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Approach to Nickel-Tin Alloy Electrodeposition and Parameters of the Nickel Tartrate Complex

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APPROACH TO NICKEL-TIN ALLOY ELECTRODEPOSITION AND PARAMETERS OF THE NICKEL TARTRATE COMPLEX

by

Kenley R. Lee

A thesis presented to the Faculty of the School of Graduate Studies in partial fulfillment of the Degree of Master of Arts

Western Michigan University
Kalamazoo, Michigan
August, 1967
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STATEMENT OF PROBLEM

The study of conditions required for the electrodeposition of a nickel-tin alloy from baths other than the fluoride bath and the acetate bath was undertaken. The research included the correlation of thermodynamic and kinetic properties of electrode processes for the electrodeposition of the alloy desired.

The research also included the determination of the formula and formation constant of the nickel tartrate complex. The tartrate ion was a possible constituent in a bath for the electrodeposition of the alloy.
INTRODUCTION

History of Nickel-Tin Alloy Electrodeposition

An equiatomic nickel-tin (1:1) alloy was originally electrodeposited by Parkinson and Cuthbertson (1)(15). Since then, numerous studies have been conducted using basically the same nickel chloride, stannous chloride, ammonium bifluoride, and sodium fluoride electrolytic bath. The fluoride ion complexes the nickelous and stannous ions, bringing their electrode potentials sufficiently close to permit their codeposition. The remarkable feature of the fluoride bath is that it permits a wide concentration variation of the metal ions without a significant change in alloy composition.

The NiSn alloy has also been electrodeposited from a nickel acetate and stannous acetate bath. The concentrations of the components in the acetate bath, however, are critical, making it undesirable for commercial usage.

There are disadvantages of the fluoride bath that make it undesirable from a commercial viewpoint. The acidity is such that the noxious hydrogen fluoride gas is given off. The current efficiency is low because with the high acid concentration, hydrogen gas is also liberated.
The optimum operating temperature for the bath is 65°C which requires extra energy, thus making it less economical. The fluoride ion is extremely corrosive which necessitates special equipment.

Physical Properties of the Alloy

The unusual physical properties of the NiSn alloy have created a great deal of interest (1). The NiSn alloy contains approximately 65 weight percent tin and 35 weight percent nickel. It is metastable; when annealed above 300°C, it recrystallizes to the more stable Ni₃Sn₂ and Ni₃Sn₄ duplex. This explains why it is not found on a nickel-tin phase diagram and therefore is not obtainable by thermal processes.

The electroplated alloy has a faint rose tint, more pleasant than the chromium blue, and is equally as tarnish resistant as a chromium plate. It has been used commercially on a wide variety of articles where corrosion resistance and a bright plate are desired. The plate ability of the alloy from the fluoride electrolyte is such that it gives a very planar and bright plate.
THEORETICAL

Nickel-Tin Alloy Electrodeposition

The objective in this theoretical treatment is to demonstrate that the feasibility of plating out a nickel-tin (1:1) alloy is enhanced if it can be shown:

1.) The total overpotentials for both the nickel and tin electrode are equal or small.

2.) The reversible electrode potential for both nickel and tin can be made equal by complex formation.

3.) The relative diffusion currents of nickel and tin can be equated by adjusting the relative concentration of nickel and tin.

The theoretical consideration for the codeposition of the nickel-tin alloy requires that the metal ion of each metal be deposited out in equal molar amounts. The situation is unique from other electroplating systems.

The object then is to select an electrochemical system from which the desired alloy can be plated, in this case a Ni:Sn (ratio 1:1) alloy. In common to all metal species in the system will be the bath condition of: pH; applied electrode potential, $E^a$; temperature; stirring rate; nonelectroactive species; and the electrode surface. Independent characteristics of the individual metal ion species that are critical to the process are: activity of
the metal ion, $a^m$; reversible electrode potential, $E^r$; diffusion coefficient; formation constants of any complexes, $K_f$; and exchange current density, $i_0$. Both common and independent parameters of the system must be adjusted or selected to permit the deposition of the desired alloy.

**Overpotential correlations to electrode kinetics**

As stated previously, in an alloy electrodeposition the applied potential, $E^a$, is the same for each metal ion couple $\text{Me}^{\text{ox}}/\text{Me}^{\text{red}}$. By definition, the applied potential for a given metal ion couple is the algebraic sum of two potentials, the reversible electrode potential, $E^r$, and the total overpotential, $\eta$, of the electrode system which is always negative for a cathodic process.

$$E^a = E^r + \eta.$$  \hspace{1cm} (1)

The total overpotential, $\eta$, is a measure of the rate determining kinetics. $\eta$ for a polarized electrode is the algebraic sum of five overpotentials as expressed by Kortüm (10) in equation (2),

$$\eta = \eta_r + \eta_y + \eta_\Omega + \eta_d + \eta_t$$ \hspace{1cm} (2)

and are as follows:

- $\eta_r$ = reaction overpotential,
- $\eta_y$ = crystallization overpotential,
- $\eta_\Omega$ = current resistance overpotential,
- $\eta_d$ = diffusion overpotential, and
- $\eta_t$ = transfer overpotential.
The full detail of an electrolysis is seldom known; in this work there are some overpotentials that were not considered important. These are overpotentials caused by kinetics that were not obviously rate limiting. The current resistance overpotential, \( \eta_\Omega \), is usually caused by some adsorbed film at the electrode interface and is generally negligible in comparison with other overpotentials. The crystallization overpotential, \( \eta_y \), is generated by an inhibiting step in forming the crystal lattice on the electrode. The diffusion overpotential, \( \eta_d \), refers to kinetics of the ions diffusing from the bulk of the solution to the cathode. It is not anticipated that \( \eta_d \) will be excessive. The experimental work anticipated will be in the range of current densities calculated by equation (3) which gives the limiting diffusion current density possible from a bath (15)

\[
I_d = 0.025Cn
\]

where

- \( I_d \) = the diffusion current density (amps cm\(^{-2}\)),
- \( C_d \) = the molar concentrations of the reducible metal,
- \( n \) = the number of electrons transferred in the reaction.

The transfer overpotential, \( \eta_t \), results from electrokinetic phenomena within the diffuse double layer. More specifically, the transfer reaction (i.e. the electrical charge transfer to the ion within the double layer) is
involved. The reaction overpotential, $\eta_r$, is caused by a chemical reaction either preceding or following the transfer reaction.

The kinetics of the transfer step and the reaction step are important and are based on the existence of exchange currents between a metal electrode and the electrolyte solution adjacent to the electrode. The cathodic current*, $i_c$, is the deposition of the ions on the metal surface and the anodic current, $i_a$, is the dissociation of the metal into the solution. These exchange currents are represented by the equation

$$M^{+n} + ne^- \xrightarrow{\eta_a} \frac{i_c}{i_a} M^0. \quad (4)$$

Figure I illustrates the currents at the metal-liquid interface. If the applied potential, $E^a$, to the electrode is equal to the reversible electrode potential, $E^r$, ($E^r = E^a$), the cathodic current will equal the anodic current, ($i_c = -i_a$). Even though there is no current through an external circuit, there is a continuous cathodic and anodic current at the electrode interface.

A cathodic current is favored by a negative potential and the anodic current is favored by a more positive potential. Thus at $E^a < E^r$, the currents will be $|i_c| > i_a$

*According to the Stockholm (European) convention, a cathodic current is negative (-), and an anodic current is positive (+).
and correspondingly at $E^a > E^r$, then $|i_c| < i_a$. The total current will be

$$i = i_a + i_c$$

which is negative (cathodic) at $E^a < E^r$ and positive (anodic) at $E^a > E^r$.

$E^a < E^r$

$E^a = E^r$

$E^a > E^r$

$FIGURE I$

Schematic Representing Partial Current Densities

The Erdey-Gruz and Volmer equation (6) has been derived for the determination of the parameters of the hydrogen electrode process and applies equally as well for most electrode reactions. The Erdey-Gruz and Volmer equation assumes the overpotential is due to the reaction and transfer overpotential. The total current density, $i$, is given by

$$i = i_a + i_c$$

or

$$i = k_a(a^{\text{red}}) \exp \left[ \frac{2nF}{RT}(E^r + \eta) \right] - k_c(a^{\text{ox}}) \exp \left[ - \frac{(1 - a)nF}{RT}(E^r + \eta) \right]$$

(6)
where \( k_a \) and \( k_c \) are reaction rate constants of the anodic and cathodic reactions respectively (13). The activities of the oxidized species and the reduced species are respectively \( a^{ox} \) and \( a^{red} \), and \( \alpha \) is the transfer coefficient.

The first term in equation (6) gives the contribution of the anodic current, and the second term gives the cathodic current. At \( E^a = E^r (\eta = 0) \), the terms are equal to each other in absolute values and are equal to the exchange current density, \( i_0 \).

\[
i_o = |k_a(a^{red})\exp[\frac{\alpha nF}{RT} E^r]| \tag{7}
\]

\[
i_o = |k_c(a^{ox})\exp[-\frac{(1-\alpha)nF}{RT} E^r]| \tag{8}
\]

If \( E^a = E^r + \eta \), then in a given bath the anodic current and the cathodic current are

\[
i_a = +i_0\exp[\frac{\alpha nF}{RT} \eta] \tag{9}
\]

\[
i_c = -i_0\exp[-\frac{(1-\alpha)nF}{RT} \eta] \tag{10}
\]

or the total current is

\[
i = i_0\exp[\frac{\alpha nF}{RT} \eta] - i_0\exp[-\frac{(1-\alpha)nF}{RT} \eta] \tag{11}
\]

At increased negative overvoltages, the cathodic current is increased exponentially and the anodic current becomes negligible.
The total cathodic current for a negatively polarized electrode then is expressed by

$$i = -i_o \exp \left[ - \frac{(1 - \alpha) n F}{RT} \eta \right]$$  \hspace{1cm} (12)

or logarithmically expressed

$$\ln |i| = \ln i_o - \frac{(1 - \alpha) n F}{RT} \eta$$

and solving for \( \eta \),

$$\eta = - \frac{RT}{(1 - \alpha) n F} \ln \frac{|i|}{i_o} = - \frac{0.06}{n(1 - \alpha)} \log \frac{|i|}{i_o} \hspace{1cm} (13)$$

The exchange current densities are seldom known accurately for a bath. However, Salt (18) and Piontelli (16) have given \( i_o \) values which are indications as to what could be expected. We shall assume \( \eta = 0.5 \) for the equations here.

For nickel, \( i_o \approx 10^{-5} \text{amp cm}^{-2} \) and at a postulated depositing current density of \( 10^{-2} \text{amp cm}^{-2} \), the \( \eta \) is

$$\eta = - \frac{0.06}{2(1 - 0.5)} \log \frac{10^{-2}}{10^{-5}} \approx -0.18 \text{volts}.$$  

For tin, \( i_o = 10^{-3} \text{amp cm}^{-2} \) and at a \( i = 10^{-2} \text{amp cm}^{-2} \) depositing current density, the overpotential \( \eta \) is,

$$\eta = - \frac{0.06}{2(1 - 0.5)} \log \frac{10^{-2}}{10^{-3}} \approx -0.06 \text{volts}.$$  

The high overpotential for nickel as well as its less noble reversible potential could prove to preclude the deposition of an alloy from a solution of the uncomplexed
metal ions. Two factors still render the proposed deposition feasible. First, the solutions used in the experiments from which the data are derived (18)(16) are not the same as those to be used in this study. Thus the transfer coefficient and the exchange current densities will probably be different than those cited. Second, in the proposed study, the metal ion will be complexed in the electrolytic solution to alter the effective metal ion activities.

Correlation of electrode potentials and ion activities with the formation of a complex

The standard reduction potentials (14) at 25°C of the stannic, stannous, and nickelous ions are:

\[
\begin{align*}
\text{Sn}^{4+} + 4e^- & \rightarrow \text{Sn} \quad E^0 = +0.007\text{V} \quad * \\
\text{Sn}^{2+} + 2e^- & \rightarrow \text{Sn} \quad E^0 = -0.140\text{V} \\
\text{Ni}^{2+} + 2e^- & \rightarrow \text{Ni} \quad E^0 = -0.250\text{V}
\end{align*}
\]

The more positive potential of the stannous electrode suggests that to attempt an electrodeposition with unit activity of the stannous and nickelous ions in solution that tin would preferentially be deposited out of solution. The same is true for a combination stannic and nickelous ions at unit activity.

*This voltage was calculated from thermodynamic data (11).
For metal ion activities other than unity, the Nernst equation relates the standard electrode potential in terms of the reversible electrode potential, $E^r$.

$$E^r = E^{0}_{25°C} - \frac{RT}{nF} \ln \frac{1}{a^{M^{n}}_a}$$  \hspace{1cm} (14)

or

$$E^r = E^{0}_{25°C} + \frac{0.059}{n} \log a^{M^{n}}$$  \hspace{1cm} (15)

where $n$ equals number of electrons transferred, and $a^{M^{n}}$ is the activity of the metal ion $M^{n}$. The electrode potential becomes more negative as the activity of the metal ion decreases.

The electrode potentials of the stannous (or stannic) and the nickelous ions must be equal in order to codeposit a nickel-tin alloy. The object then would be to reduce the activity of the stannous ion in solution to a point where the alloy $\mid$ Sn$^{++}$ electrode potential is equal, or within 0.05v of the electrode potential of the alloy $\mid$ Ni$^{++}$ electrode (12). A method must be chosen that will not significantly reduce the nickelous ion activity or electrode potential. At more negative voltages, hydrogen gas will be plated out. This is especially true in an acidic bath, and nickelous electroplating baths must be acidic. However, while the activity of the metal ion, $a^{M^{n}}$, in solution can be reduced by lowering the concentration
of the ion, this is not practical in an actual deposition as the concentration would be very low and hard to maintain in the bath.

An effective way to reduce the activity of the metal ion would be to complex the ion with ligand, \( X^b \), of charge \( b \) to form the complex \( MX_p^{(n - pb)} \).

\[
M^n + pX^b = MX_p^{(n - pb)}.
\] (16)

The formation constant, \( K_f \), for the reaction is

\[
K_f = \frac{a^{MX}}{(a^M)(a^X)^p}
\] (17)

where \( a^M \), \( a^X \), and \( a^{MX} \) are the activities of the metal ion, ligand ion, and the complex, respectively, ignoring charges on the symbols.

Solving for \( a^M \),

\[
a^M = \frac{a^{MX}}{(a^X)^p K_f}
\] (18)

and then by substituting into equation (15), the following equation is given,

\[
E^r = E^0 + \frac{0.059}{n} \log \frac{a^{MX}}{(a^X)^p K_f}
\] (19)

This gives then a workable equation to determine the effects of a complexing ligand on the metal ion electrode potential.
In a polarographic analysis (2), it was observed that (Ni^{2+}) and (Sn^{4+}) had the same half-wave potential (-0.50v) versus saturated calomel electrode (S.C.E.). The supporting electrolyte was 5.0M CaCl₂. This suggested that the chloride ion was complexing the stannic and nickelous ions so that each of them had the same half-wave potential.

To electroplate a metal alloy, the reversible electrode potentials need to be equal or at least within 0.05 volts of each other (12). The possibility of equating the standard reversible potentials of the electrodes in a plating system by comparison of their respective half-wave potentials appears to be legitimate. This assumes of course that the same supporting electrolyte is being used in both cases.

The general equation for equating a half-wave potential, \( E_{\text{1/2}} \), with standard reversible electrode potential (9) for the same metal ion couple is

\[
E_{\text{1/2}} = E^0 + E^S + \frac{0.0591}{n} \log a^S
\]

where \( a^S \) is the activity of the metal in mercury at saturation and \( E^S \) is the potential of the cell, \( M(s)/M^2/M(Hg)_{\text{satd}} \).
By observation, the potential, $E^s$, of the above cell would equal zero at unit activity of the metal in the mercury and the term

$$\frac{0.0591}{n} \log a^s$$

would also be zero. Thus at unit activities, the half-wave potential would be the same as the standard electrode potential ($E_{1/2}^s = E^o$) of the metal ion couple $M^n/M$. This example illustrates the reason for variance of the half-wave potential in respect to the standard reduction potential, mainly because of the activity of the metal in the saturated amalgam.

Table I illustrates the difference of half-wave potentials and the reversible electrode potentials of several metals (9). The metals listed are those that can be compared to the $\text{(Sn}^{+4})$ and $\text{(Ni}^{++})$ ions for which data are not available.

Table I

Comparative List of Half-wave Potentials and Reversible Electrode Potentials

<table>
<thead>
<tr>
<th>ion</th>
<th>$E^o$(S.C.E.)</th>
<th>$E^s$</th>
<th>$E_{1/2}$(S.C.E.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pb$^{++}$</td>
<td>-0.372</td>
<td>-0.006</td>
<td>-0.388</td>
</tr>
<tr>
<td>Cd$^{++}$</td>
<td>-0.647</td>
<td>-0.050</td>
<td>-0.578</td>
</tr>
<tr>
<td>Zn$^{++}$</td>
<td>-1.008</td>
<td>0</td>
<td>-0.997</td>
</tr>
<tr>
<td>Tl$^+$</td>
<td>-1.582</td>
<td>+0.003</td>
<td>-0.459</td>
</tr>
</tbody>
</table>
This indicates then that the reversible electrode potentials for the Ni\(^{++}\) and Sn\(^{4+}\) in the 5.0M CaCl\(_2\) bath may be nearly equal if the half-wave potential is equal. If this is due to the complexing of chloride ions, the potentials are not likely to be changed excessively upon concentration changes of the metal ion because a large excess of complexing chloride ion is present.

The stepwise reduction of the stannic ion to stannous and then to the free metal is unlikely. The polarogram probably represents the potential of the four electron reduction, which is the potential in question for the alloy deposition.

\[
\text{Sn}^{4+} + 4\text{e}^- \rightarrow \text{Sn} \quad E^0 = +0.007\text{v}
\]

\[
\text{Sn}^{2+} + 2\text{e}^- \rightarrow \text{Sn} \quad E^0 = -0.140\text{v}
\]

This is attributed to the fact that the standard potentials of the two half cell reactions are not very far apart. The established one step reduction of the cupric ion is an analogous example (9).

The polarographic determination of the maximum diffusion currents of each metal is significant to the design of the electroplating system. One of the most important features of polarography is that the maximum diffusion currents of a metal can be found in relation to the molar concentration. If the molar concentration of each metal in the alloy plating bath is adjusted so the diffusion of each metal ion species into the electrode
is equal, an equiatomic electrodeposition is expected. This assumes the metal ions are subsequently reduced at the electrode.

Summary

The general case of the electrodeposition of a 1:1 alloy has been considered. The applied potential is the sum of the overpotential and the reversible potential. The electrode kinetics of such a process are related to the overpotential of the individual species plating out. The excessive overpotential of the nickel may prevent its deposition.

The effect of complex formation of the metal ion on the electrode potentials is also pointed out. From polarographic data it is indicated that nickel and tin have the same electrode potential in a concentrated chloride bath which implies complex formation. The chloride solution is proposed as a possible alloy electroplating bath.

The relative molar diffusion current densities of the nickel and tin reduction can be equated from polarographic data. In the alloy plating system, these currents can be adjusted by changing the metal ion concentration.
Determination of the Formula and Formation Constant of a Nickel Tartrate Complex

The tartrate ion was considered as a possible constituent for the alloy plating bath. The complexing properties with nickel and tin ions were not known. The determination of the formula and formation constant of the nickel tartrate ion was given precedence. The following is a theoretical summary of the methods used.

**Zero current potentiometric method**

A potentiometric method is available for the analysis of reducible metal complexes. The potentiometric determinations of the formula number, p, and formation constant, $K_f$, are possible from the half cell potential measurements.

The above method, however, is only directly applicable to systems for which the zero current potential can be measured directly. Where the metal ion of the complex is part of a system in which it is not possible to measure the zero current potentials, different techniques must be used to determine the zero current potentials.

The general equation for the reduction of a metal may be written

$$M^n + n-e^- = M,$$

(21)
and the equation involving the formation of a single complex is

\[ Mn + pX_b = MX^{n-pb} \]  \hspace{1cm} (22)

where

- \( n \) = number of electrons exchanged in reduction,
- \( Mn \) = reducible metal ion,
- \( M \) = free metal,
- \( X_b \) = uncomplexed ligand of charge \( b \),
- \( p \) = number of ligands per metal ion, and
- \( MX_p \) = complex.

The potential of the half cell reaction is given by the Nernst equation

\[ E^F = E^0 - \frac{RT}{nF} \ln \frac{a}{a^M} \]  \hspace{1cm} (23)

where \( a^M \) is the activity of the metal ion in solution.

The formation constant, \( K_f \), for the complex can be represented:

\[ K_f = \frac{a^{MX}}{(a^M)(a^X)^p} \]  \hspace{1cm} (24)

where \( a^X \) is the activity of the ligand species and \( a^{MX} \) the activity of the complex. For convenience, the activities may be substituted by the molar concentrations of the species, and the equation becomes

\[ K_f = \frac{[MX]}{[M][X]^p}. \]  \hspace{1cm} (25)

The half cell potential of the complexed ion is then written combining equations (23) and (25),
\[ E^r = E^o - \frac{RT}{nF} \ln \frac{K_f [X]^p}{[MX]} \]  \hspace{1cm} (26)

or

\[ E^r = E^o - \frac{RT}{nF} \ln K_f + \frac{RT}{nF} \ln [MX] - \frac{RT}{nF} \ln [X]^p . \]  \hspace{1cm} (27)

Equation (27) can now be differentiated by partials to obtain

\[ \left( \frac{\partial E^r}{\partial (\ln [X])} \right)_{[MX]} = -\frac{RT}{nF} p \]  \hspace{1cm} (28)

where \( E^o, R, T, n, F, \) and \( K_f \) are obviously constants, and by experimental conditions, \([MX]\) may also be held essentially constant. This is possible for a stable complex (large value of \( K_f \)) by keeping the total metal ion concentration constant and the total ligand ion concentration in very large excess of the total metal ion concentration.

The zero current potentials of irreversible electrodes are not obtainable by direct measurements. One possible solution to the problem is to use a polarized electrode system. The electrode is polarized by small cathodic and anodic currents, and from a plot of the current-potential data, the zero current potential of the electrode can usually be interpolated. The above data are plotted on an applied voltage versus polarizing current graph and a smooth curve is drawn through the
points. Where the curve intercepts zero current ($i = 0$), the reversible potential, $E^r$, is given as shown in Figure II.

For the proposed study, data must be obtained at several ligand concentrations to obtain the reversible potentials needed to determine the parameters of the complex.

![Figure II](image)

**Figure II**

Plot: Voltage versus polarizing current at several different ligand ion concentrations

[X'] [X''] [X''']

$[X'] < [X''] < [X''']$
Thus, from a graph similar to Figure II, the reversible potential, $E^r$, may be obtained at different ligand concentrations. From this data, equation (28) can be graphed.

![Graph](image)

Figure III

$E^r$ versus $-\ln[X]$

The slope, $s$, of the line in Figure III will then be

$$s = -\frac{3E^r}{\delta \ln [X]} = \frac{RT}{nF} p .$$

(29)

The calculation of $p$ may then be expressed as

$$p = s \frac{nF}{RT} ,$$

(30)

and the nearest whole number chosen as the actual $p$.

The numerical value of $n$ may be determined using equation (27) and by experimentally maintaining the ligand ion concentration, $[X]$, constant and in large excess of that needed by the complex. The reversible electrode potentials are determined at various complex concentrations.
By graphing $E^\circ$ versus $\ln[MX]$ the slope, $m$, will be

$$m = \frac{\partial E^\circ}{\partial \ln[MX]} = \frac{RT}{nF},$$

which gives a check on the electrode reaction for the value of $n$. The intercept ($E^\circ = 0$) will be

$$E^\circ - \frac{RT}{nF} \ln K_f - \frac{RT}{nF} \ln K_f$$

and will give $K_f$ from the corresponding calculation.

**Polarographic method**

A polarographic method for the determination of the formula and the formation constant, $K_f$, of certain stable metal complexes has been developed. Heyrovský and Káta (6) give a detailed summary of the method originally mentioned by Heyrovský and Ilkovič (5), and worked out in greater detail by von Stackelberg and von Freyhold (20), and by Lingane (13). Vlček (21) has given a method for the determination of a thermodynamic formation constant by extrapolating the polarographic data to zero concentration of the supporting electrolyte. The theoretical summary given will only be detailed to the extent necessary for this thesis.

As mentioned previously, a complexed metal ion exhibits a more negative electrode potential than a corresponding uncomplexed metal ion. Similarly, the
polarographic half-wave potential of a complexed metal ion, \( (E_{1/2})_{c} \), is less than the polarographic half-wave potential of the uncomplexed metal ion \( (E_{1/2})_{u} \). The formation constant, \( K_f \), is determined from measurements of the shift of the half-wave potentials at various ligand concentrations.

The general reaction for a dropping mercury electrode is written

\[
MX_p^{(n - pb)} + ne^- + Hg = M(Hg) + pX^{-b}
\]  

(33)

where a competitive complexing reaction is occurring and

- \( MX_p^{(n - pb)} \) = dissociating metal complex,
- \( M(Hg) \) = free metal atom in the mercury,
- \( n \) = number of electrons gained per atom,
- \( b^- \) = charge on the ligand ion,
- \( X^- \) = ligand ion, and
- \( p \) = ratio of ligand ions to metal ion or formula number.

The general polarographic wave equation can be written

\[
E^a = E_{1/2} - \frac{RT}{nF} \ln \frac{i}{i_d - i}
\]  

(34)

where

- \( E^a \) = applied potential,
- \( i \) = current at electrode at \( E^a \),
- \( i_d \) = maximum diffusion current, and
- \( E_{1/2} \) = half-wave potential of the metal ion.

Equation (34) can also be expressed as

\[
\frac{RT}{nF} = \frac{E_{1/2} - E^a}{\ln \frac{i}{i_d - i}}
\]  

(35)
and by plotting \((E_\frac{1}{2} - E^a)\) versus \(\ln \frac{i}{i_d - i}\), a graph similar to Figure (IV) is obtained.

\[ (E_\frac{1}{2} - E^a) \]

\[ \ln \frac{i}{i_d - i} \]

Figure IV

\((E_\frac{1}{2} - E^a)\) versus \(\ln \frac{i}{i_d - i}\)

The slope, \(m\), will be

\[ m = \frac{RT}{nF} \]  \hspace{1cm} (36)

and \(n\) can be determined from equation

\[ n = \frac{RT}{mF} \]  \hspace{1cm} (37)

If \(n\) is representative of the reaction, it will be nearly a whole number and reasonable. The plot in Figure IV should also be linear. If these conditions are not satisfied, it is very likely that the electrode process is irreversible and kinetically hindered by a secondary reaction. In such case, the further evaluation of the polarographic results to obtain \(K_f\) and \(p\) is apparently meaningless.
The reversible amalgam electrode potential, \( E_f \), for the free metal ion is given (6) by the Nernst equation

\[
E_f = E^0 - \frac{RT}{nF} \ln \frac{[M]}{[M^+]} \quad (38)
\]

where \([M]\) and \([M^+]\) are the effective concentrations respectively of the reduced metal and the uncomplexed metal ion at the electrode interface. The activities of the species considered will be represented as molar concentrations which for most practical purposes are adequate.

Introducing the formation constant, \( K_f \),

\[
K_f = \frac{[MX_p]}{[M^+]^p[X]^p} \quad (39)
\]

into equation (38), changes the electrode potential \( E_f \) to \( E_c \) (\( E_c \) is the electrode potential of the complexed metal ion),

\[
E_c = E^0 - \frac{RT}{nF} \ln K_f \frac{[M]}{[MX_p]} \quad (40)
\]

or

\[
E_c = E^0 - \frac{RT}{nF} \ln K_f \quad -p \frac{RT}{nF} \ln [X] - \frac{RT}{nF} \ln \frac{[M]}{[MX_p]} \quad (41)
\]

where the metal ion activity is changed because of complex formation.

Introducing diffusion current conditions into the Nernst equations (38) and (41), they now can be
expressed as

\[ E_f = E^0 - \frac{RT}{nF} \ln \frac{i}{i_d} \]  \hspace{1cm} (42)

and

\[ E_c = E^0 - \frac{RT}{nF} \ln K_f - p \frac{RT}{nF} \ln [X] - \frac{RT}{nF} \ln \frac{i}{i_d} \] \hspace{1cm} (43)

By subtracting equation (42) from equation (43) and introducing \( i = \frac{i_d}{2} \) (the current at half-wave potential \( E_{1/2} \)), the equation becomes

\[ (E_{1/2})_c - (E_{1/2})_f = - \frac{RT}{nF} \ln K_f - p \frac{RT}{nF} \ln [X] \] \hspace{1cm} (44)

Equation (44) can be differentiated to determine \( p \) knowing \( (E_{1/2})_f \) is constant.

\[ \frac{\Delta(E_{1/2})_c}{\Delta \ln [X]} = -p \frac{RT}{nF} \] \hspace{1cm} (45)

By graphing \( E_{1/2} \) versus \( \ln [X] \) for various solutions containing a large excess of ligand ions, the slope, \( Q \), will equal

\[ Q = p \frac{RT}{nF} \] \hspace{1cm} (46)

from which \( p \) may be determined.

The formation constant, \( K_f \), can now be calculated from the previously obtained values of \( n \) and \( p \) and by using equation (44). Two half-wave potentials are needed, \( (E_{1/2})_f \) for a free metal ion solution and \( (E_{1/2})_c \) for a complexed metal ion solution at ligand ion concentration, \([X]\). The incorporation of several half-wave
potentials at different ligand ion concentrations is advisable for a more accurate determination of $K_f$.

Figure V is an illustration of $(E_{f/2})_c$ versus $\ln [X]$, and the intercept is

$$(E_{f/2})_f - \frac{RT}{nF} \ln K_f$$

according to equation (44). This gives the formation constant upon calculation.

\begin{center}
\begin{tikzpicture}
    \draw[->] (0,0) -- (6,0) node[right] {$\ln [X]$};
    \draw[->] (0,0) -- (0,6) node[above] {$(E_{f/2})_c$};
    \draw (0,6) -- (6,0);
\end{tikzpicture}
\end{center}

Figure V

$(E_{f/2})_c$ versus $\ln [X]$

Spectrophotometric method

The absorbance, $A_i$, of a particular species in a solution is given by Beer's law as

$$A_i = a_i b C_i$$

(47)

where

- $a_i =$ molar absorption coefficient of species $i$,
- $b =$ length of light path, and
- $C_i =$ molar concentration of species $i$. 

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For an equilibrium reaction in solution, the equation is written

$$M + pX = MX_p$$  \hspace{1cm} (48)

disregarding charges on the species and assuming only one combination of species $M$ and $X$ are formed. Now the total absorbance, $A^0$, of the equilibrium solution at a particular wavelength is given by

$$A^0 = A_m + A_x + A_{mx}$$  \hspace{1cm} (49)

which is the total light absorbed by all species.

If ligand $X$ is assumed to be a nonabsorbing species, then

$$A_x = 0$$  \hspace{1cm} (50)

and

$$A^0 = A_m + A_{mx}$$  \hspace{1cm} (51)

According to equations (47) and (49), $A^0$ can be defined by

$$A^0 = a_m b [M] + a_{mx} b [MX_p]$$  \hspace{1cm} (52)

The total solution concentrations of the ligand, $C_x$, and the metal, $C_m$, is that amount added experimentally to the solutions. Using the reaction equation (48), it can be said that

$$C_m = [MX_p] + [M]$$  \hspace{1cm} (53)

and

$$C_x = p [MX_p] + [X]$$  \hspace{1cm} (54)
Yoe and Jones (23) have described a molar-ratio method for the determination of $p$ for a light absorbing complex $MX_p$. The method is carried out by graphing the absorbance, $A_0$, of a solution against the ratio $(C_X : C_m)$ where $C_X$ is the total metal ion concentration. In experimental application, $C_m$ is held constant while $C_X$ is varied widely and the absorbance measured at several concentrations of $C_X$. For a stable complex, it can be seen from equation (52) that $A_i$ is proportional to $C_X$ as long as $p(C_X) < C_m$ and forms a straight line on the graph. For $p(C_X) > C_m$, the absorbance is constant and forms another straight line parallel to the base line, $(C_X : C_m)$, assuming the ligand ion is transparent. By extrapolating the two straight lines, they will intersect at

$$C_X : C_m = p$$

where $p$ is the formula ratio of the complex.

The method is applicable where the molar extinction coefficients $a_m$ and $a_{mx}$ are different and if the complex formed is stable or does not dissociate appreciable. In the case of the formation of one complex species, the method is precise. However, if more than one complex is present in any appreciable amount, the method will indicate this by nonlinearity of the lines in the graph,
and will not necessarily be useful in determining the formula numbers of the various complexes present.

The formation constant, $K_f$, by definition is

$$K_f = \frac{[MX]^p}{[M][X]^p} \quad (56)$$

for the reaction given in equation (48).

The concentration of each species in the solution has to be determined either by a direct or indirect method to find $K_f$. By knowing the concentration of the reactants added, and by determining the concentration of one of the constituents in the resultant solution, the other concentration can be deduced using the $p$ obtained previously and equation (48).

To determine the free metal ion concentration, $[M]$, equation (52) must be changed to

$$\frac{A^0}{b} = a_m [M] + a_{mx}(C_m - [M]), \quad (57)$$

or

$$\frac{A^0}{b} = (a_m - a_{mx}) [M] + a_{mx} C_m, \quad (58)$$

$$[M] = \frac{A^0}{b} \frac{a_m - a_{mx}}{a_m - a_{mx}} = \frac{A^0}{b(a_m - a_{mx})} - \frac{a_{mx} C_m}{(a_m - a_{mx})} \quad (59)$$

The data needed to determine $[M]$ can be found experimentally. The total absorbance of the solution, $A^0$, at a given wavelength can be measured directly where $b$ is
the cell length. By using equation (47), $a_m$ can be
determined from the measurement of the absorbance of a
noncomplexing solution of the metal ion of known
concentration. $a_{mx}$ can be determined similarly under the
condition that the ligand ion is in great excess over
that of the metal ion needed. $C_m$ is known by working
with known concentrations of metal ion as is $C_x$ in the
solution.

Now that $[M]$ can be found, $[MX_p]$ can be determined
by
\[
[MX_p] = C_m - [M]
\]
and
\[
\]
Equation (56) then becomes
\[
K_f = \frac{[MX_p]}{[M][X]^p} = \frac{[MX_p]}{[M] (C_x - p[MX_p])^p} .
\]

The formation constant, $K_f$, is readily attainable
from absorbance measurements on solutions in which there
is an absorbance change due to the formation of a complex.
As the method is given here, either or both the metal ion
species and the complex species can absorb light at a
given wavelength. However, it should be emphasized that
the absorption coefficients, $a_{mx}$ and $a_m$, have to be
significantly different from each other to make the data
useful.
Summary

Three methods are given to determine the formula and the formation constant of a nickel tartrate complex.

A zero current potentiometric method of determining the parameters of complex formation is given. This method is directly applicable to reversible electrode potential measurements and also irreversible electrodes assuming the zero current potential can be interpolated from polarized electrode data.

A polarographic method is outlined. The half-wave potential shifts at various ligand ion concentrations are measured. The limitations of the method are discussed.

The spectrophotometric method for the determination of the parameters for a colored complex is also presented. Both the formula and the formation constant can be determined using the methods outlined. The application and limitations of the method are discussed.
EXPERIMENTAL AND RESULTS

Determination of the Formula and Formation Constant for Nickel Tartrate Complex

Potentiometric method

The measurement of the nickel electrode potential was attempted. The nickel electrode potential cannot be measured with zero current methods because it is an irreversible electrode. The exact cause of its irreversible nature is not known. However, it was felt that the potential could be determined by a polarization method outlined in the theoretical section.

The polarization of the nickel electrode was done by impressing various amounts of cathodic and anodic currents on the nickel electrode, independent of the voltage measuring circuit as shown on Figure VI. The polarizing current was determined by measuring the current resistance drop across a precision resistor that was in the polarizing circuit.

The nickel electrode potential was measured versus a saturated calomel electrode (S.C.E.). The potential was measured with a model K-2 Leeds and Northrup potentiometer which was calibrated with a N.B.S. standardized cell. Another method of potential measurement was also
Figure VI
Polarized Electrode Potentiometric Measurement Cell Schematic

$E_1$ = measured nickel electrode
$E_2$ = polarized nickel electrode
$E_3$ = saturated calomel electrode
$R_1$ = potential dividing resistor
$R_2$ = precision resistor
$P$ = potentiometer
$PS$ = power supply
$S$ = S.P.D.T. switch
$B$ = beaker
—used and found very convenient. This was the adaptation of a zeromatic Beckman pH meter (8) by increasing its sensitivity. The meter sensitivity could be increased tenfold which meant the full scale deflection was 140 millivolts. The instrument was standardized with the K-2 potentiometer. The error of the adapted zeromatic was less than one millivolt. This provided an instantaneous and accurate voltage reading device with very low current drain on the circuit measured.

The following experimental laboratory procedures were observed in an attempt to obtain meaningful potentiometric data:

1.) The cell was placed in a constant temperature bath.
2.) The nickel electrodes were annealed and electropolished.
3.) The electrode was vibrated vigorously in the solution.
4.) The solution was both stirred and unstirred.
5.) The cell was flushed with nitrogen gas to eliminate oxygen.
6.) The electrode was polarized for several hours at one current density value.
7.) The polarizing anodic and cathodic current densities ranged from $10^{-3}$ amp cm$^{-2}$ to $10^{-6}$ amp cm$^{-2}$.
8.) The concentration ranges of NiCl$_2$ in cell was 0.01M to 0.2M. The Na$_2$C$_6$H$_5$O$_7$ concentration ranged from 0.1M to 1.0M. The pH of the solutions was usually 6, however some runs were tried at more acidic conditions (pH = 2).
The determinations of the parameters of the nickel tartrate complex were not attainable by this method. The potential measurements were not reproducible enough. Typical data are given in the appendix.

Spectrophotometric method

Absorbance spectrograms were made on a Beckman DB in the visible light range of a 0.04M NiCl₂ solution, a 0.04M NiCl₂ and 0.04M Na₂C₄H₄O₆ solution, and a 0.04M Na₂C₄H₄O₆ solution. The nickel chloride solution had an absorbance maximum at 392₅₅ (A₀ = 0.21) and the nickel chloride, sodium tartrate solution had an absorbance maximum at 393₅₅ (A₀ = 0.48). The tartrate ion did not absorb at these wavelengths.

Further work with a Beckman DU spectrophotometer showed that the peak actually had a maximum at 400₅₅ for a nickel chloride, sodium tartrate solution. Since the DU instrument was used to measure the absorbance of the experimental solutions, the 400₅₅ value was used for the determination of Kᵢ and p, but 393₅₅ was still used to obtain the data for Figure VIII as the discrepancy between the two instruments had not been noticed at this point.

It was noted that the nickel tartrate complex was very slow to form. Figure VII is a graph of absorbance plotted against the concentration of nickel chloride and
Figure VII

Absorbance at 393\text{m}$\mu$ Versus Molar Concentration of Nickel Chloride and Sodium Tartrate

\[ \text{[NiCl}_2\text{]} = \text{[Na}_2\text{C}_4\text{H}_4\text{O}_6\text{]} \]

- at 15 hours
- at 1 hour
sodium tartrate at equal molar concentrations. The absorbance was measured at one hour and at fifteen hours. The graph demonstrates the time dependence of the complex formation. Meaningful data could not be taken until the solutions had stood for a day.

For the experimental data needed for a molar ratio plot, solutions were made up containing the same concentration of nickel chloride (0.049M NiCl₂). The sodium tartrate was added in a mole ratio to nickel chloride as indicated in Figure VII. The solutions were adjusted to pH = 6.0 and allowed to stand over night. The absorbance was measured in a 1.00 cm cell on the Beckman DU at 400nm.

The experimental procedure for the determination of the formation constant was done by successive dilutions of a solution that contained 0.049M NiCl₂ and 0.050M Na₂C₄H₄O₆. The solutions were adjusted to pH = 6.0 and allowed to stand 40 hours. The absorbance of the solutions was measured at 400nm and the results are in Table II. Most of the solutions were measured in a 1.0 cm cell on the DU spectrophotometer. The solutions (8) through (10) were also measured on the Beckman B with 5.00 cm cells.

From Figure VIII it is observed that the two straight lines intersect at the point where the mole ratio of nickel
## Table II

Absorbance of Nickel Tartrate Complex and Calculated $K_f$

<table>
<thead>
<tr>
<th>Trial No.</th>
<th>$[\text{Ni}^{++}]$</th>
<th>$[\text{C}_4\text{H}_4\text{O}_6^{-}]$</th>
<th>$A_{400\mu\text{m}}^0$ 1.0 cm cell</th>
<th>$A_{400\mu\text{m}}^0$ 5.0 cm cell</th>
<th>$K_f$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.0490</td>
<td>0.0500</td>
<td>0.545</td>
<td></td>
<td>4.4 x 10²</td>
</tr>
<tr>
<td>2</td>
<td>0.0390</td>
<td>0.0400</td>
<td>0.423</td>
<td></td>
<td>4.3</td>
</tr>
<tr>
<td>3</td>
<td>0.0343</td>
<td>0.0350</td>
<td>0.366</td>
<td></td>
<td>4.3</td>
</tr>
<tr>
<td>4</td>
<td>0.0294</td>
<td>0.0300</td>
<td>0.321</td>
<td></td>
<td>6.8</td>
</tr>
<tr>
<td>5</td>
<td>0.0245</td>
<td>0.0250</td>
<td>0.254</td>
<td></td>
<td>4.0</td>
</tr>
<tr>
<td>6</td>
<td>0.0196</td>
<td>0.0200</td>
<td>0.202</td>
<td></td>
<td>4.5</td>
</tr>
<tr>
<td>7</td>
<td>0.0147</td>
<td>0.0150</td>
<td>0.148</td>
<td></td>
<td>4.0</td>
</tr>
<tr>
<td>8</td>
<td>0.0098</td>
<td>0.0100</td>
<td>0.094</td>
<td>0.462</td>
<td>**</td>
</tr>
<tr>
<td>9</td>
<td>0.0073</td>
<td>0.0075</td>
<td>0.069</td>
<td>0.345</td>
<td>**</td>
</tr>
<tr>
<td>10</td>
<td>0.0049</td>
<td>0.0050</td>
<td></td>
<td>0.215</td>
<td>**</td>
</tr>
<tr>
<td>11</td>
<td>0.0490</td>
<td>0.0000</td>
<td>0.250</td>
<td>($a_M = 5.1$)</td>
<td></td>
</tr>
<tr>
<td>12</td>
<td>0.0490</td>
<td>0.5000</td>
<td>0.603</td>
<td>($a_{MX} = 12.3$)</td>
<td></td>
</tr>
</tbody>
</table>

* Measured on Beckman B.

** The calculated value of $K_f$ would be inaccurate at these concentrations.
Figure VIII

Molar Ratio Absorbance Study
Absorbance versus molar ratio
of sodium tartrate to nickel chloride
(pH = 6, cell length = 1.0 cm)
to tartrate is a ratio of one to one; thus it can be concluded that the major nickel tartrate complex present has a formula number of one. The formula of the complex is then $\text{Ni(C}_4\text{H}_4\text{O}_6$).

Using the above information and the formulas derived in the theoretical section of this thesis, the stability constant of the nickel tartrate complex was calculated using the data in Table II. The $K_f$ calculated for each set of data is listed in Table II.

**Polarographic method**

The determination of the formation constant, $K_f$, and the formula number, $p$, using polarography was attempted. The supporting electrolyte for this determination was $0.02\text{M}$ and $0.1\text{M NaNO}_3$. This supporting electrolyte was chosen because it appeared to be the least likely to interfere by complexing the metal. Also, the concentration was low so as to approach the conditions for the determination of a thermodynamic formation constant. Gelatin was present at $0.002\%$ as a suppressor. The half-wave potentials and diffusion currents were measured from the polarograms as described by Willard, Merritt, and Dean (21). The drop time of the mercury was approximately 2.5 seconds. The polarograph used was a Sargent Model XV.
From the data tabulated in Table III and plotted in Figure IX, n can be calculated using equation (35).

\[
\text{Slope } m = - \frac{\Delta(E_{1/2} - E^\circ)}{\Delta(\ln \frac{1}{d} - \frac{1}{d})} = -0.99v -(-1.06v) = -0.206
\]

\[
n = -\frac{RT}{mF} = \frac{0.0591}{0.206} = 0.29
\]

This is not a reasonable number of electrons exchanged in the reaction. In the reduction of the nickelous ion (Ni^{2+}), the expected number, n, of gained electrons should be two per atom and, in any case, an integral number. As suggested in the theoretical section, this indicates the dropping mercury electrode reaction is irreversible and the use of this method is not valid for the determination of \(K_f\) and \(p\). For example, the \(p\) was calculated to be 26.4, assuming \(n = 2\). The formation constant, \(K_f\), was calculated to be \(4 \times 10^{-9}\), assuming \(p = 1\) and using the polarographic data obtained in the laboratory.

**Determination of Nickel and Tin Polarographic Parameters**

Solutions were made up of varying concentrations of nickel chloride and stannic chloride in 5.0M calcium chloride and 5.0 x 10^{-3} weight percent of gelatin as a suppressor. The diffusion currents and \(E_{1/2}\) were then measured on a recording polarograph at 25°C.
Table III

Polarograph Currents at Various Voltages for a Nickel Tartrate Complex

<table>
<thead>
<tr>
<th>$E^a$(S.C.E.)</th>
<th>$i_{mm}^*$</th>
<th>$\frac{i}{i_d - i}$</th>
<th>$\log \frac{i}{i_d - i}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>-0.93</td>
<td>24</td>
<td>0.28</td>
<td>-0.553</td>
</tr>
<tr>
<td>-0.94</td>
<td>32</td>
<td>0.43</td>
<td>-0.367</td>
</tr>
<tr>
<td>-0.95</td>
<td>38</td>
<td>0.52</td>
<td>-0.284</td>
</tr>
<tr>
<td>-0.96</td>
<td>47</td>
<td>0.65</td>
<td>-0.187</td>
</tr>
<tr>
<td>-0.97</td>
<td>56</td>
<td>0.78</td>
<td>-0.108</td>
</tr>
<tr>
<td>-0.98</td>
<td>68</td>
<td>0.91</td>
<td>-0.051</td>
</tr>
<tr>
<td>-0.99</td>
<td>76</td>
<td>1.00</td>
<td>0</td>
</tr>
<tr>
<td>-1.00</td>
<td>84</td>
<td>1.09</td>
<td>+0.037</td>
</tr>
<tr>
<td>-1.01</td>
<td>95</td>
<td>1.22</td>
<td>+0.086</td>
</tr>
<tr>
<td>-1.02</td>
<td>101</td>
<td>1.30</td>
<td>+0.114</td>
</tr>
<tr>
<td>-1.03</td>
<td>110</td>
<td>1.42</td>
<td>+0.152</td>
</tr>
<tr>
<td>-1.04</td>
<td>122</td>
<td>1.61</td>
<td>+0.207</td>
</tr>
<tr>
<td>-1.05</td>
<td>126</td>
<td>1.68</td>
<td>+0.225</td>
</tr>
<tr>
<td>-1.06</td>
<td>132</td>
<td>1.82</td>
<td>+0.260</td>
</tr>
<tr>
<td>-1.07</td>
<td>137</td>
<td>1.96</td>
<td>+0.292</td>
</tr>
</tbody>
</table>

*Current expressed in millimeters from polarogram

1mm = 0.015 microamp.

$i_d$ = 152mm

$E^a = -0.99$ volts (S.C.E.)

$[\text{Ni(NO}_3\text{)}_2] = 5 \times 10^{-4}$ M

$[\text{Na}_2\text{C}_4\text{H}_4\text{O}_6] = 3 \times 10^{-3}$ M
Figure IX

Polarographic Diffusion Current and Voltage Graph of a Nickel Tartrate Complex

$log \frac{i}{l_d - i}$ versus Applied Voltage

$E^a$, Volts (S.C.E.)
The half-wave potentials of nickel chloride and stannic chloride solutions were determined at several concentrations. They were equal for the most part, and the half-wave potentials were (-0.48v) to (-0.50v) (S.C.E.). Instrumental difficulties were encountered with the polarograph response and more accurate data were not obtainable.

The maximum diffusion current, $i_d$, was determined at a fixed nickel chloride concentration. The stannic chloride was then added at increasing increments of concentration to the same nickel chloride solution. The increase in maximum diffusion current, $\Delta i_d$, was determined for each solution, that is,

$$\Delta i_d^{\text{Sn}} = (i_d)^{\text{total}} - (i_d)^{\text{Ni}}.$$  

In Figure X, the increment diffusion current ($\Delta i_d$) from the data in Table IV due to the tin reduction versus the stannic concentration is graphed, and the point where the maximum diffusion current of the two metals were equal (0.55 $\mu$A) was determined. The concentration of stannic chloride at this point is projected from the graph. The molar ratio of stannic chloride to nickel chloride is (1.4:1.0) for equal maximum diffusion currents.
Figure X

Molar Concentration of Tin Versus Polarographic Diffusion Current of Tin

\[ [\text{Ni}^{++}] = 2.32 \times 10^{-4} = 5.5 \times 10^{-1} \text{ micro amp} \]

- = diffusion current of tin
- = diffusion current of nickel

\( (\Delta I_d)_{SN} \) - micro amp
Table IV

Nickel and Tin Diffusion Current Data

<table>
<thead>
<tr>
<th>Solution Number</th>
<th>Ion Concentrations</th>
<th>$I_d$</th>
<th>$\Delta I_d$</th>
<th>$E_2$(S.C.E.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>$[\text{Ni}^{+4}] = 2.32 \times 10^{-4}$</td>
<td>0.55μA</td>
<td>0.00μA</td>
<td>-0.47V</td>
</tr>
<tr>
<td></td>
<td>$[\text{Sn}^{+4}] = 0$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>II</td>
<td>$[\text{Ni}^{+4}] = 2.32 \times 10^{-4}$</td>
<td>0.75μA</td>
<td>0.20μA</td>
<td>-0.49V</td>
</tr>
<tr>
<td></td>
<td>$[\text{Sn}^{+4}] = 1.27 \times 10^{-4}$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>III</td>
<td>$[\text{Ni}^{+4}] = 2.32 \times 10^{-4}$</td>
<td>0.90μA</td>
<td>0.45μA</td>
<td>-0.49V</td>
</tr>
<tr>
<td></td>
<td>$[\text{Sn}^{+4}] = 2.54 \times 10^{-4}$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>IV</td>
<td>$[\text{Ni}^{+4}] = 2.32 \times 10^{-4}$</td>
<td>1.34μA</td>
<td>0.79μA</td>
<td>-0.50V</td>
</tr>
<tr>
<td></td>
<td>$[\text{Sn}^{+4}] = 3.81 \times 10^{-4}$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>V</td>
<td>$[\text{Ni}^{+4}] = 0$</td>
<td>0.65μA</td>
<td></td>
<td>-0.50V</td>
</tr>
<tr>
<td></td>
<td>$[\text{Sn}^{+4}] = 2.54 \times 10^{-4}$</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Nickel-Tin Alloy Electrodeposition

For a solution made up as a possible electroplating bath, the molar ratio of stannic chloride to nickel chloride (0.7:1.0) was used due to an erroneous calculation. The solution contained 0.75M NiCl₂, 0.50M SnCl₄, and 3.36M CaCl₂. The calcium chloride was added as a supporting electrolyte and complexing agent.

The electroplating was done in the apparatus shown in Figure XI. The cathode surface was the end of a 0.75 inch copper bar with the area of 2.85 cm². The end of the bar was flush with the surface of the rubber stopper in which it was mounted. This was done to avoid edge effects. For analysis of the plate, the copper bar was removed and the plate was turned off on a lathe. During the electrodeposition of the plate, the solution was not agitated.

The cathode was electropolished before attempting each plate. This was accomplished by placing concentrated H₃PO₄ in the plating apparatus. The anodic current density was increased until the evolution of oxygen gas (iₐ ≈ 200ma) at the electrode surface was visually evident and then decreased slightly (17). The H₃PO₄ electrolyte was stirred vigorously at the electrode surface with a vibrating electric stirrer. The surface
obtained was very brilliant. It was discovered that the electropolished surface was smoother when the copper bar was first annealed at an elevated temperature.

The plating was done with nickel and tin anodes placed in the solution. The exposed areas of the nickel and tin anodes were calculated to be equal. This was done in order to replenish the bath in a nearly uniform manner with nickel and tin. An unusual feature of the circuit was the use of silicon diodes placed between the anodes (Figure XI) to block any corrosion currents between them. The solutions used for electroplating were replaced often so as to avoid serious concentration changes.

The E.M.F. source was a nickel-cadmium battery capable of 6 volts and several amperes. The current was controlled by using a variable resistor in series. The current measurement was done with an ordinary laboratory Weston ammeter. No attempt was made to measure polarizing voltage. A special electrode was built, however, to measure this, but the course of the search did not merit its use.

The plating of the alloy was attempted at several current densities as given in Table V. The current densities were maintained above those predicted by equation (3) to assure a diffusion controlled reaction.
$E_1$ = nickel anode
$E_2$ = tin anode
$E_3^{Cu}$ = copper cathode
$D^S$ = silicon diode
$S$ = rubber stopper
$G$ = glass tube
$R$ = voltage divider
E.M.F. = 6 volt nickel-cadmium battery

**Figure XI**

Electroplating Cell Schematic
The plates obtained contained only small amounts of tin. The plates were black, rough, and crumbly.

The copper electrode surface was amalgamated with mercury for one day before an electrolysis was attempted. This was an attempt to simulate polarographic conditions. The resulting plate was not obviously different from those obtained previously.

Because the parameters of the tin tartrate complexes were not known and the lack of time, the use of a tartrate ion electroplating bath for a nickel-tin alloy deposition was not attempted.

Table V

Tabulation of Deposits Obtained from a Bath of Calcium Chloride, Stannic Chloride, and Nickel Chloride

<table>
<thead>
<tr>
<th>Current Density $10^{-3}$ amp cm$^{-2}$</th>
<th>Appearance of Plate</th>
<th>Molar Ratio of Sn: Ni in Plate</th>
</tr>
</thead>
<tbody>
<tr>
<td>75</td>
<td>Rough, Black</td>
<td>0.06</td>
</tr>
<tr>
<td>1</td>
<td>Matte, Black</td>
<td>trace</td>
</tr>
<tr>
<td>100</td>
<td>Rough, Black</td>
<td>0.10</td>
</tr>
<tr>
<td>100</td>
<td>Rough, Black</td>
<td>0.10</td>
</tr>
<tr>
<td>*75</td>
<td>Excessive Treeing</td>
<td>trace</td>
</tr>
</tbody>
</table>

*The surface of the copper electrode was first amalgamated with mercury.
Analysis of deposits

Standard solutions were made up of nickel sulfate and stannous chloride. The nickel sulphate solution was standardized by the electrodeposition of the nickel onto a platinum electrode. Knowing the actual weight of electroplated nickel and the volume of the solution used, the concentrations were readily calculated.

The standard tin solution was made up from pure tin metal that was dissolved in concentrated hydrochloric acid. This method was accurate enough for the work here.

The alloy analysis for total nickel and tin was performed by first dissolving the alloy in concentrated hydrochloric acid. The solution was then diluted to a known volume and analyzed for nickel and tin content.

Polarography was utilized for the analysis of tin. The supporting electrolyte used was 260g liter$^{-1}$ ammonium chloride, 0.2 weight percent gelatin, and the addition of concentrated hydrochloric acid to maintain the acidity at a constant value. The diffusion current, $i_d$, was found in terms of equivalent molar tin using the standard solution.

The analysis of nickel was adapted from a method outlined by Sandell(19). The method involves the extraction of a dimethylglyoxime chelate with successive
volumes of chloroform. The absorbance of the chloroform solution was measured on the spectrophotometer at 375μm. A Beer's law study was made using the standardized nickel sulfate solution.

All chemicals used in this search were of analytical quality, A.C.S. or better. The tartaric acid was optically active, d-configuration. The electrode used in the potentiometric measurements was a 0.040 inch diameter wire obtained from International Nickel Company.

All work involving solutions was done at room temperature.
SUMMARY OF RESEARCH

Alloy Deposition

The polarographic determination of the half-wave potentials of \((\text{Sn}^{++})\) and \((\text{Ni}^{++})\) were confirmed to be equal in a 5.0M CaCl\(_2\) supporting electrolyte. The relative molar diffusion currents of the nickelous and stannic ions were determined.

The electrodeposition of a NiSn alloy was not obtained from a concentrated chloride bath containing nickelous chloride and stannic chloride. The plate obtained was very rough and contained only small amounts of tin. The use of silicon diodes in the anode branch of the electroplating cell was effective in preventing corrosion between the nickel anode and the tin anode.

Formula and Formation Constant for Nickel Tartrate

The determination of the formation constant and the formula for a nickel tartrate complex was attempted by three methods.

The potentiometric method was not successful because the nickel electrode system was irreversible. The determination of the zero current potentials from
polarized electrode data was unsuccessful because reproducibility was not found.

The polarographic method was not applicable. On examination of the data, the amalgam electrode reaction was irreversible; therefore the data were not applicable.

The spectrophotometric method was applicable. The formula of nickel tartrate is $\text{Ni(C}_4\text{H}_6\text{O}_6$ and the formation constant is $4 \times 10^2$. This is for a $25^\circ\text{C}$ solution and the complex was formed from sodium tartrate and nickel chloride. The concentrations ranged from $0.05\text{M}$ to $0.015\text{M}$ of both nickel chloride and sodium tartrate. The complex absorbance maximum was found to be $400\text{m}$. It was also noted that the formation of the nickel tartrate from a sodium tartrate, nickel chloride solution was slow. The solution would reach equilibrium only after standing a day or so.
APPENDIX

Typical Data from Polarized Nickel Electrode
Potentiometric Measurements at
25°C, 0.5M NiCl₂, 0.5M C₄H₄O₆, and pH = 2.0

<table>
<thead>
<tr>
<th>Polarizing Current* (microamp cm⁻²)</th>
<th>Time Lapse at Each Current Setting (minutes)</th>
<th>Potential of Electrode (volts) Versus S.C.E.</th>
</tr>
</thead>
<tbody>
<tr>
<td>-10</td>
<td>3</td>
<td>-0.285</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>-0.275</td>
</tr>
<tr>
<td></td>
<td>6</td>
<td>-0.268</td>
</tr>
<tr>
<td></td>
<td>7</td>
<td>-0.266</td>
</tr>
<tr>
<td>+10</td>
<td>1</td>
<td>-0.140</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>-0.146</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>-0.154</td>
</tr>
<tr>
<td></td>
<td>14</td>
<td>-0.152</td>
</tr>
<tr>
<td>+5</td>
<td>1</td>
<td>-0.166</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>-0.163</td>
</tr>
<tr>
<td></td>
<td>6</td>
<td>-0.158</td>
</tr>
<tr>
<td>-5</td>
<td>1</td>
<td>-0.204</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>-0.196</td>
</tr>
<tr>
<td></td>
<td>11</td>
<td>-0.189</td>
</tr>
<tr>
<td></td>
<td>31</td>
<td>-0.166</td>
</tr>
<tr>
<td></td>
<td>59</td>
<td>-0.146</td>
</tr>
<tr>
<td></td>
<td>98</td>
<td>-0.141</td>
</tr>
<tr>
<td></td>
<td>120</td>
<td>-0.140</td>
</tr>
<tr>
<td>+5</td>
<td>5</td>
<td>-0.130</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>-0.132</td>
</tr>
<tr>
<td>-5</td>
<td>1</td>
<td>-0.148</td>
</tr>
<tr>
<td></td>
<td>17</td>
<td>-0.146</td>
</tr>
<tr>
<td>0</td>
<td>30</td>
<td>------</td>
</tr>
<tr>
<td>+10</td>
<td>1</td>
<td>-0.164</td>
</tr>
<tr>
<td>-10</td>
<td>1</td>
<td>-0.188</td>
</tr>
</tbody>
</table>

*(-) cathodic current, (+) anodic current

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BIBLIOGRAPHY


2. R. Egland, unpublished work.


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VITA

The author was born and raised on a fruit farm near Bangor, Michigan. He attended the public school system there. Upon graduation from high school in 1957, he attended Moody Bible Institute for one academic year.

In 1958 he entered Western Michigan University and, majoring in chemistry and physics, obtained a Bachelor of Science Degree in 1962. He subsequently entered graduate study in chemistry at the same university. He was a participant in a National Science Foundation summer research grant in 1962 and also received two teaching assistantships during his graduate study. In August 1964, he began working for The Dow Chemical Company where he is currently employed as a research chemist.