solvent will hereafter be referred to as 1:1 M NaCl-KCl. The general method of attack was the study of galvanic cells without junction of the type



where M is either cobalt or nickel,  $MCl_2$  the corresponding chloride,  $N_{MCl_2}$  the mole fraction of  $MCl_2$ , and G is graphite. The electromotive force, e. m. f., of each cell was measured as a function of concentration of  $MCl_2$  and temperature. The concentration range was  $10^{-4}$  to  $5 \times 10^{-2}$  mole fraction of solute and the temperature range  $660^\circ$  to  $750^\circ C.$  Practical equilibrium constants, defined as  $K_N = N_{CoCl_2}/N_{NiCl_2}$ , for the desired reaction were calculated from the e. m. f. data. In addition, activity coefficients of the solutes were calculated. A possible reason for the deviation of such mixtures from ideality is the formation of complexes in the solution. This possibility has been considered and dissociation constants for possible complex equilibria have been calculated.

The electrode potentials of metals in the 1:1 M NaCl-KCl solvent relative to the chlorine electrode have not been definitely established. Such information would allow an accurate thermodynamic description of the solutions and would be useful for planning electrochemical separations in this potentially useful solvent.

A discussion of earlier work and electrochemical theory directly related to this research is now in order. Many galvanic cells utilizing molten electrolytes have been studied. Pioneer work in the field was done by Lorenz (35, p. 1-257) and later by Drossbach

(11, p. 1-143). During the 1930's in the United States Hildebrand and his students did extensive work on cells of the type



where M is the metal investigated,  $MX_x$  is metal halide, RX is alkali metal halide, and  $X_2$  a halogen (22, p. 722-729; 23, p. 4257-4261; 42, p. 4641-4654; 52, p. 4655-4661). In addition to extensive references to e. m. f. work found in the already mentioned review articles and theses, an annotated bibliography on fused salt voltaic cells has been prepared by W. C. Spindler and R. E. Panzer (49, p. 1-46).

Much of the early work concerning fused salt cell potentials dealt with decomposition potentials rather than reversible electrode potentials. Decomposition potentials are usually obtained by dipping two inert electrodes into the electrolyte and gradually increasing the applied potential across the electrodes. Cell current, I, is plotted as a function of applied potential, V. Depending on the purity of the electrolyte and the nature of the electrodes, the cell current will gradually increase until in the region of the decomposition potential of the electrolyte the slope of the I-V plot will increase sharply. To obtain the decomposition potential the current-potential line above

the sharp break is extrapolated to the applied potential axis. The total potential across the electrodes of a cell through which current is passing may be attributed to several factors. There is a potential related to the chemical reactions occurring at the electrodes and the concentrations of the reacting species; this potential is given at any instant by the Nernst equation. The remaining potential may be related to resistance in the cell, e. g., resistive layers on the electrodes and resistance of the electrolyte, and what is termed activation overpotential. This overpotential arises due to the necessity for supplying an activation energy when appreciable current passes through the cell. Due to these problems exact thermodynamic significance is not usually attributed to decomposition potentials although resistive polarization and activation overpotential are supposedly eliminated by extrapolation to zero current.

Early work on cell potentials must also be reviewed in the light of recent studies concerning the dehydration of melts. It has been found that without taking careful precautions most melts contain water, or products of hydrolysis reactions which may affect electrode potentials (17, p. 1458-1459; 32, p. 516-519; 36, p. 354-356).

Accurately reproducible reference electrodes are a necessity if accurate thermodynamic data is to be obtained from measurements

of cell e. m. f. 's. The preparation of such electrodes and their evaluation has been the subject of several recent papers. A few examples of reference electrodes for use in chloride melts are listed below.

- (a) Ag / pure AgCl / asbestos plug / (44, p. 31-32)
- (b) Na (9, p. 340-350)  
or Na-Sn / glass diaphragm / Na<sup>+</sup> melt (28, p. 502-507)
- (c) Ag / AgCl in 1:1 M NaCl-KCl / glass diaphragm / Na<sup>+</sup> melt  
or AgCl in LiCl-KCl eutectic (3, p. 438-439)
- (d) Ag / AgCl in 1:1 M NaCl-KCl / asbestos fiber sealed in  
silica (15, p. 715)
- (e) Ag / AgCl in 1:1 M NaCl-KCl / porcelain conductive to Na<sup>+</sup>  
(31, p. 896-899)
- (f) Pt / Pt<sup>++</sup> in 1:1 M LiCl-KCl / glass frit / (39, p. 16-22)
- (g) graphite-Cl<sub>2</sub> / glass diaphragm or asbestos fiber /  
(45, p. 151-152;  
15, p. 717-718)

The Cl<sub>2</sub>/Cl<sup>-</sup> electrode has been often used and is accepted as the proper reference electrode for obtaining thermodynamic data for metal chlorides in chloride melts by e. m. f. measurements.

However, the hope of finding an acceptable substitute which is more easily prepared, less fragile, less temperature sensitive, and more stable has led to the investigation and development of other reference electrodes. In some cases the Cl<sub>2</sub>/Cl<sup>-</sup> electrode has necessarily

been replaced, for instance, in cases where it is desired to study a lower valence state of a metallic ion capable of being oxidized by chlorine. In some work only relative potentials are desired and thus a more easily handled reference electrode is used.

It is important carefully to consider the possibility of junction potentials and variations of chemical potentials of reacting species in different melts when comparing electrode potentials. For instance, Yang and Hudson point out the difficulties involved in converting electrode potentials  $E_a$ , based on the reference electrode

$\text{Ag} / \text{AgCl} (N_{\text{AgCl}})$  in LiCl-KCl eutectic / Pyrex membrane /

to potentials,  $E_b$ , based on the  $\text{Cl}_2/\text{Cl}^-$  electrode (55, p. 986-990).

One might assume that this could be simply done providing e. m. f. data,  $E_c$ , for the cell

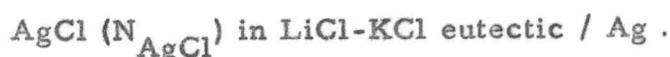
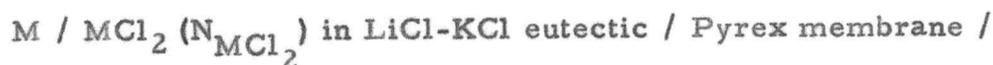
$\text{Ag} / \text{AgCl} (N_{\text{AgCl}})$  in LiCl-KCl eutectic /  $\text{Cl}_2$ -graphite

were available. Yang and Hudson point out that such conversion involves a term  $\Delta E$ ,

$$\Delta E = E_a + E_c - E_b \quad (1)$$

$$\Delta E = \frac{1}{F} \left\{ \left[ \mu_{\text{Cl}^-} \text{ in } \text{MCl}_2 (N_{\text{MCl}_2}) \text{ in LiCl-KCl eutectic} \right] - \left[ \mu_{\text{Cl}^-} \text{ in AgCl } (N_{\text{AgCl}}) \text{ in LiCl-KCl eutectic} \right] \right\} - E_m \quad (2)$$

where  $F$  is the Faraday Constant and  $\mu_{\text{Cl}^-}$  is the chemical potential of the chloride ion, and  $E_m$  is a junction potential for the cell



By studying several metals for which both the potentials  $E_a$  and  $E_b$  could be experimentally determined and knowing the potential,  $E_c$ , of their reference electrode relative to the  $\text{Cl}_2/\text{Cl}^-$  electrode, it was shown that in certain cases  $\Delta E$  is not inappreciable and may amount to 20 mv with concentration of metal chloride as low as  $2 \times 10^{-2}$  and AgCl  $6 \times 10^{-2}$  mole fraction. It was found that  $\Delta E$  varies with the nature of the metal ion and that in general those metal chlorides which showed larger deviation from ideality in solution showed higher values of  $\Delta E$ .  $\Delta E$  was found to decrease with decreasing concentration of the metal chloride being studied and to be generally insensitive to temperature and concentration of AgCl up to 0.6 mole fraction of

AgCl.  $\Delta E$  was found to vary with the nature of the glass diaphragms used for housing the reference electrodes. It was decided to use the  $\text{Cl}_2/\text{Cl}^-$  electrode in cells without junction in the present work in order to avoid the problems outlined in this paragraph.

∥ The possibility of errors due to thermal e. m. f. 's in the cell potential measuring circuit are greatly increased when working with high temperatures. This possibility has been generally recognized by recent workers in the field and a method of correcting for such e. m. f. 's is found in the literature (6, p. 4). A correction term is determined experimentally utilizing the electrodes and lead wires of the circuit to be used in the actual cell e. m. f. determination. ∥

Temperature control and measurement which are necessary in establishing accurate data has been improved in recent years. It is desirable to have a furnace and control system which will maintain a uniform, known temperature throughout a volume slightly larger than the melt volume. Temperature measurement with the thermocouples has been thoroughly discussed in the literature (7, p. 1-90; 41, p. 247-279). Tube furnaces capable of maintaining large uniform temperature zones are not generally available commercially. Details concerning construction of such furnaces, although beyond the scope of the present work, are found in the literature.

It is felt that although considerable work has been done toward the establishment of electrode potentials and electromotive series in various melts, there is much constructive work yet to be done to establish the reliability of data for systems already studied and to obtain data for systems of current interest which have not yet received attention.

In order to obtain accurate thermodynamic information from an electrochemical cell certain conditions must be met. The simple cell is composed of two dissimilar electrodes which dip into the electrolyte and are connected by an external metallic circuit. The cell must be so arranged that the cell reaction -- that is, the oxidation-reduction reaction in which the various constituents of the phases of the cell take part and which is bound with the passage of current, must proceed at the electrodes without direct contact of the reactants. Thus, reaction may proceed only with passage of current through the external circuit. There may be no junctions of dissimilar electrolytes within the cell. Provided a given cell closely approximates the conditions for thermodynamic reversibility and the cell reaction is known, well-known thermodynamic relationships may be applied to relate the free heat content change of the cell reaction,

the cell potential, and the activities of the reactants taking part in the cell reaction.

Thermodynamics tells us that no reaction proceeding at a finite rate is reversible. Electrochemists have therefore adopted the well-known Poggendorf Method of measuring cell potentials whereby the potential of the cell is exactly balanced by a known opposing potential; thus, no current is allowed to flow in the external circuit and provided the cell is properly constructed the cell reaction does not proceed. Use of the compensation principle is not, however, enough to insure the reversibility of the cell. Kortum and Bockris list several observations which indicate that an electrode is not behaving reversibly (30, p. 581).

1. Fluctuations occur in the e. m. f.
2. Two apparently identical electrodes in the same solution give a different e. m. f.
3. Changes occur in e. m. f. when the electrode is shaken.
4. The potential does not rapidly return to the equilibrium value after polarization.

A criterion of reversibility of a cell is continuity of a plot of cell current against cell potential across the zero cell current axis. In the present work, the measured potential varied by not more than  $\pm 1$  m. v. by changing the direction from which the zero cell current

was approached. Of course, a reversible process is only a useful hypothetical tool since such processes do not obtain in reality. In any given case, reversibility is a matter of degree and what may be an acceptable approximation in one case may be poor in another. For instance, reproducibility of electrode potentials to within one or two millivolts is deemed good in fused salt work and rather poor for many cells utilizing aqueous electrolytes. Irreversibility in a galvanic cell, the potential of which is being measured by the compensation method, will lead to a potential lower than the reversible value.

The free heat content change,  $\Delta G$ , for a given reaction is a measure of the isothermal maximum work obtainable from the reaction at constant pressure exclusive of pressure volume work. It thus follows that the relationship between the free heat content change,  $\Delta G$ , for a given reaction and the reversible potential,  $E$ , of a cell having the same overall reaction is

$$\Delta G = -nFE \tag{3}$$

where  $n$  is the number of electrons involved per unit advancement of the cell reaction and  $F$  is the Faraday Equivalent, 96,500 coulombs. For a hypothetical reaction



the van't Hoff Isotherm gives

$$\Delta G = \Delta G_o + RT \ln \frac{a_C^c a_D^d}{a_A^a a_B^b} \quad (4)$$

where R is the gas constant, T, the absolute temperature, and a the activity. Combining equations 3 and 4 gives the Nernst Equation.

$$E = E_o - \frac{RT}{nF} \ln \frac{a_C^c a_D^d}{a_A^a a_B^b} \quad (5)$$

At equilibrium  $\Delta G = 0$  and  $E_o$  is related to the equilibrium constant, K, for the reaction by the equation

$$E_o = \frac{RT}{nF} \ln K . \quad (6)$$

The entropy change for the reaction at a given concentration of reactants is obtained by combining the equation

$$\left( \frac{\partial \Delta G}{\partial T} \right)_P = -\Delta S \quad (7)$$

with equation (3).

Thus,

$$\Delta S = nF \left( \frac{\partial E}{\partial T} \right)_P \quad . \quad (8)$$

Then from the Gibbs Hilmholz Equation one may obtain  $\Delta H$ .

$$\Delta G = \Delta H - T \Delta S \quad . \quad (9)$$

The mole fraction of component  $i$  as used in this work will be defined as

$$N_i = \frac{n_i}{\sum n} \quad (10)$$

where  $n_i$  is the total number of moles of component  $i$  and  $\sum n$  is the total number of moles in the bath. One may define a cation mole fraction, an anion mole fraction, or mole fraction of a component such as  $\text{NiCl}_2$ . When referring to a cation fraction,  $\sum n$  refers to the total number of moles of cations in the bath; when referring to an anion fraction,  $\sum n$  will be the total number of moles of anions. Other possible definitions of mole fraction in fused salt work are found in the literature (16, p. 247).

The relationship between activity and mole fraction concentration of a given component is given by

$$a_i = N_i \gamma_i \quad (11)$$

where  $a_i$  is the activity,  $N_i$  the mole fraction, and  $\gamma_i$  the activity coefficient of component  $i$ .

The practical equilibrium constant for a reaction



was defined as

$$K_N = \frac{N_C^c N_D^d}{N_A^a N_B^b} \quad (12)$$

where the mole fractions refer to the analytically determined mole fraction concentrations of the bath.

Direct e. m. f. data concerning the two systems of interest in this work has been found in only one place in literature. S. N. Flengas and T. R. Ingrahm in a series of articles describe the experimental

determination of an electromotive force series in 1:1 M NaCl-KCl (13, p. 1139-1149; 14, p. 1245-1259; 15, p. 714-721). The reference electrode on which their system is based is

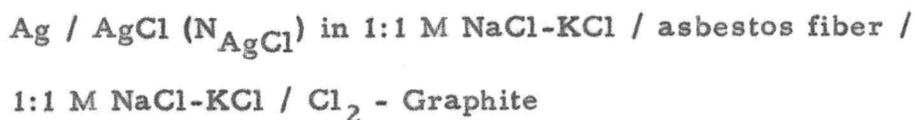


where  $N_{\text{AgCl}}$  is the mole fraction of AgCl and is on the order of  $6 \times 10^{-2}$ . The asbestos fiber is sealed into a short length of silica tubing and serves to separate the melt of the reference electrode from the melt in the indicator electrode compartment and also as a bridge between the two compartments. Among others the following two cells were studied at the temperatures of  $705^{\circ}$  and  $710^{\circ}\text{C}$  respectively.



According to these investigators the junction potentials of these cells are justifiably neglected on the basis that there is a high concentration of the same ionic species on both sides of the junction. It is to be

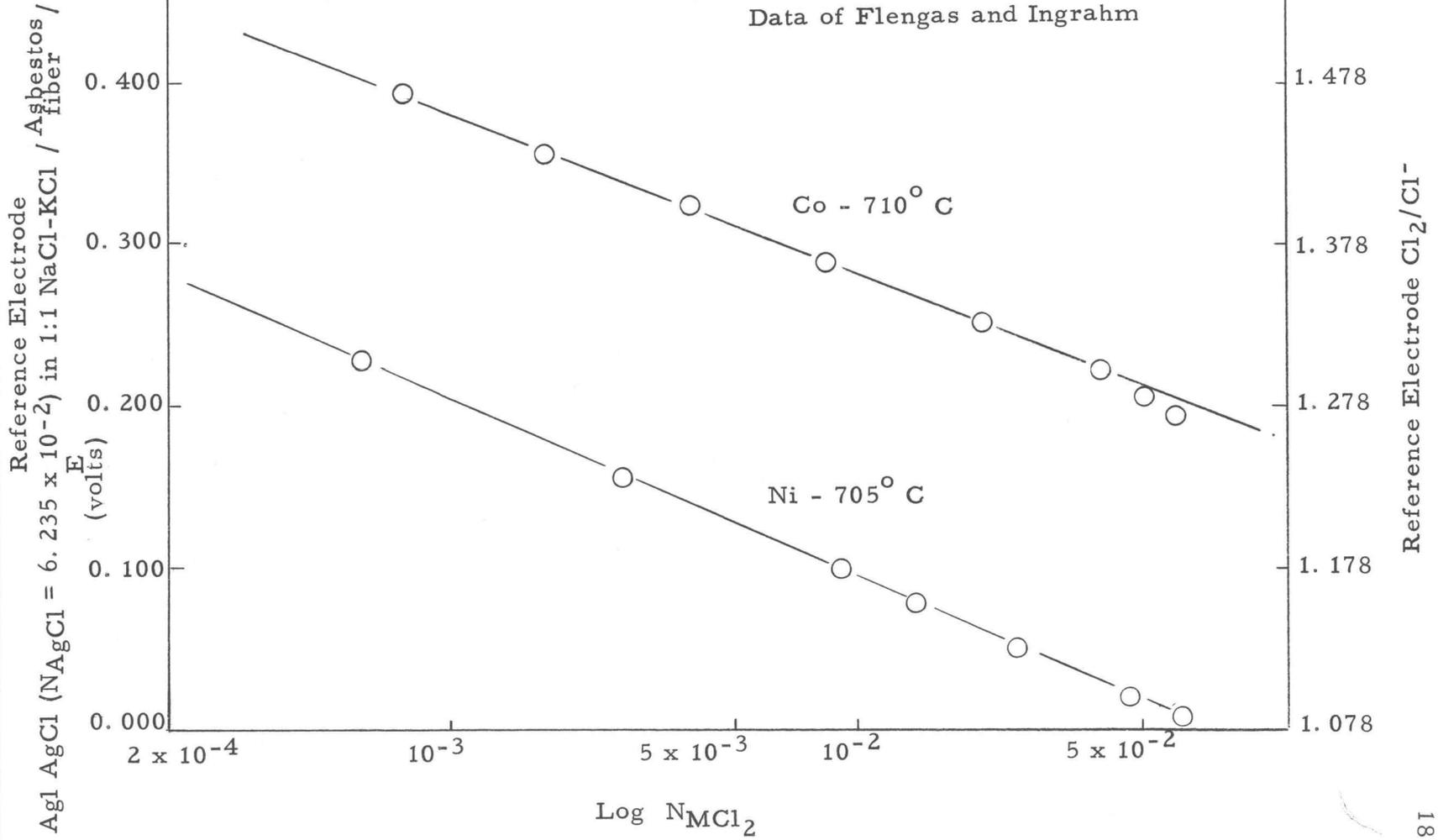
noted, however, that their concentrations fall within the region where Yang and Hudson found  $\Delta E$  to be appreciable in some cells. Also, the cell



was studied, thus supposedly relating the potential of their reference electrode to that of the chlorine electrode. On the basis of their experimental data and cell e. m. f. data derived from thermal data, it was concluded that the system  $\text{AgCl} (N_{\text{AgCl}})$  in 1:1 M NaCl-KCl behaves ideally over the whole concentration range from 700° to 900°C; thus the activity coefficient for AgCl was taken to be unity over the whole concentration range. The standard states were stated to be the pure metals and metal halides at one atmosphere pressure and the temperature of the experiment. Evidence was given by Flengas and Ingrahm and also has been given elsewhere in the literature that there is a negligible junction potential between the solutions  $\text{AgCl} (N_{\text{AgCl}})$  in 1:1 M NaCl-KCl and 1:1 M NaCl-KCl up to  $N_{\text{AgCl}}$  equal to approximately 0.5 (51, p. 741).

Figure 1 shows the data of Flengas and Ingrahm with respect to the two metals of interest. These e. m. f. 's are not corrected for

Figure I  
Data of Flengas and Ingrahm



the thermal e. m. f. 's. The values on the

$\text{Ag} / \text{AgCl} (N_{\text{AgCl}})$  in 1:1 M NaCl-KCl / asbestos fiber /

reference scale have been corrected to the same concentration,

$N_{\text{AgCl}}$ , of AgCl. The values on the  $\text{Cl}_2 / \text{Cl}^-$  scale are calculated from their comparison of the

$\text{Ag} / \text{AgCl} (N_{\text{AgCl}})$  in 1:1 M NaCl-KCl / asbestos fiber /

electrode with the  $\text{Cl}_2 / \text{Cl}^-$  electrode without considering junction potentials or the problem of variation chemical potential of chloride ion in different melts. Their experimental value of  $E_0$  for the  $\text{AgCl}_2$  cell at  $700^\circ\text{C}$ , 0.845 volts, was used in the calculation. As has been previously pointed out, neglect of these effects may contribute errors of the order of 20 m. v.

## II. EXPERIMENTAL EQUIPMENT AND PROCEDURE

### A. Furnace and Temperature Control

The furnace was a type 86, multiple unit, electric crucible furnace manufactured by the Hevi Duty Electric Company. The throat of the furnace was 3 inches in diameter and 5 inches deep. No modification was made in the furnace other than placing a soft iron tube in the throat to cut down magnetic flux in the e. m. f. measuring circuit.

A schematic diagram of the furnace and temperature control system is shown in Figure IIA. Power was furnished continuously to the furnace by a variable transformer. Additional power entered the circuit by way of the secondary of the Kenyon type S14940 transformer. The primary of this transformer was fed by line voltage and switched on and off by the Brown Electronik Potentiometer Pyrometer, model number 156C16PS-21, automatic temperature control. The Brown control was activated by the chromel-alumel thermocouple situated between the furnace coil and the iron tube. The voltage ratio of the Kenyon transformer was 115:5 and proper phase relation was

Figure II A

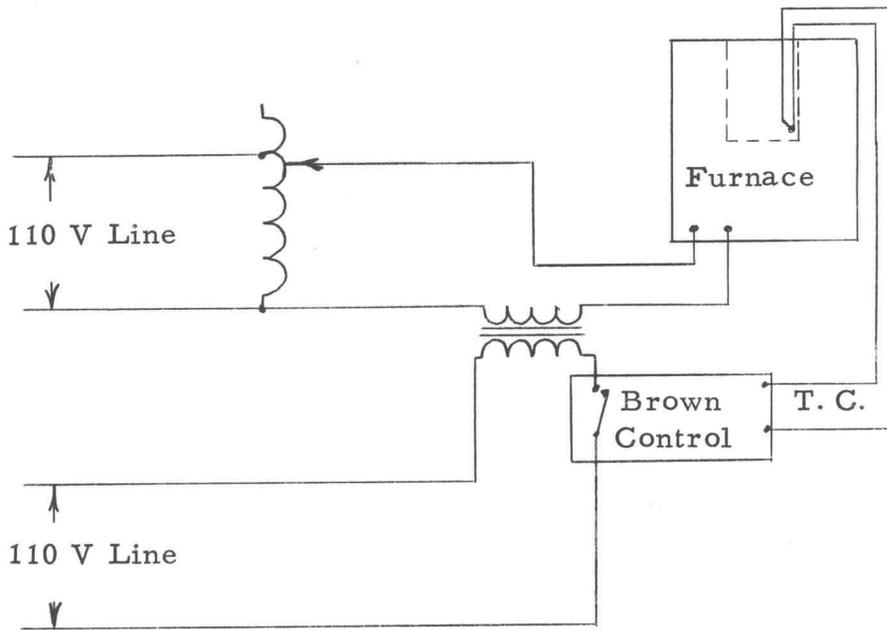
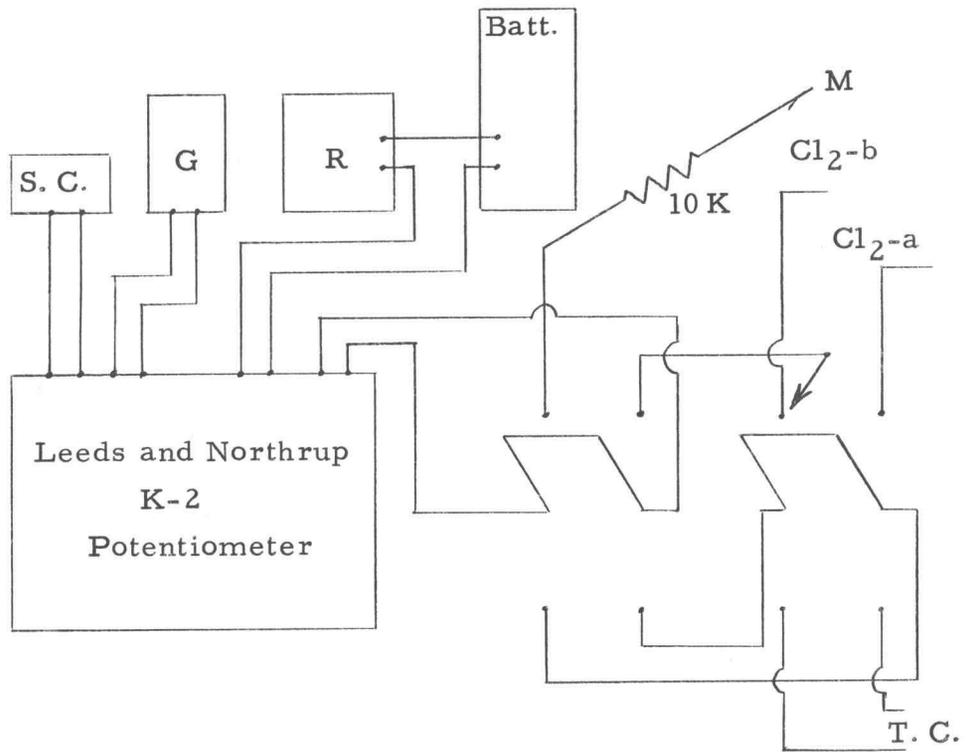


Figure II B



necessary to make the 5 volts of the secondary add to the Variac voltage.

The desired temperature was first roughly established with the variable transformer and the Brown control was then set and used as a fine control. The furnace could be set and left for many hours at a given temperature; long term fluctuations of melt temperature as indicated by an immersed thermocouple were no more than  $\pm 2^{\circ}\text{C}$ .

#### B. Temperature Measurement

All temperature measurements were made with calibrated chromel-alumel thermocouples which were interchanged from time to time to check any instability in a given couple. The couples were calibrated by the cooling curve method under conditions closely approximating those under which they were to be used. During calibration the hot junction, housed in 7 mm Vycor tubing, was immersed to a depth of 4 cm, and the cold junction was placed in an ice bath. Thermal e. m. f. 's were measured potentiometrically. Detailed information on fabrication, calibration, and use of thermocouples is given by Roeser and Wensel (41, p. 247-279) of the National Bureau of Standards. Antimony, which satisfied the purity

requirements of Roeser and Wensel, was used as the calibration standard. A corrected line of thermocouple e. m. f. versus temperature was drawn through the experimentally determined point at  $630.5^{\circ}\text{C}$  parallel to the curve for chromel-alumel thermocouples given by Dike (8, p. 82). Temperature measurement is estimated to have been accurate to  $\pm 3^{\circ}\text{C}$  over the temperature range of interest,  $660^{\circ}$  to  $750^{\circ}\text{C}$ .

### C. Reagents and Materials

Reagents and electrode materials were as follows:

1. 'Baker Analyzed', reagent grade NaCl and KCl for experiments I, II, IV, V.
2. 'Baker Analyzed', reagent grade NaCl and KCl further treated by the Hays' process (21) and twice recrystallized for experiment III.
3. Reagent grade nickel shot (99.8%) was obtained from the Matheson Coleman and Bell Division of the Matheson Company. Rods for use as electrodes were prepared from this material by Mr. Kato of the U. S. Bureau of Mines in Albany, Oregon.
4.  $\text{NiCl}_2$  was prepared from the nickel shot by dissolution in concentrated HCl, crystallization, and subsequent drying.

5. Cobalt metal of high purity was obtained from Dr. W. J. Kroll. The cobalt electrodes were made from this sheet metal by spot welding several strips together.
6.  $\text{CoCl}_2$  was prepared from the cobalt metal by dissolution in concentrated HCl, crystallization, and subsequent drying. This material was used for experiment IV. 'Baker Analyzed', reagent grade  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$  was dried and used in experiment V.
7. Oil pumped nitrogen gas was passed over copper turnings at  $500^\circ\text{C}$  and twice over  $\text{Mg}(\text{ClO}_4)_2$ .
8. Chlorine gas (Matheson Company) was passed over  $\text{Mg}(\text{ClO}_4)_2$ .
9. Spectrographically pure graphite (United States Carbon Company) was used for all graphite parts.

All salts were subjected to heat treatment in a Thelco vacuum oven, serial No. 19-F-12, for 6 hours at  $120^\circ\text{C}$ ; during this period dry nitrogen was allowed to pass slowly through the oven. Subsequently the NaCl and KCl were weighed out and mixed 1:1 molar. This mixture was placed in the cell and subjected to a vacuum of  $10^{-2}$  mm of mercury for 12 hours at  $500^\circ\text{C}$ . After this treatment the cell was flooded with chlorine gas, the salts melted and chlorinated in the presence of carbon for two hours (36, p. 354-356; 38). Chlorine was bubbled through the melt using the chlorine electrodes. The melt

was then ready for use. It was necessary to further dehydrate the chlorides of nickel and cobalt by heating the powdered, partially dried materials in a stream of dry HCl for 4 hours; 400°C was used for NiCl<sub>2</sub> and 170°C for CoCl<sub>2</sub> (5, p. 1154 and p. 1131).

The metal electrodes were washed, anodized in concentrated HCl, rinsed and heated to red heat in hydrogen, then cooled in hydrogen and placed in the cell.

### C. Cell Design

Schematic cutaway diagrams of the vacuum envelope, crucible, chlorine electrode, and partition tube are shown in Figures III and IV. The lower portion of the vacuum envelope is a Vycor cup topped by an inner 71/60 standard taper Vycor joint. Within the Vycor envelope is the graphite crucible which contains the melt. In the bottom of the crucible is a shallow hole large enough to accept the open end of a 19 mm Vycor partition tube. A Vycor chimney is set into the crucible so that vaporized salt will collect on its walls. Some of this condensed salt may be returned to the bath by raising the temperature of the cell sufficiently. The upper part of the cell is Pyrex and has openings on top for two chlorine reference

Figure III  
Cell  
Design

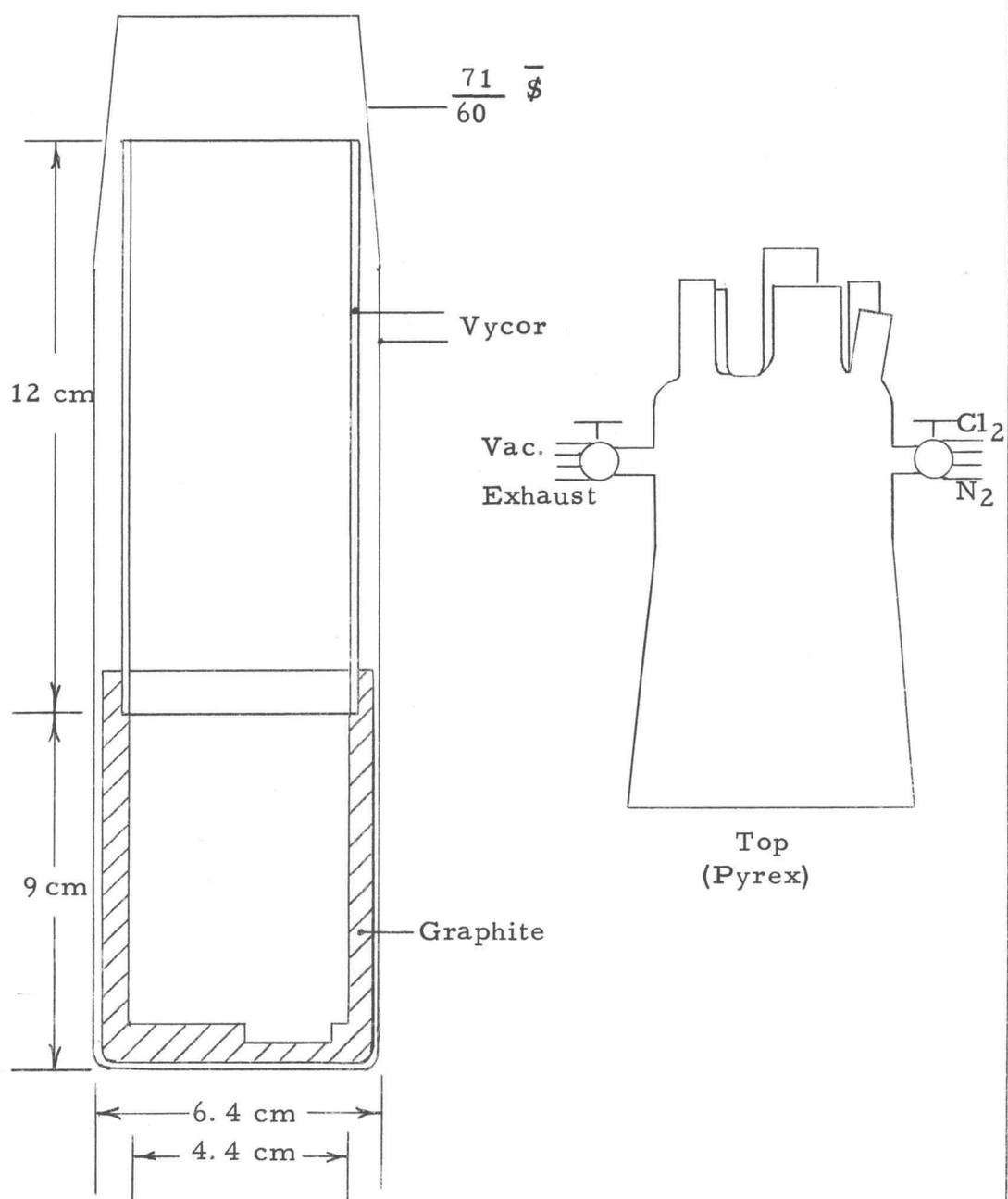
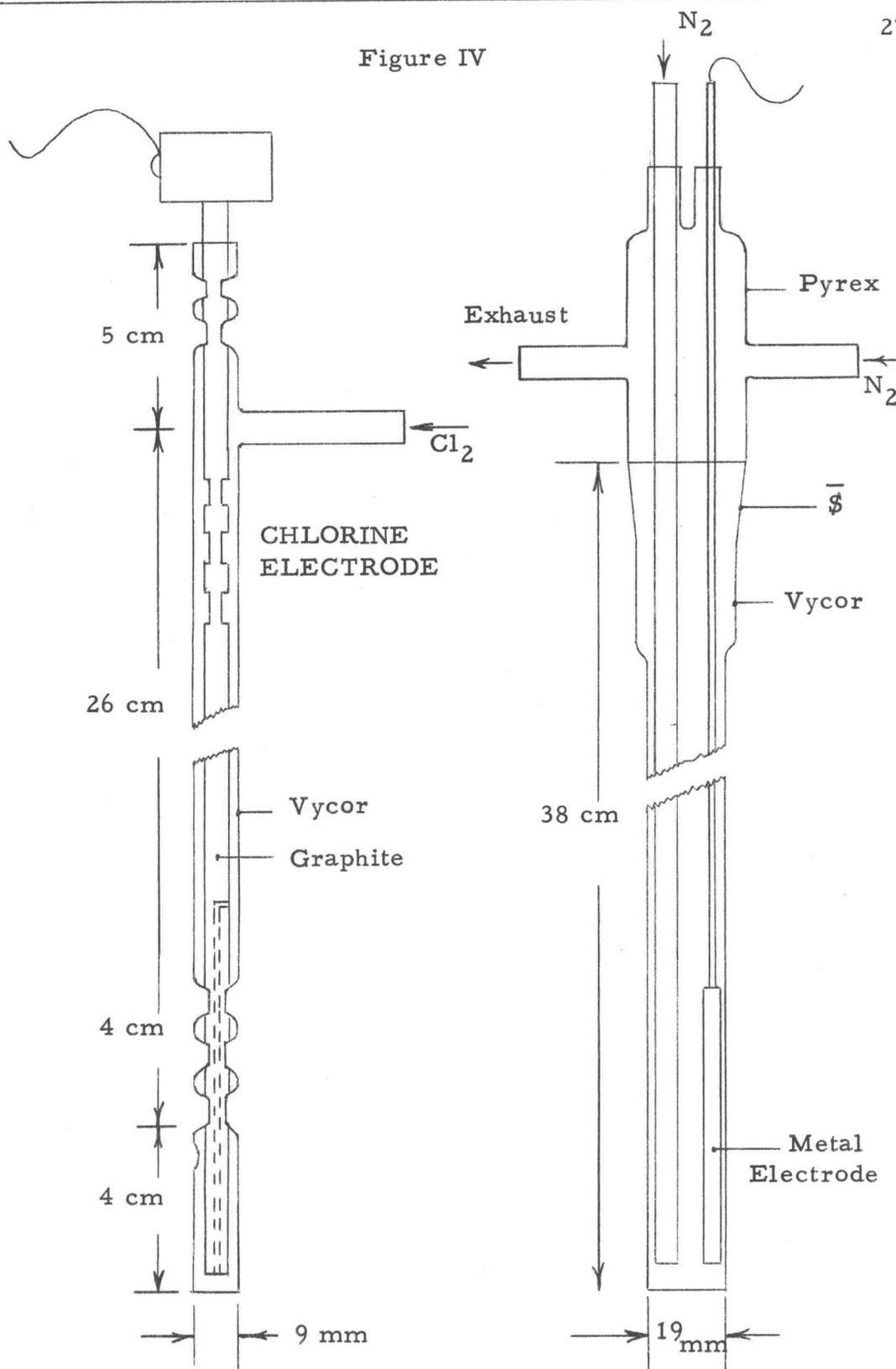


Figure IV



electrodes, a stirrer, the partition tube, sampling, and one thermocouple protection tube. Provision is made for gas inlet, vacuum, and exhaust through side arms with stopcocks. Brass cooling rings were machined to fit around the outer Pyrex joint and around the Vycor glass just below the joint. Graphite cloth was placed between the glass and the cooling ring for better thermal contact. 1/4" copper tubing, silver soldered into grooves in the rings, carried cooling water continuously during an experiment. Cooling allowed more comfortable working of the cell components, prevented more rapid deterioration of the stopcock grease in the large joint, and prevented the slipping down of the Pyrex top over the Vycor inner joint.

The chlorine electrode was designed to allow chlorine to pass through a 1/4" graphite rod into the melt. The fragility of the bored rod made the protective Vycor sheath necessary. The sheath also acted to prevent shorting of the two chlorine electrodes in the cell by a scum of graphite which accumulated on the surface of the melt. The constrictions near the top of the graphite rod reduced the thermal conductivity. The chlorine gas was pre-heated to some extent by its passage along and through the graphite rod before its entry into the melt. The Vycor was lathe-paddled into lathe-cut grooves in the graphite as shown. The graphite was flamed with an oxy-hydrogen

torch in air on the end to be immersed which resulted in a finely divided surface layer of graphite on the electrode. After thorough washing by boiling in concentrated HCl and in distilled water, the electrodes were dried and then heated in chlorine gas for several hours at 500°C. The electrodes were then immersed in the melt and chlorination was begun. Usually after two hours of chlorination the potential between the two reference electrodes was less than 1 mv. During actual measurement of a cell potential the chlorine gas was given a parallel path through the cell so that bubbling through the melt was almost stopped. The ends of the electrodes were positioned 1 cm from the bottom of the crucible. All exit gases from the cell passed through a sulfuric acid trap the entry tube of which was just barely immersed below the surface of the acid. If after hours of chlorination the electrodes were not within 2 to 3 millivolts of one another, a current of several hundred milliamps was passed first one way and then the other through these electrodes. This commonly used technique usually would result in bringing the two electrodes into close agreement.

The tube at the right in Figure IV housed the metal electrode. This tube could be raised so that its end was 2 to 3 cm. from the bottom of the crucible during stirring after addition of metal chlorides

to the bath or during temperature equilibration. Approximately one-half hour before an e. m. f. measurement was to be made the tube was pushed into the hole in the crucible bottom, thereby making it difficult for chlorine from the reference electrode to enter the metal electrode housing. (In experiments I and II the partition tube was seated over a truncated cone attached to the crucible bottom.) Provision was made to bubble dry nitrogen gas into the melt in this compartment as shown. This did not prove necessary since, within experimental error, the same readings were obtained with or without the nitrogen bubbling.

The thermocouple protection tube was a 7 mm Vycor tube closed at one end and immersed to within one cm of the bottom of the crucible.

Stirring was done with a flat paddle of Vycor fashioned on the end of a 7 mm Vycor rod. The paddle was turned by a Palo Myers, model 7605, variable speed motor. This type of stirring was not established until measurement 23 of experiment II.

Rubber tubing of appropriate sizes was used to join the inserted components to the cell top, thus making the cell air tight.

### E. Potentiometer Circuit

This circuit was the standard potentiometer circuit as shown in Figure IIB. Two double pole double throw switches were arranged so that the potential of the thermocouple, that between the electrodes of the cell, or that between the chlorine electrodes, could be measured. A 10,000 ohm resistor to prevent polarization was always in series in the circuit when the cell potential was being measured. A National Bureau of Standards calibrated standard cell No. 630177 was used to calibrate the working standard cell No. 401895. The galvanometer was a Leeds and Northrup Company, catalog number 2420b galvanometer, with a sensitivity of 25 microvolts per mm and an internal resistance of 26 ohms.

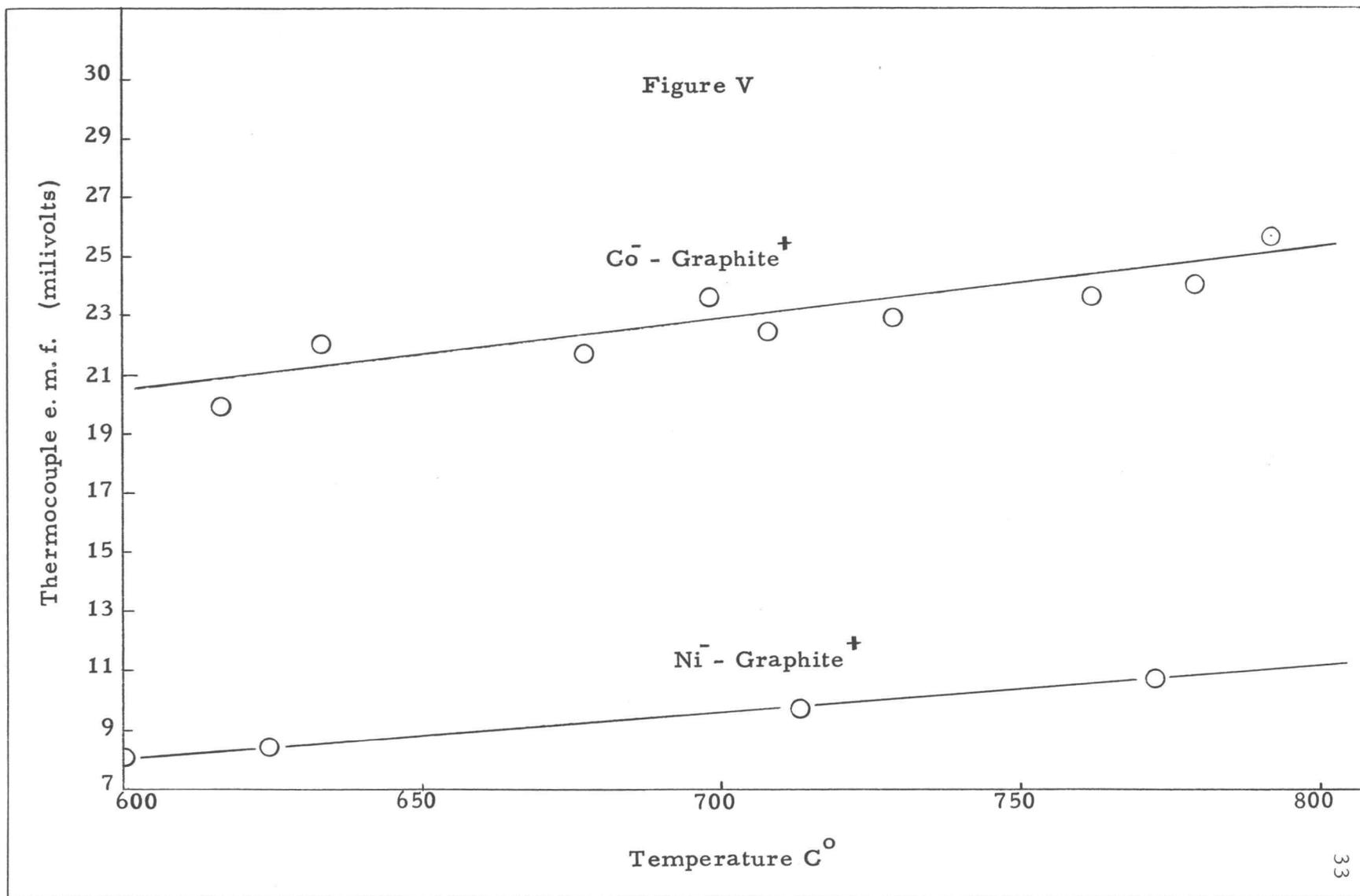
### F. Thermal E. M. F. 's in the Cell Circuit

To evaluate thermal e. m. f. 's in the cell potential measuring circuit the cell was set up exactly as it would be in use except that the melt was replaced by powdered graphite and the cell was flooded with dry nitrogen. No chlorine gas was allowed to enter the cell. The electrodes were immersed in the powdered graphite and the

e. m. f. of the couples Ni-G and Co-G were read as the cell temperature was raised. Pertinent values are shown plotted in Figure V. The polarities are indicated in the figure.

### G. Experimental Procedure

All glassware and graphite was thoroughly cleaned and dried before use. Stopcocks and ground joints were greased. Each run was begun with one mole of NaCl and one mole of KCl in the graphite crucible. After preparation of the solvent melt and chlorine electrodes solute was added in weighed amounts and the melt stirred. Pellets of solute which were easily handled were tried but abandoned for the powdered material which it was felt dissolved more rapidly. Additions were made through the top of the raised metal electrode protection tube. As previously mentioned, good stirring was not established until reading 23 of experiment II; lack of stirring necessitated long waits for dispersal of the solute. After stirring, the partition tube was lowered, stirring stopped, and the potential measured after one-half hour. The metal electrode was positioned in the melt only during potential measurements. As soon as a steady reading was obtained, usually 3 to 4 minutes after immersion, the



metal electrode was raised from the melt. A melt sample was then taken, the partition tube raised, temperature setting changed, and stirring was resumed until the new temperature had been reached. This procedure was repeated until e. m. f. 's had been obtained for several concentrations and at least two temperatures for each concentration.

Analysis of the melt samples was done spectrophotometrically. The method of Soine (48, p. 1-62) involving a tetracyanonickel complex was used for nickel and the chloride complex (43, p. 283) was used for cobalt. The analysis gave the amount of nickel or cobalt in a weighed sample of melt from which the number of moles of these salts could be calculated. Assuming the NaCl and KCl were present in the ratio 1:1 molar the mole fraction of the solute could be calculated.

### III. RESULTS

The experimental data from experiments II through V are given in tables I through IV. Values of  $E$ , the cell e. m. f., have been corrected for thermal e. m. f. 's. Experiment I was exploratory and no e. m. f. data were taken.

Experiment II differed from those subsequent in that the cell was never cooled below  $650^{\circ}\text{C}$  after the initial melting. Also, the chimney described in Section II-C was not used. At night the cell was filled with  $\text{Cl}_2$  and sealed. Many more points were obtained at given concentrations than in subsequent experiments; however, in addition to being time consuming it was feared that the results might be affected by loss of salts by vaporization. Mole fractions have been calculated on the assumption that the solvent composition remains 1:1 M NaCl-KCl. The vapor pressures of these salts differ and are appreciable in the range of temperatures used. Therefore, in experiments III through V the chimney was used, fewer points were taken, and the cell was filled with  $\text{Cl}_2$ , sealed, and allowed to cool to room temperature at night. Thus, duration of these experiments was considerably less than that of experiment II.

TABLE I  
Experiment II

NiCl <sub>2</sub> added to melt, g	Temperature C°	E <sub>Ni</sub>	Concentration, N <sub>NiCl<sub>2</sub></sub> × 10 <sup>2</sup>
0.3408	705	1.229	0.189
	682	1.236	
	734	1.222	
	785	1.209	
	696	1.222	
0.2276	698	1.199	0.341
	743	1.197	
	698	1.206	
	680	1.208	
	698	1.200	
	773	1.186	
	745	1.195	
0.2722	780	1.151	0.688
	750	1.154	
	720	1.158	
	691	1.171	
	712	1.168	
	727	1.161	
	748	1.163	
	767	1.153	
	717	1.164	
	719	1.152	
0.5906	721	1.151	0.919
	743	1.146	
	789	1.136	
	770	1.140	
	750	1.141	
1.568	745	1.120	1.66
	729	1.125	
	708	1.130	
	689	1.133	
	762	1.112	

TABLE I (continued)

## Experiment II

NiCl <sub>2</sub> added to melt, g	Temperature C°	E <sub>Ni</sub>	Concentration, N <sub>NiCl<sub>2</sub></sub> × 10 <sup>2</sup>
2. 771	787	1. 108	
	809	1. 068	
	782	1. 081	3. 05
	745	1. 091	
	719	1. 100	3. 10
	698	1. 104	
5. 183	679	1. 110	3. 20
	765	1. 054	5. 14
	762	1. 055	
	748	1. 055	
	748	1. 061	
	729	1. 065	
	712	1. 074	
	686	1. 079	

Attention should be called to the variation of mole fraction of added salt as shown in the proper column of Table I. It will be noticed that the analytically determined mole fraction does not agree with a nominal mole fraction calculated from the amount of metal salt added to the bath. Also, there is variation in analytically determined mole fraction for a given nominal bath composition. These variations are outside the limits of error of the analytical method. Several

TABLE II  
Experiment III

NiCl <sub>2</sub> added to melt, g	Temperature C°	E <sub>Ni</sub>	Concentration, N <sub>NiCl<sub>2</sub></sub> × 10 <sup>2</sup>
0.0806	751	1.301	0.0392
	700	1.304	0.0411
0.1199	703	1.263	0.086
0.1430	760	1.235	0.151
	705	1.240	0.154
1.2	731	1.175	0.658
	696	1.180	0.638
	740	1.166	0.750
3.6	752	1.104	2.21
	700	1.122	2.20
7.3	753	1.070	4.88
	700	1.085	5.06

explanations are offered to clarify this situation. One possibility is the slight solubility of the metal electrode in its molten salt which would lead to increases in mole fraction concentration. Another is the attack of the metal electrode by small amounts of chlorine inside the partition tube. During experiment II the metal electrode was twice accidentally left in the melt with the partition up which led to appreciable increases in solute concentration. Touching the graphite crucible bottom with the metal electrode should also lead to metal

TABLE III  
Experiment IV

CoCl <sub>2</sub> added to melt, g	Temperature C°	E <sub>Co</sub>	Concentration, N <sub>CoCl<sub>2</sub></sub> x 10 <sup>2</sup>
0.0896	698	1.486	0.0398
	750	1.483	0.0375
0.120	748	1.452	0.103
	698	1.459	
0.270	693	1.463	0.0888
	691	1.429	0.201
0.499	752	1.423	0.209
	755	1.386	0.439
3.39	708	1.396	0.452
	743	1.322	1.97
4.77	698	1.333	2.01
	698	1.296	4.35
9.84	745	1.282	4.32
	745	1.241	8.51
	696	1.258	8.41

solution since the crucible would probably act as a chlorine electrode. Sampling would decrease the total moles of solvent but should not affect the 1:1 M solvent ratio. Vaporization seemed negligible in experiments III, IV, and V. However, with these possibilities taken into account, the analytical results indicated that uniform dispersal of the solute in this solvent was very difficult to

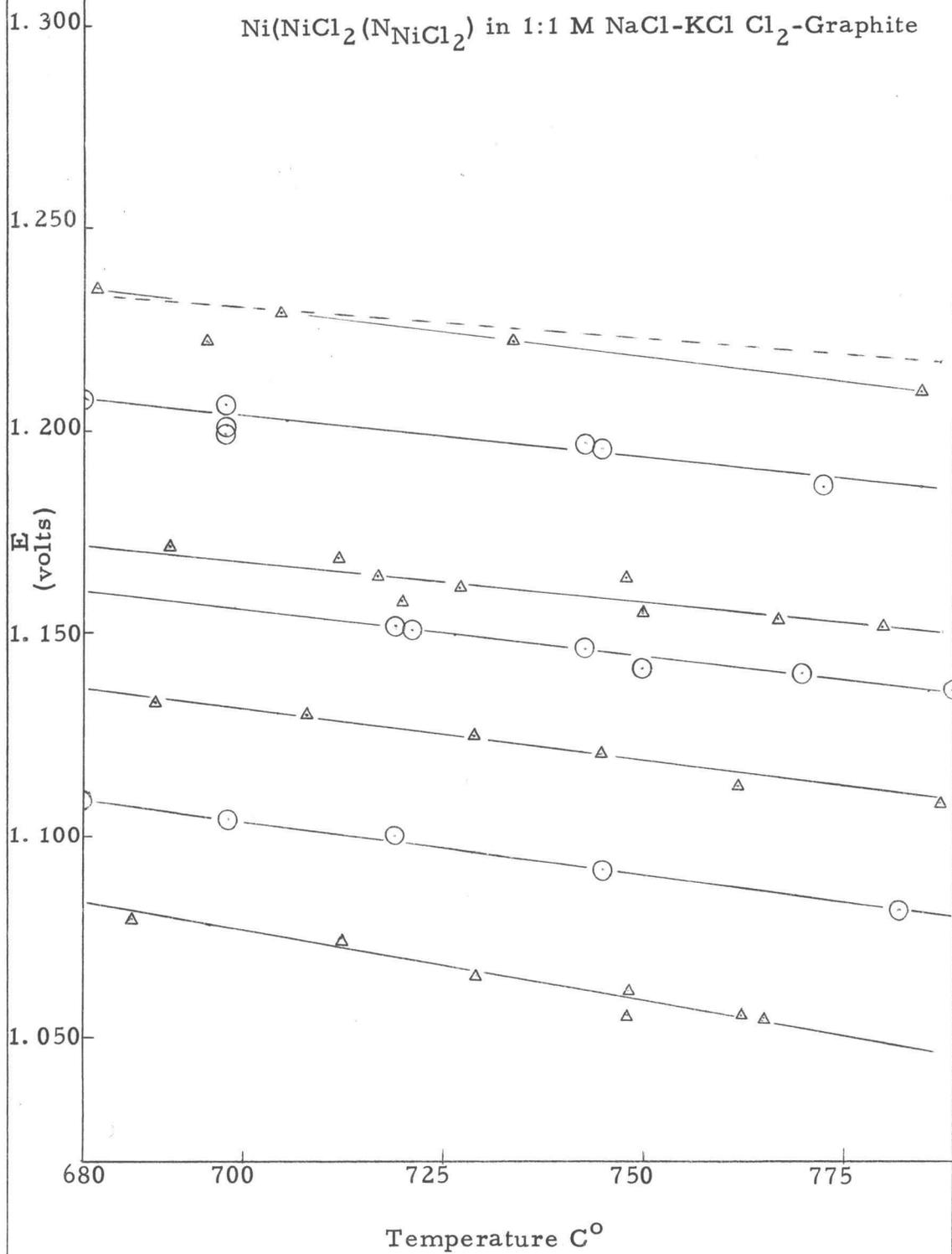
TABLE IV  
Experiment V

CoCl <sub>2</sub> added to melt, g	Temperature C°	E <sub>Co</sub>	Concentration, N <sub>CoCl<sub>2</sub></sub> x 10 <sup>2</sup>
0.0336	743	1.511	0.0164
	698	1.521	0.0164
0.0698	755	1.480	0.0444
	736	1.477	0.0493
	700	1.483	0.0490
0.0995	700	1.459	0.0966
	760	1.448	0.0920
0.234	755	1.427	0.178
	700	1.435	0.170
0.6587	752	1.382	0.480
	696	1.392	0.480
1.236	696	1.355	1.08
	757	1.344	1.06
2.993	755	1.303	2.39
	696	1.317	2.47
6.728	757	1.254	5.73
	691	1.272	5.52

achieve and that after two hours of stirring some variation in bath composition was to be expected.

In Figure VI the e. m. f. data for experiment II is plotted against temperature. Straight lines were drawn through the data points at a given nominal concentration and e. m. f. of the cell then

Figure VI  
Experiment II



taken from the plot at  $680^{\circ}$ ,  $700^{\circ}$ , and  $750^{\circ}\text{C}$  for the various concentrations. Similar plots were used to derive e. m. f. values at these temperatures from the data of experiments III, IV, and V. Provided the analytical results agreed to within 5% for a given nominal concentration an average of the analytical results was taken. Where deviations of concentration were greater than 5% an attempt was made to correct the data to a single concentration using the Nernst Equation. This was necessary only for one set of points in experiment I as shown by the dotted line near these points in Figure VI.

In Figure VII plots of cell e. m. f. versus logarithm of mole fraction of solute at  $700^{\circ}\text{C}$  are shown.

In Table V the least-squares slopes, intercepts, and standard deviations for the data at  $680^{\circ}$ ,  $700^{\circ}$ , and  $750^{\circ}$  are given. These slopes and intercepts were calculated assuming  $\log N$  to be exact and the error to be in  $E$ . Since there is definitely uncertainty in  $\log N$  as well, a trial calculation was run on the data for experiments II and III at  $700^{\circ}\text{C}$  using the statistical least-squares equations taking into account errors in both axes (53, p. 258). To three significant figures the values were the same as in the simpler calculation. E. m. f. -  $\log N_{\text{MCl}_2}$  data of experiments IV and V for Co were treated also as

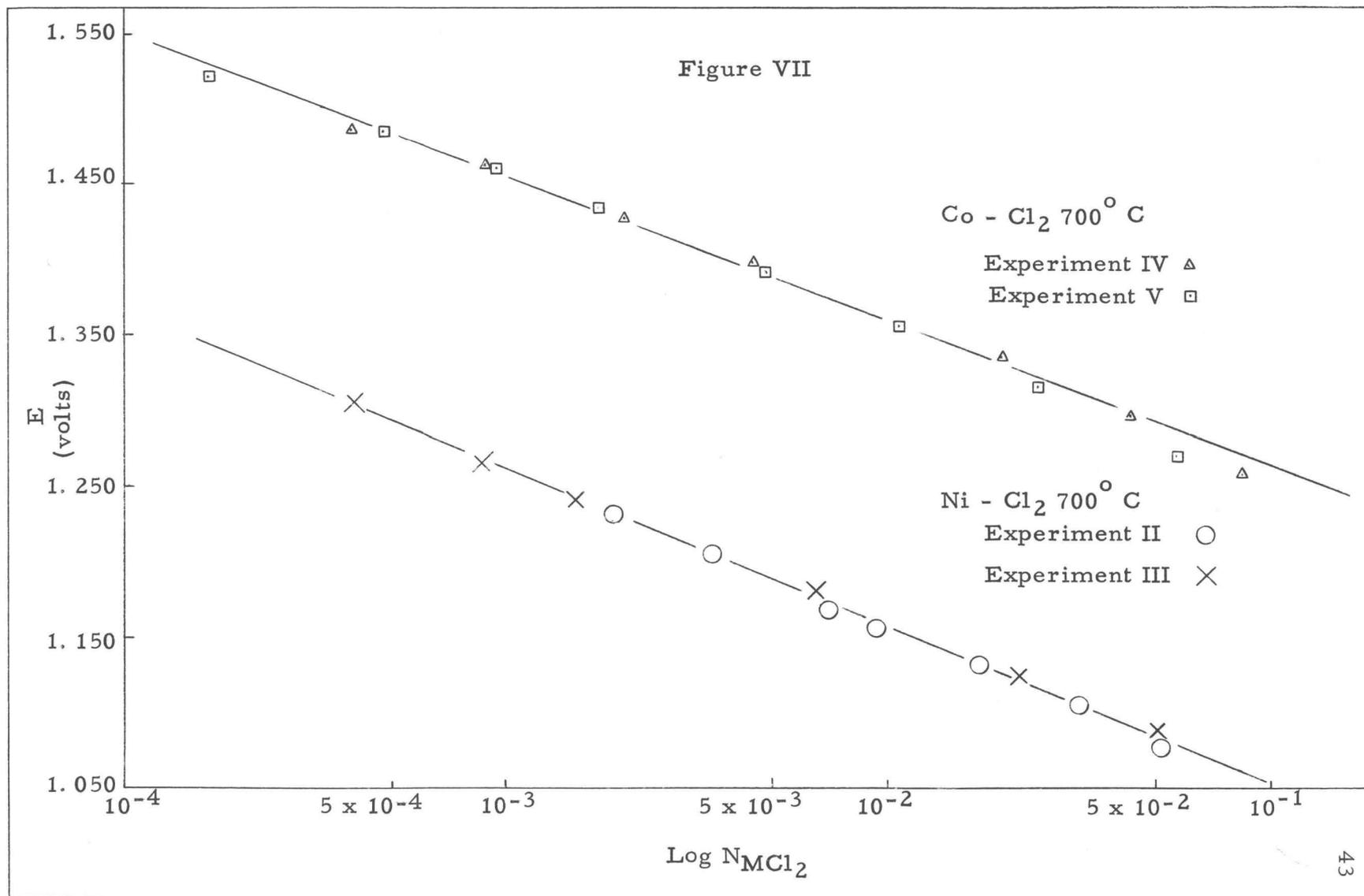


TABLE V

Cell	Temperature	$\frac{dE}{d \log N_{MCl_2}}$ , b	Intercept, a (Volts)	Standard Deviation (Millivolts)
Ni-Cl <sub>2</sub>	680	-0.103	0.954	3
	700	-0.105	0.945	3
	750	-0.112	0.920	3
Co-Cl <sub>2</sub>	680	-0.0947	1.172	4
	700	-0.0962	1.144	4
	750	-0.101	1.166	5

straight line data although curvature is evident at both high and low concentrations. The highest concentration and the two lowest concentrations were not considered in the least-squares treatment. However, neglect of the higher point is felt to be justified on the basis of higher possible error in the determination of concentration in this region. It is probable that the calculated slopes are valid in the very low concentration range.

## IV. DISCUSSION OF RESULTS

The Nernst equations for the two cells of interest in this work corresponding to the reactions



may be written

$$E_{\text{Ni}} = E_{\text{o-Ni}} - \frac{RT}{2F} (2.303) \log \frac{a_{\text{NiCl}_2}}{a_{\text{Cl}_2} a_{\text{Ni}}} \quad (13)$$

$$E_{\text{Co}} = E_{\text{o-Co}} - \frac{RT}{2F} (2.303) \log \frac{a_{\text{CoCl}_2}}{a_{\text{Cl}_2} a_{\text{Co}}} \quad (14)$$

The standard states are chosen as the pure metals and pure liquid salts, with the properties of the pure substances, at one atmosphere pressure and the temperature of the experiment. The standard state for the chlorine gas is taken as the pure gas at one atmosphere pressure and the temperature of the experiment. In the present work care was taken that the gas pressure within the cell did not exceed

atmospheric pressure. It is felt that within experimental error the activity of chlorine gas is unity. Assuming the solubility of the metal salt in the corresponding metal is negligible,  $a_{Ni} = 1$  and  $a_{Co} = 1$ . Equations 13 and 14 then may be written

$$E_{Ni} = E_{o-Ni} - \frac{RT}{2F} (2.303) \log N_{NiCl_2} - \frac{RT}{2F} (2.303) \log \gamma_{NiCl_2} \quad (15)$$

and

$$E_{Co} = E_{o-Co} - \frac{RT}{2F} (2.303) \log N_{CoCl_2} - \frac{RT}{2F} (2.303) \log \gamma_{CoCl_2} \quad (16)$$

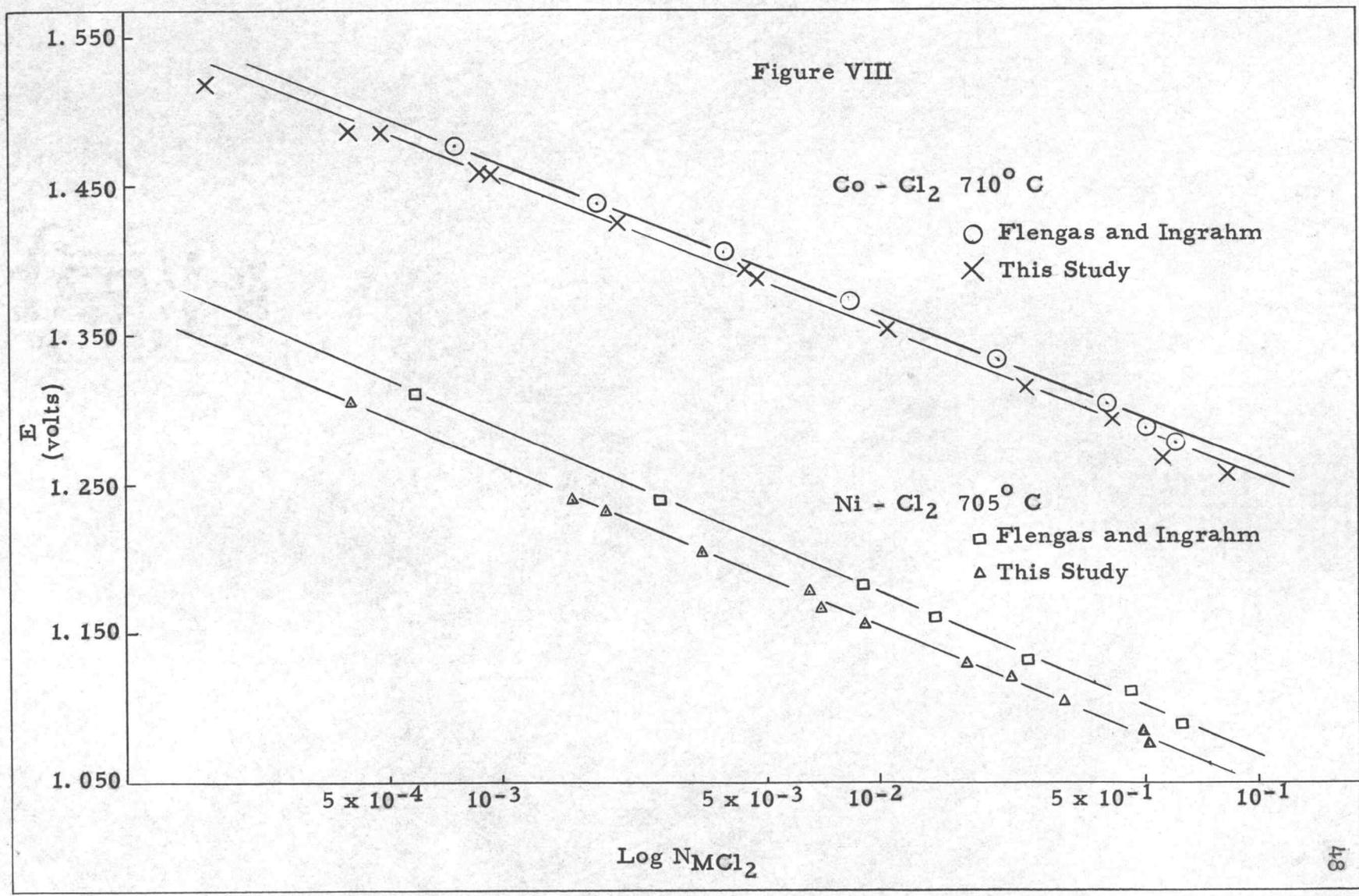
Values for the term  $\frac{2.303 RT}{2F}$  at  $680^\circ$ ,  $700^\circ$ , and  $750^\circ C$  are 0.0945, 0.0965, and 0.1015. Agreement of the experimental value of the slope,  $\frac{dE}{d \log N_{MCl_2}}$ , with these values indicates constancy of the activity coefficient term over the given concentration range. The experimental values of  $\frac{dE_{Co}}{d \log N_{CoCl_2}}$ , -0.0947, -0.0962, and

-0.101, show that  $\gamma_{\text{CoCl}_2}$  is constant. Slopes for the nickel cell are not in good agreement with the values above. Flengas and Ingrahm also noted a similar departure of this slope from the calculated value (15, p. 715). The magnitude of the departure seems to be outside the limit of experimental error in the present case. Thus  $\gamma_{\text{NiCl}_2}$  varies over the concentration range studied in this work. For both cells the experimental slopes are considered to be in close enough agreement with the values of  $\frac{RT(2.303)}{2F}$  to justify use of the two electron reaction.

A comparison of the data obtained in this work with that obtained by Flengas and Ingrahm is possible (13, p. 1145; 14, p. 1256). Figure VIII shows such a comparison; the data of Flengas and Ingrahm is shown in this figure corrected for thermal effects (15, p. 716). In the light of Yan and Hudson's discussion on the conversion of electrode to potentials based on the

Af / AgCl ( $N_{\text{AgCl}}$ ) in 1:1 M LiCl-KCl / Glass diaphragm

reference electrode to potentials based on the  $\text{Cl}_2\text{-Cl}^-$  reference electrode, a similar conversion being necessary for this comparison, the agreement between the sets of data for cobalt is considered



reasonable. However, this point will be discussed further in a later paragraph.

Activity coefficients for the cobalt and nickel chlorides may be calculated by utilizing values of  $E_o$  calculated from thermal data. The following values of  $E_o$  were estimated from the data tabulated by Hamer, et. al. (20, p. 11).

	<u>680°</u>	<u>700°</u>	<u>750°</u>
$E_{o-Ni}$	0.904	.895	.870
$E_{o-Co}$	1.02	1.01	0.997

The values corresponding to liquid  $CoCl_2$  were arrived at by extrapolating Hamer's data for the liquid salt to the desired temperatures. However, no data are given for liquid  $NiCl_2$ ; therefore, a line was drawn through the melting point for  $NiCl_2$  (40, p. 202) with a slope greater than that for the  $CoCl_2$  data by an amount equal to the difference in slopes of the  $FeCl_2$  and  $CoCl_2$  data. The quantity  $-2FE_o$  equals the change in free heat content involved in forming one mole of liquid metal salt at the temperature indicated. These values of  $E_o$  may be substituted into equations 15 and 16 along with the appropriate experimental data to calculate activity coefficients. However, one should understand that the values

of these activity coefficients and subsequently derived values of thermodynamic functions which depend upon the value of  $E_o$  are subject to the error involved in estimating  $E_o$ . The activity coefficients calculated for  $\text{CoCl}_2$  are over the concentration range  $4 \times 10^{-4}$  to  $4 \times 10^{-2}$  mole fraction and are 0.027, 0.029, and 0.037 at  $680^\circ$ ,  $700^\circ$ , and  $750^\circ\text{C}$  respectively. However, the activity coefficient of nickel varies regularly over the same concentration and temperature range. An equation may be written to describe this variation. Thus

$$E_{\text{Ni}} = E_{o-\text{Ni}} - \frac{RT (2.303)}{2F} \log N_{\text{NiCl}_2} - \frac{RT}{2F} (2.303) \log [(\Delta P') N_{\text{NiCl}_2}]^k \quad (17)$$

where

$$\gamma_{\text{NiCl}_2} = [(\Delta P') N_{\text{NiCl}_2}]^k \quad (18)$$

$$\Delta P = E_{\text{intercept}} - E_{o-\text{Ni}} \quad (19)$$

$E_{\text{intercept}}$  is the intercept on  $N_{\text{NiCl}_2} = 1$  of the  $E_{\text{Ni}} - \log N_{\text{NiCl}_2}$  plot as calculated by the least-squares treatment.

$$\Delta P = - \frac{kRT}{2F} (2.303) \log \Delta P' \quad (20)$$

The value of  $k$  is calculated from the experimental value of

$$\frac{d E_{\text{Ni}}}{d \log N_{\text{NiCl}_2}} \quad (21)$$

$$\frac{-RT (2.303)}{2 F} - \frac{kRT (2.303)}{2 F} = \frac{d E_{\text{Ni}}}{d \log N_{\text{NiCl}_2}}$$

Values of  $k$  and  $\Delta P'$  are given in Table VI from which  $\gamma_{\text{NiCl}_2}$  may be calculated.

Comparison of activity coefficients for the  $\text{NiCl}_2$  calculated from equation 18 and the data of Table IV shows that values of  $\gamma_{\text{NiCl}_2}$  are consistently higher than values of  $\gamma_{\text{CoCl}_2}$ ; e. g., at  $700^\circ\text{C}$  and  $N = 1 \times 10^{-3}$ ,  $\gamma_{\text{CoCl}_2} = 0.029$  and  $\gamma_{\text{NiCl}_2} = 0.17$ . This indicates that on the basis of the chosen standard state the deviation of  $\text{CoCl}_2$  from ideality is consistently greater than that for  $\text{NiCl}_2$ . Accordingly, the term  $\Delta E$ , defined and discussed by

TABLE VI

$C^\circ$	$k$	$\Delta P' \times 10^6$
680 $^\circ$	0.0899	1.312
700 $^\circ$	0.0881	1.312
750 $^\circ$	0.103	17.34

Yang and Hudson (equation 2, this thesis), which would correspond closely to the difference between the data of Flengas and Ingrahm and that of the present work as shown in Figure VIII, should be greater for the cobalt comparison than for the nickel comparison. That this is not the case is not explainable at this time.

Much effort has been made in recent years to explain the deviation of fused salt solutions from ideality on the basis of complex ion formation. Conductivity and solubility measurements and cryoscopic and spectrophotometric studies along with the behavior of electrodes in these solutions have been used to demonstrate the existence of complex ions (54, p. 599). The deviations from ideality of the  $\text{NiCl}_2 - \text{NaCl} - \text{KCl}$  and  $\text{CoCl}_2 - \text{NaCl} - \text{KCl}$  solutions of the present work, described by the activity coefficients of  $\text{NiCl}_2$  and  $\text{CoCl}_2$  in the preceding paragraph may be described in terms of complex formation. As a possibility let us consider formation of the

complex ion  $\text{NiCl}_4^{2-}$ . In this derivation the activities of the various species will be assumed equal to their concentrations, and all the deviation ascribed to complex formation (25, p. 803-829). Consider the reaction



where R represents alkali metal. Let  $N_{\text{NiCl}_2}$  represent the nominal mole fraction of  $\text{NiCl}_2$  in the melt,  $a$  the fraction of the nominal mole fraction of  $\text{NiCl}_2$  which is in the complexed state. R may be either sodium or potassium and as an approximation for dilute solutions the mole fraction of RCl in a 1:1 molar NaCl-KCl solvent is taken as unity. Then for the association constant we may write

$$K_a = a \frac{N_{\text{NiCl}_2}}{(1-a)N_{\text{NiCl}_2}} \quad (22)$$

and from 22

$$K_a = \frac{a}{1-a} \quad (23)$$

$$\frac{1}{1+K_a} = \frac{a}{K_a} \quad (24)$$

Thus

$$(1-a) N_{\text{NiCl}_2} = \frac{1}{1+K_a} N_{\text{NiCl}_2} = a_{\text{NiCl}_2} \quad (25)$$

and

$$\gamma_{\text{NiCl}_2} = \frac{1}{1+K_a} \quad (26)$$

Using the activity coefficient of  $\text{NiCl}_2$  mentioned in the preceding paragraph corresponding to  $N_{\text{NiCl}_2} = 1 \times 10^{-3}$  one thus obtains a value of 4.88 for  $K_a$ . For  $\text{CoCl}_2$  at the same nominal mole fraction  $K_a = 33$ . Gruen has presented considerable evidence for the existence of chloro complexes of cobalt and nickel in chloride melts (18, p. 74-76; 19, p. 393-397). However, it is felt that the values of  $K_a$  given here must be taken as illustrative rather than having exact physical significance since, as previously mentioned,  $\gamma_{\text{MCl}_2}$  depends upon the values of  $E_o$  estimated from thermal data. With regard to treating deviations from ideality in terms of complexes note should be taken of the recent objection to this procedure by Blander,

Blankenship, and Newton (1, p. 1260-1261). These authors treat the problem by a statistical mechanical approach in a series of recent papers.

A different, and perhaps more satisfactory, choice of standard states is possible in the present work. Although the approach is common in aqueous electrochemistry, it has not been frequently applied to fused salt systems. By rearranging equations 15 and 16 one may obtain

$$E_{\text{Ni}} + \frac{RT}{2F} (2.303) \log N_{\text{NiCl}_2} = E_{\text{o-Ni}} - \frac{RT}{2F} (2.303) \log \gamma_{\text{NiCl}_2} \quad (27)$$

$$E_{\text{Co}} + \frac{RT}{2F} (2.303) \log N_{\text{CoCl}_2} = E_{\text{o-Co}} - \frac{RT}{2F} (2.303) \log \gamma_{\text{CoCl}_2} \quad (28)$$

By plotting the left hand sides of equations 27 and 28 against appropriate functions of the concentrations,  $N_{\text{NiCl}_2}$  and  $N_{\text{CoCl}_2}$ , and stipulating by definition that  $\gamma$  approaches one as  $N$  approaches zero one may experimentally define  $E_{\text{o}}$ . The standard states of the metal salts will still correspond to the liquid salts,  $N = 1$ , but now the properties of the salts in their standard states must be those of the salts in the solvent at infinite dilution. Table VII contains values of  $E_{\text{o}}$  obtained by plotting values of the left hand sides of equations 27

and 28 against the square roots of the appropriate concentrations and extrapolating to  $N = 0$ .

TABLE VII

	$E_o$		
$T, C^o$	$680^o$	$700^o$	$750^o$
$E_o_{Co-Cl_2}$	1.177	1.169	1.149
$E_o_{Ni-Cl_2}$	0.980	0.969	0.949

On the basis of these values  $\gamma_{CoCl_2} = 1.1$  over the concentration range  $4 \times 10^{-2}$  to  $4 \times 10^{-4}$  for the temperatures  $680^o$ ,  $700^o$ , and  $750^oC$ . Again the activity coefficients for  $NiCl_2$  will vary regularly with concentration as given by equations 17 through 21; however, using the values of  $E_o$  given in Table VII the values of  $k$  given in Table VI are appropriate but not the values of  $\Delta P'$ . Appropriate values of  $\Delta P'$  are  $1.145 \times 10^3$ ,  $6.661 \times 10^2$ , and  $5.780 \times 10^2$  at  $680^o$ ,  $700^o$ , and  $750^oC$  respectively. Calculation of activity coefficients for  $NiCl_2$  now show that deviations from unity are small and have both positive and negative values.

The difference between the values of  $E_0$  corresponding to the two standard states which have been described is of interest. By multiplying this difference by  $nF$  one obtains the free heat content change involved in transferring one mole of the salt from one standard state, e. g., that of the pure liquid salt with the properties of the pure liquid salt, to the second standard state, that of the pure liquid salt with the properties of the infinitely dilute solute. This energy might be judiciously related to the bond energies involved in formation of the chloro complexes.

The final subject to be discussed in this thesis is the calculation of the practical equilibrium constant,  $K_N$ , for the reaction



Adding the following equations gives the desired reaction and the energy change which is involved.



At equilibrium

$$- nF (E_{\text{Co}} - E_{\text{Ni}}) = 0 \quad (32)$$

and

$$E_{\text{Co}} = E_{\text{Ni}} \quad (33)$$

At equilibrium the concentrations must therefore be such that the equation

$$(E_{\text{O-Co}} - E_{\text{O-Ni}}) - \frac{RT (2.303)}{2F} \log \frac{N_{\text{CoCl}_2} \gamma_{\text{CoCl}_2}}{N_{\text{NiCl}_2} \gamma_{\text{NiCl}_2}} = 0 \quad (34)$$

is satisfied.

Values of  $K_N$  are obtained by utilizing the intercepts and slopes given in Table V. Table VIII contains values of  $K_N$  calculated by applying the appropriate least-squares equations in the form

$$E = a + b \log N_{\text{MCl}_2} \quad (35)$$

to the condition of equation 33. Concentrations of  $\text{CoCl}_2$  were chosen which would avoid necessity for excessive extrapolation of

TABLE VIII

$$K_N = \frac{N_{\text{CoCl}_2}}{N_{\text{NiCl}_2}}$$

CoCl <sub>2</sub> (Mole Frac.)	K <sub>N</sub> 680°C	K <sub>N</sub> 700°C	K <sub>N</sub> 750°C	K <sub>N</sub> <sup>1</sup> 705°C
5 x 10 <sup>-2</sup>	100	96	73	57
1 x 10 <sup>-2</sup>	89	85	64	50
6 x 10 <sup>-3</sup>	86	83	60	47

<sup>1</sup>Derived from the data of Flengas and Ingrahm

the data for nickel. Also found in Table VIII are values of K<sub>N</sub> derived graphically by the same principle from the data of Flengas and Ingrahm, shown in Figure I.

The tabulated values neglect activity coefficient effects due to the common presence of the two metal chlorides in the solvent at the given concentrations. Therefore, the values given in the table will not necessarily agree with values of K<sub>N</sub> determined by direct equilibration and analysis studies in the same concentration range. Neglecting errors due to activity coefficient effects, and assuming

the necessary extrapolation of the nickel data is valid, elementary error theory would predict a probable error of 7% in the values of  $K_N$  determined in this study.

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