A POLAROGRAPHIC STUDY OF THE COPPER-FORMAMIDINE DISULFIDE DIHYDROCHLORIDE SYSTEM IN AQUEOUS SOLUTION

BY

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A THESIS

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INTRODUCTION
Many studies have been made on the solid complexes of thiourea with various metal ions. However, much less information is available on these systems in solutions. The copper(II)-thiourea system is especially intriguing.

Copper(II) complexes of thiourea (tu) are reported to be unstable (1) (2). Only one reference makes any attempt to describe the reaction products (3). They report that formamidine disulfide dihydrochloride (FDS•2HCl) and a copper(I) complex of thiourea result when cupric chloride is added to thiourea. However, it is felt by this author that inadequate proof is presented for the presence of FDS•2HCl as a reaction product. In addition, if FDS•2HCl is formed, it is surprising that complexation was not observed between the FDS•2HCl and the copper present in the solution. If FDS•2HCl can form complexes with copper, it would appear that cupric ions might be stabilized in the presence of thiourea.

The FDS•2HCl-tu system has been the subject of several redox studies (4) (5) (6). However, no attempt has been made to study the complexing ability of FDS•2HCl. It is, therefore, the purpose of this research to study the properties of FDS•2HCl as a chelating agent in the copper(II)-thiourea system.

The study of this system poses many problems—the low pK_a of thiourea, the low solubility of thiourea complexes, the lack of stability of FDS•2HCl in aqueous solutions, and the lack of highly colored copper complexes with FDS•2HCl. Infrared analyses
of the solid complexes of the copper complexes of FDS*2HCl and
polarographic analyses of aqueous solutions of these complexes
were undertaken.
Solid Complexes of Thiourea. The solid complexes of manganese(II), nickel(II), cadmium(II), mercury(II), zinc(II), cobalt(II), iron(II), and calcium(II) with thiourea (tu) were prepared in 1906 by Rosenheim and Meyer (7). Rathke in 1884 showed the existence of complexation between copper(I) and thiourea (8). Kohlschütter prepared many thiourea complexes of cuprous salts (9).

The structures of the compounds Zn(tu)₂Cl₂, Pb(tu)₂Cl₂, Ni(tu)₄Cl₂, Ni(tu)₂(NCS)₂ and Cu(tu)₃Cl have been determined by X-ray crystallography (10) (11). In each case only sulfur-metal bonds were found. Infrared studies on complexes of platinum(II), palladium(II), zinc(II), nickel(II) (12) (13), cobalt(II) (14), copper(I), manganese(II), mercury(II), cadmium(II), lead(II) (10), and iron(II) (15) (16) with thiourea indicate only metal to sulfur bonding. Far-infrared spectra studies by Adams and Cornell (17) agree with the above conclusions. However, Rivest (18) argues on the basis of infrared analysis that thiourea bonds through nitrogen to titanium.

Oxidation of Thiourea. Many oxidizing agents may be used to convert thiourea to formamidine disulfide (FDS). Werner (14) in 1912 found that iodine in neutral or acid solutions would oxidize thiourea to formamidine disulfide disulfide dihydroiodide (FDS·2HI). In basic solutions iodine oxidized thiourea to free sulfur. Hydrogen gas reduced FDS·2HNO₃ back to thiourea. In another article Werner (5) found that thiourea in the presence of strong acids could be
oxidized by HNO₂ to produce FDS·2HX where X is the anion of the strong acid utilized. In the presence of weak acids, such as acetic acid, thiocyanic acid is produced. Preisler and Berger (6) oxidized thiourea with hydrogen peroxide to obtain formamidine disulfide. They titrated thiourea with ceric sulfate to obtain FDS and backtitrated with stannous sulfate.

For the oxidation of thiourea to formamidine disulfide in 1 N H₂SO₄ at platinum electrodes at 30°C, Preisler and Berger report Eₒ' = +0.420 volts referred to the normal hydrogen electrode (6).

Cu(II)-Thiourea. Several references state that copper(II) complexes of thiourea are unstable and therefore do not exist (1) (2). Only a single polarographic wave is observed corresponding to the reduction of a copper(I) complex of thiourea when copper(II) and thiourea are put into a solution of 0.1 N potassium nitrate (1). The following reaction occurs when cupric chloride is added to thiourea (3).

\[ 2 \text{CuCl}_2 + 2 \text{CSN}_2\text{H}_4 \rightarrow 2 \text{CuCl} + (\text{CSN}_2\text{H}_4)_2\text{Cl}_2 \]

Irreversible Polarography. Only a minority of electrode processes proceed reversibly at the dropping mercury electrode (D.M.E.). The slow establishment of equilibrium between the oxidized and reduced forms of the depolarizer is considered to be the cause of irreversibility (19a).

To interpret such electrode processes it is necessary to
introduce kinetic considerations. If the reaction occurring at the D.M.E. can be written simply as

\[ \text{O} + \text{ne} \rightleftharpoons \text{R} \]

where O is the species being reduced and R is the product of the reduction, and if, for simplicity, the electrode process is of the first order, then

\[ \frac{dN_0}{dt} = \frac{dN_R}{dt} = k_f h C_0 - k_b h C_R \]

where the C's are the concentrations and the k's are the formal rate constants. A substance which undergoes a chemical transformation must overcome an energy barrier. An electrical field exists about the surface of the D.M.E. This field favors electrochemical reduction and therefore hinders the reaction to occur in the other direction. The fraction \( \alpha E \) of the potential favors the cathodic reaction; the fraction \( (1 - \alpha)E \) hinders the anodic reaction. The parameter \( \alpha \) is called the transfer coefficient (20a).

Irreversible cathodic half-wave potentials are more negative than reversible half-wave potentials (21a). The difference between the half-wave potential of an irreversible wave and the reversible half-wave potential \( E^0 \) is the polarographic overpotential \( \eta_{1/2} \) (19a).

\[ \eta_{1/2} = (E_{1/2})_{\text{irrev.}} - E^0 \]

The slope of an irreversible wave differs from the slope of a reversible wave. A plot of \( \frac{i}{i_d} \) vs. \( E_{d,e} \) may be linear, but
The apparent number of electrons involved in the half-reaction as determined from the slope according to the equation for reversible waves is smaller than the actual number of electrons consumed in the electrode process (19a).

The following equation may be applied for irreversible waves at 25°C

\[ E_{d,e.} = E_1^\frac{1}{2} - \frac{0.05915}{\alpha n} \log \frac{i}{i_d - i} \]

where \( E_{d,e.} \) is the potential at the dropping mercury electrode, \( E_1^\frac{1}{2} \) is the half-wave potential, \( \alpha \) is the transfer coefficient, \( n \) is the number of electrons in the reduction half-reaction occurring at the D.M.E., \( i \) is the current at the end of the drop life of the D.M.E. at the potential \( E_{d,e.} \), and \( i_d \) is the diffusion current (21b). This equation is derived in the Appendix.

This equation derived from kinetics for irreversible processes is very similar to the equation for reversible waves

\[ E_{d,e.} = E_1^\frac{1}{2} - \frac{RT}{nF} \ln \frac{i}{i_d - i} \]

or, at 25°C

\[ E_{d,e.} = E_1^\frac{1}{2} - \frac{0.05915}{n} \log \frac{i}{i_d - i} \]

The equation for irreversible waves differs only in the coefficient of the log term and by the fact that the currents are those at the ends of the drop lives (21b). The irreversible half-wave potential
is not a thermodynamic half-wave potential as is the reversible half-wave potential.
Apparatus

All polarograms were run on a Fisher Model 65 Electropode with a Fisher Model 66 Recording Accessory. The polarographic cell was prepared from a standard 150 x 25 mm o.d. test tube. The dropping mercury electrode was prepared from 75 mm of Fisher Scientific Electropode Capillary Tubing (catalog number 13-776-5). The mercury pressure was adjusted by raising or lowering the mercury reservoir containing triply distilled mercury and reading the mercury height directly from the buret. A Fisher Scientific Special 2½-inch Calomel Reference Electrode (catalog number 13-776-10) was inserted in saturated potassium chloride solution in one test tube. Electrical contact between the calomel electrode and the polarographic cell was through a saturated potassium chloride-agar salt bridge. The inert electrolyte was 2.0 M HCl, 0.5 M KCl. The polarographic apparatus is shown in Figure I.

Procedure

To provide maximum accuracy in reading voltage values from the graph, the voltage values were observed at the end as well as the beginning of each polarogram. The appropriate current sensitivity was so chosen that the polarographic wave covered as much of the full range of the recorder as possible. Current measurements were taken from the maxima of the recorder excursions since these maxima represent true current values at the termination of
Figure I

DIAGRAM OF THE POLAROGRAPHIC CELL
drop life. All current readings were corrected for residual current. Potentials as read from the Applied Potential Dial on the polarograph were checked against a Leeds and Northrup Students' Potentiometer (catalog number 7645) using a Leeds and Northrup Reflecting Type Galvanometer 2h35-b and were found to agree within ±.002 volts. A polarogram of 1.0 x 10⁻³ M CuCl₂, 1.0 M NH₄OH, 1.0 M NH₄Cl gave half-wave potentials at -.22 volts and -.51 volts vs. S.C.E. in agreement with E₁/₂ values published by Meites (21c).

The capillary constant (m²/3t¹/₂) measured at 25°C and -0.25 volts in 2.0 M HCl, 0.5 M KCl was 2.31 mg²/³sec⁻¹/₂. The mercury level was maintained at a height of 27.0 cm and the drop time (at 25°C and -0.25 volts) was 3.68 seconds in solution.

Prior to analysis solutions were deaerated with nitrogen gas for ten to fifteen minutes. The nitrogen was bubbled through alkaline pyrogallol and a constant temperature solution of 2.0 M HCl, 0.5 M KCl before it entered the cell. The pyrogallol served to remove any traces of oxygen from the nitrogen gas. The 2.0 M HCl, 0.5 M KCl solution presaturated the nitrogen to prevent evaporation of the analysis solution.

Materials

Fisher Certified Reagent Grade thiourea, Fisher Certified anhydrous CuCl₂, Fisher Certified A.C.S. KCl, and Fisher Reagent A.C.S. HCl were used without further purification. The cupric
chloride was dried in an oven before use. The melting point of
the thiourea was 180°C in agreement with a literature value (22).

All distilled water was run through a Barnstead Mixed Bed
Hose Type Ion Exchange Column No. 8902 before being used to make
up all solutions. Fisher Laboratory gelatin U.S.P. served as maxi­
mum suppressor. The mercury metal used in this work was continuous
vacuum triply distilled mercury from Bethlehem Apparatus.

Preparation of FDS•2HCl. Formamidine disulfide dihydrochloride
(FDS•2HCl) was prepared from Fisher Certified Reagent Grade thiou­
rea. A quantity of 7.6 grams of thiourea was dissolved in 75 ml
of 3 N hydrochloric acid. This solution was placed in an ice water
bath and 7.5 ml of 30% hydrogen peroxide added slowly while stir­
ing. An amount of 320 ml of ethanol was added followed by 83 ml
of concentrated HCl. The crystalline precipitate which formed was
filtered off by suction, washed several times with ethanol, and
dried over phosphorus pentoxide (6). The structure of FDS•2HCl is
illustrated in Figure III.

Characteristics of FDS•2HCl. The infrared spectra of formami­
dine disulfide dihydrochloride is given in Table I on page 21.
All IR Spectra were recorded in KBr pellets on a Beckman IR 8
(catalog number 70802).

The FDS•2HCl melted and decomposed at 130-147°C. This is in
contrast to a value of 155°C as reported by Werner (23). However,
the melting and decomposition point of FDS•2HCl as prepared by
Figure II

\[
\begin{align*}
\text{A} & : \quad \text{H}_2\text{N} - \text{C} - \text{NH}_2 \\
\text{B} & : \quad \text{H}_2\text{N} - \text{C} - \equiv \text{NH}_2 \\
\text{C} & : \quad \text{H}_2\text{N} - \text{C} - \text{NH}_2
\end{align*}
\]

RESONANCE CONFIGURATIONS OF THIOUREA

Figure III

\[
\begin{align*}
\text{H}_2\text{N} & \equiv \text{NH} \cdot \text{HCl} \\
\text{S} & \equiv \text{S} \\
\text{H}_2\text{N} & \equiv \text{NH} \cdot \text{HCl}
\end{align*}
\]

STRUCTURE OF FORMAMIDINE DISULFIDE DIHYDROCHLORIDE
Nutritional Biochemicals Corporation was 127-140°C. A mixture of the two melted and decomposed at 134-148°C indicating that both products were the same.

When 0.120± gm of FDS•2HCl was dissolved in 5.0 ml of distilled water, the freezing point was depressed by 0.60 ± .005°C.

\[ \Delta T = K_f \cdot m \]

\[ \Delta T = \text{freezing point depression} \]

\[ K_f = \text{molal freezing point depression constant} \]

\[ m = \text{molality} \]

\[ m = \frac{\Delta T}{K_f} = \frac{0.6}{1.86} = 0.32 \text{ moles/1000 gm H}_2\text{O} \]

\[ \frac{0.120\mu \text{ gm}}{5 \text{ gm H}_2\text{O}} = \frac{x \text{ gm}}{1000 \text{ gm H}_2\text{O}} \]

\[ x = 2\mu \text{ gm/1000 gm H}_2\text{O} \]

\[ \text{Mol. Wt.} = \frac{\text{gm}}{\text{mole}} = \frac{2\mu}{0.32} = 75 \text{ gm/mole} \]

Since one mole of FDS•2HCl ionizes in water to yield three moles of ions as follows

\[ \text{FDS•2HCl} \rightleftharpoons (\text{FDS•2H})^{+2} + 2\text{Cl}^- \]

and since freezing point depression is a colligative property, the molecular weight should be

\[ 75 \times 3 = 220 \text{ gm/mole} \]

The actual molecular weight of FDS•2HCl is 223.16 gm/mole. The experimentally determined molecular weight was off by 1.3%.

Repeating the freezing point experiment, 0.2074 gm of FDS•2HCl
was dissolved in 5.0 ml of H₂O as before. The freezing point depression was 1.0°C. This gave a molecular weight of 230 gm/mole in error by 3.1%.

It should be noted at this point that these molecular weight determinations were made within one hour after the FDS·2HCl was put into solution since FDS·2HCl was found to decompose overnight in aqueous solution producing free sulfur.

Preparation of Cut₃Cl. The compound Cu(SCN₂H₄)₃Cl was prepared by the method of Kohlschütter (9). A quantity of 22.8 gm of thiourea was added to 100 ml of water and heated to 70°C. Then 9.85 gm of CuCl was added while stirring with a magnetic stirrer. The solution was cooled to 10°C and filtered. The infrared spectra of this compound is reported in Table I on page 21 and is in good agreement with the values reported by Swaminathan and Irving (10).

Preparation of Cu(I) Complex of FDS·2HCl. A copper(I) complex of FDS·2HCl was prepared by placing 100 ml of 2 N HCl in an ice bath, adding 1.12 gm of formamidine disulfide dihydrochloride followed by 3.96 gm of cuprous chloride, and adding an additional 150 ml of 2 N HCl. The precipitate was filtered and washed with HCl until the filtrate was colorless. The compound decomposes over a period of a day or two. The product was analyzed by electrodeposition and found to contain 29.4% Cu. If the formula of the complex were Cu₂(S₂C₂N₂H₆Cl₂)Cl₂, it should contain 30.2% copper. The infrared spectra is recorded in Table I on page 21.
Preparation of Cu(II) Complex of FDS·2HCl. A Cu(II) complex of formamidine disulfide dihydrochloride was prepared by dissolving 2.79 gm of FDS·2HCl in 100 ml of 2 N HCl at 0°C. In addition, 0.24 gm of CuCl$_2$ was dissolved in 50 ml of 2 N HCl. The CuCl$_2$ solution was added to the FDS·2HCl solution and stirred with a magnetic stirrer. Another 100 ml of 2 N HCl was added. An IR of the precipitate is given in Table I on page 21. The Cu(II) complex of FDS·2HCl decomposes more readily than the Cu(I) complex.
RESULTS
Infrared Spectra

The infrared spectra of thiourea, formamidine disulfide dihydrochloride, Cu\textsubscript{4}Cl\textsubscript{3}, and two copper complexes of FDS\textsubscript{2}HCl are given in Table I. Several shifts in absorption peaks are noted. The 1460 cm\textsuperscript{-1} peak of thiourea is shifted to larger values in the other four compounds. The 730 cm\textsuperscript{-1} peak of thiourea decreases in frequency. The 1600 cm\textsuperscript{-1} peak of thiourea shifts to a larger value for FDS\textsubscript{2}HCl but remains essentially constant for the three complexes. The 1650 cm\textsuperscript{-1} band of FDS\textsubscript{2}HCl is lowered in all three complexes.

Polarography of FDS\textsubscript{2}HCl

The FDS\textsubscript{2}HCl Wave. A polarogram of FDS\textsubscript{2}HCl is shown in Figure IV. Both the rate constant \(k_{f,h}^0\) (see Appendix) and \(\alpha n_a\) (see page 7) are often drastically altered by the presence of maximum suppressors. The value \(n_a\) is the number of electrons in the rate determining step. Adsorption of a maximum suppressor onto the mercury drop surface might change the structure of the electrical double layer around the drop and might hinder certain orientations of the electroactive ion with respect to the drop surface. Therefore, no maximum suppressor was used.

The wave is well-defined and indicates a one step reduction. The wave is irreversible since a plot of \(E_{d,e}\) vs. \(\log \frac{i}{i_{d-1}}\) does
Table I

ABSORPTION MAXIMA IN CM⁻¹ OF THIOUREA, FDS·2HCl, AND THEIR COPPER COMPLEXES

<table>
<thead>
<tr>
<th>THIOUREA</th>
<th>FDS·2HCl</th>
<th>Cu₄Cl⁺</th>
<th>FDS·2HCl + CuCl</th>
<th>FDS·2HCl + CuCl₂</th>
</tr>
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<tr>
<td>3100-3400(b)</td>
<td>2900-3300(b)</td>
<td>3460(m)</td>
<td>2950-3450(b)</td>
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</tr>
<tr>
<td>2680(w)</td>
<td>2700(w)</td>
<td>2660(w)</td>
<td>2710(w)</td>
<td></td>
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<tr>
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<td>2320(w)</td>
<td>2310(w)</td>
<td>2320(w)</td>
<td></td>
</tr>
<tr>
<td>2100(w)</td>
<td>1650(s)</td>
<td>1590(s)</td>
<td>1600(s)</td>
<td>1610(s)</td>
</tr>
<tr>
<td>1600(s)</td>
<td>1510(sh)</td>
<td>1570(s)</td>
<td>1510(m)</td>
<td>1510(w)</td>
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<tr>
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<td></td>
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</tr>
<tr>
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<td>1050(s)</td>
<td>1080(w)</td>
<td>1045(w)</td>
<td></td>
</tr>
<tr>
<td>730(s)</td>
<td>700(m)</td>
<td>710(s)</td>
<td>690(s)</td>
<td>695(m)</td>
</tr>
<tr>
<td>620(s)</td>
<td>640(m)</td>
<td></td>
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</tbody>
</table>

s = sharp, m = medium, w = weak, b = broad, sh = shoulder, v = very

a not assigned to specific modes; bNH₂ bending; cN-C-N stretching; dNH₂ rocking, N-C-N stretching, and C=S stretching; eC=S stretching and N-C-N stretching (12)
Polarograms of solutions containing (a) \(5 \times 10^{-4}\) M FDS•2HCl, 2.0 M HCl, 0.5 M KCl; (b) 2.0 M HCl, 0.5 M KCl.
not yield a straight line of appropriate slope as predicted by the
equation for reversible waves. A plot of \( E_{d,e} \) vs. \( \log \frac{i}{i_d-i} \) for
an aqueous solution of \( 5 \times 10^{-4} \) M FDS\( \cdot \)2HCl, 2.0 M HCl, 0.5 M KCl
is given in Figure V.

From the equation

\[
E_{d,e.} = E_l - 0.0592 \log \frac{i}{i_d-i}
\]

\( E_l \) and \( \alpha n \) can be evaluated. In the FDS\( \cdot \)2HCl system, between
-0.030 volts and -0.090 volts, the slope gives a value for \( \alpha n_a \)
of 0.82. Since \( n_a \) must obviously be an integer, the logical
choice would be to assign the value of either one or two to \( n_a \).

The value of \( \alpha n_a \) is evaluated near the foot of the wave,
between -0.030 and -0.090 volts in this case, because the current
is dependent on the concentration of the reducible species at the
surface of the D.M.E. At the foot of the wave the concentration
of the reducible species remains virtually constant.

According to the Ilkovic equation

\[
id = 607.0 n D^{1/2} C m^{2/3} t^{1/6}
\]

\[
p^{1/2} = \frac{i_d}{607.0 n C m^{2/3} t^{1/6}}
\]

The concentration \( C \) of FDS\( \cdot \)2HCl was 0.50 millimoles/liter. The
value of \( m^{2/3} t^{1/6} \) measured at 25°C and -0.25 volts in the sup-
porting electrolyte was 2.31 mg\(^{2/3}\) sec\(^{-1/2}\). The diffusion current
Figure V

-0.05 - 0.00 - 0.05 - 0.10 - 0.15 - 0.20
-0.5  -0.0  0.0  0.5  1.0

Plot of $\log \left( \frac{i}{i_d-i} \right)$ vs. $E_{d.e.}$ for FDS•2HCl

- $5 \times 10^{-4}$ M FDS•2HCl
- 2 M HCl
- 0.5 M KCl
- No suppressor
$i_d$ for the FDS•2HCl wave was about 4.0 microamps. We shall allow the number of electrons $n$ gained by each FDS•$2H^+$ ion to be equal to two.

$$D^{1/2} = \frac{4.0}{(607.0)(2)(0.50)(2.31)} = 2.87 \times 10^{-3}$$

$$D = 8.24 \times 10^{-6} \text{ cm}^2/\text{sec}$$

$D$ is the diffusion coefficient and is the proportionality constant from Fick's first law.

The diffusion current constant $I$ is defined by

$$I = \frac{i_d}{C m^{2/3} t^{1/6}}$$

$$I = \frac{4.0}{(0.50)(2.31)} = 3.48$$

For the simple mechanism

$$0 + n_a e \rightarrow I$$

$$I + (n - n_a)e \rightarrow R$$

the half-wave potential obtained by measuring maximum currents is given by (21d)

$$E_{1/2} = -0.2412 + \frac{0.05915}{\alpha n_a} \log \left( \frac{1.349 k_{f,h} t^{1/2}}{D^{1/2}} \right)$$

The half-wave potential for FDS•2HCl was seen to be equal to -0.078 volts in our system and $\alpha n_a$ was seen to equal 0.82. The drop time measured at 25°C and -0.25 volts in the supporting electrolyte was 3.68 sec/drop. Substituting
\[-0.078 = -0.2412 + \frac{0.05915}{0.82} \log \frac{(1.349)(3.68)^{1/2}}{(8.24 \times 10^{-6})^{1/2}} k_{f,h}^0 \]

\[\log 893 k_{f,h}^0 = 2.2635\]

\[k_{f,h}^0 = 0.204 \text{ cm/sec}\]

The value \(k_{f,h}^0\) is the rate constant for the electrode reaction when the electrode potential \(E\) equals the reference value \(-0.2412\) volts vs. S.C.E. where the potential \(E\) is referred to the S.C.E.

The dimensionless parameter \(\lambda\) is defined as follows:

\[\lambda = \frac{k_{f,h} t^{1/2}}{D^{1/2}}\]

This parameter \(\lambda\) is equal to 0.76 at the half-wave potential \((20b)\). Rearranging this equation

\[k_{f,h} = \frac{\lambda D^{1/2}}{t^{1/2}}\]

and substituting in

\[k_{f,h} = \frac{(0.76)(8.24 \times 10^{-6})^{1/2}}{(3.68)^{1/2}}\]

\[k_{f,h} = 1.14 \times 10^{-3} \text{ cm/sec}\]

The constant \(k_{f,h}\) is the potential-dependent heterogeneous rate constant for an irreversible reaction.

At the half-wave potential

\[
\frac{k_{f,h}}{D^{1/2}} = \frac{1.14 \times 10^{-3}}{(8.24 \times 10^{-6})^{1/2}} = 0.399 \text{ sec}^{-1/2}
\]
Effect of Gelatin as Maximum Suppressor. In Table II are given the half-wave potentials of FDS·2HCl at various concentrations of gelatin. These $E_1$ values were evaluated graphically by plotting $E_{\text{d.e.}}$ as a function of $\log \frac{i}{i_{\text{d-1}}}$ When $\log \frac{i}{i_{\text{d-1}}}$ equals zero, $E_{\text{d.e.}}$ equals $E_1$.

It is apparent that gelatin interferes with the electrode process. Certain orientations of the FDS·2HCl molecule at the electrode surface are disallowed by the addition of gelatin. Gelatin becomes adsorbed onto the mercury surface making it more difficult for FDS·2HCl molecules to reach the surface of the mercury drop. More energy is required to reduce the FDS·2HCl as gelatin is added. At concentrations of gelatin greater than 0.0468 gm/100 ml of solution, $E_2$ remains essentially constant.

The energy required to reduce FDS·2HCl at the D.M.E. has reached a large enough value to overcome the effect of any further addition of gelatin.

Effect of Height of Mercury Column. If a wave is diffusion controlled, the following equation should be obeyed (21g)

$$\frac{i_d}{h_{\text{corr}}}^{1/2} = k$$

where $i_d$ is the diffusion current, $h_{\text{corr}}$ is the height of the mercury column corrected for back pressure due to the interfacial tension at the drop surface, and $k$ is a constant. In Table III is listed the height of the wave of $5 \times 10^{-4}$ M FDS·2HCl in 2.0 M HCl,
<table>
<thead>
<tr>
<th>Conc. of Gelatin (gm/100 ml soln.)</th>
<th>$E_{\frac{1}{2}}$ (volts vs. S.C.E.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0000</td>
<td>-0.068</td>
</tr>
<tr>
<td>0.0178</td>
<td>-0.078</td>
</tr>
<tr>
<td>0.0468</td>
<td>-0.103</td>
</tr>
<tr>
<td>0.0925</td>
<td>-0.094</td>
</tr>
<tr>
<td>0.1743</td>
<td>-0.096</td>
</tr>
<tr>
<td>0.1803</td>
<td>-0.094</td>
</tr>
</tbody>
</table>

Variation of $E_{\frac{1}{2}}$ with concentration of gelatin in solutions containing $5 \times 10^{-4}$ M FDS•2HCl, 2.0 M HCl, 0.5 M KCl at a mercury column height of 23.75 cm at 25°C.
<table>
<thead>
<tr>
<th>h, cm&lt;sup&gt;a&lt;/sup&gt;</th>
<th>i&lt;sub&gt;d&lt;/sub&gt; /µa</th>
<th>i/h&lt;sup&gt;3/2&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>24.4</td>
<td>4.24</td>
<td>0.87</td>
</tr>
<tr>
<td>22.3</td>
<td>3.80</td>
<td>0.81</td>
</tr>
<tr>
<td>20.1</td>
<td>3.85</td>
<td>0.86</td>
</tr>
<tr>
<td>18.0</td>
<td>3.48</td>
<td>0.83</td>
</tr>
</tbody>
</table>

<sup>a</sup>h is corrected for back pressure

Effect of h<sub>corr</sub> on i<sub>d</sub> at -0.40 volts vs. S.C.E. in solutions containing 5 x 10<sup>-4</sup> M FDS•2HCl, 2.0 M HCl, 0.5 M KCl, 0.18% gelatin.
0.5 M KCl, 0.18% gelatin as a function of the height of the mercury column. The diffusion current increases as $h^{corr}$ increases. The quantity $i/ht^{\frac{1}{2}}$ remains essentially constant indicating that the electrode process is diffusion controlled.

Polarography of CuCl$_2$-Thiourea

The effect of adding thiourea to a solution of cupric chloride is shown in Table IV. The half-wave potential of the first wave becomes increasingly more negative as thiourea is added to $5 \times 10^{-4}$ M CuCl$_2$ in a 2.0 M HCl, 0.5 M KCl, 0.005% gelatin solution. The half-wave potential of the second wave increases from -0.26 volts for a cupric chloride solution, to -0.33 volts when thiourea is added. The half-wave potential of the second wave remains constant at concentrations of thiourea greater than $1 \times 10^{-3}$ molar.

Another effect is apparent from the polarograms of this system as shown in Figure VI. The height of the first wave diminishes as the concentration of thiourea is increased. The height of the second plateau remains essentially constant. Some other reducible species must be forming to cause the increase in height of the second wave.

Copper(II) is reduced to copper(I) in the first wave. The height of this wave is proportional to the concentration of copper(II) at the electrode surface. That the height of the
Table IV

HALF-WAVE POTENTIALS, VOLTS VS. S.C.E., IN 2 M HCl, 0.5 M KCl, .005% GELATIN

<table>
<thead>
<tr>
<th>Concentration</th>
<th>Potential</th>
<th>Concentration</th>
<th>Potential</th>
<th>Concentration</th>
<th>Potential</th>
</tr>
</thead>
<tbody>
<tr>
<td>$5 \times 10^{-4}$ M CuCl$_2$</td>
<td>-.026</td>
<td>$5 \times 10^{-4}$ M CuCl$_2$</td>
<td>-.033</td>
<td>$5 \times 10^{-4}$ M CuCl$_2$</td>
<td>-.086</td>
</tr>
<tr>
<td>$1 \times 10^{-3}$ M tu</td>
<td>-.26</td>
<td>$2 \times 10^{-3}$ M tu</td>
<td>-.33</td>
<td>$3 \times 10^{-3}$ M tu</td>
<td>-.33</td>
</tr>
<tr>
<td>$5 \times 10^{-4}$ M FDS$\cdot$2HCl</td>
<td>-.078</td>
<td>$5 \times 10^{-4}$ M CuCl$_2$</td>
<td>-.031</td>
<td>$5 \times 10^{-4}$ M CuCl$_2$</td>
<td>-.044</td>
</tr>
<tr>
<td>$2.5 \times 10^{-3}$ M FDS$\cdot$2HCl</td>
<td>-.19</td>
<td>$5 \times 10^{-3}$ M FDS$\cdot$2HCl</td>
<td>-.39</td>
<td>$5 \times 10^{-3}$ M FDS$\cdot$2HCl</td>
<td>-.41</td>
</tr>
</tbody>
</table>
Figure VI

Polarograms of solutions containing $5 \times 10^{-4}$ M CuCl$_2$, 2.0 M HCl, 0.5 M KCl, 0.005% gelatin, and (a) $1 \times 10^{-3}$ M tu; (b) $2 \times 10^{-3}$ M tu; (c) $3 \times 10^{-3}$ M tu, at 25°C and at a mercury column height of 27.0 cm Hg.
first wave diminishes as thiourea is added is due to the diminishing concentration of copper(II) in solution. Values of $\alpha n$ are reported in Table V. These values were calculated from the equation

$$\alpha n = \frac{-0.0542 \Delta \log \frac{i}{i_d-1}}{\Delta E_{d.e.}}$$

where $i$ and $E_{d.e.}$ were measured at the ends of the drop lives.

Polarography of CuCl$_2$-FDS•2HCl

Polarograms of solutions containing both FDS•2HCl and CuCl$_2$ were recorded. The half-wave potentials are recorded in Table IV. As the concentration of FDS•2HCl is increased in a solution of 5 x 10$^{-4}$ M CuCl$_2$, 2.0 M HCl, 0.5 M KCl, the half-wave potentials of all three waves become more negative. As can be seen from Figure VII, the limiting currents of both the second and third waves increase with increasing FDS•2HCl concentration. The height of the first wave, however, varies by very little.

If average currents are used rather than the currents at the ends of the drop lives, the equation describing irreversible waves becomes

$$E_{d.e.} = E_{1/2} - \frac{0.05915}{\alpha n} \log \frac{i}{i_d-1}$$
<table>
<thead>
<tr>
<th></th>
<th>(a)</th>
<th>(b)</th>
<th>(c)</th>
</tr>
</thead>
<tbody>
<tr>
<td>FIRST WAVE</td>
<td>1.88</td>
<td>1.93</td>
<td>1.89</td>
</tr>
<tr>
<td>SECOND WAVE</td>
<td>.51</td>
<td>.63</td>
<td>.49</td>
</tr>
</tbody>
</table>

Values of $\alpha n$ for solutions containing $5 \times 10^{-4} \text{ M}$ CuCl$_2$, 2.0 M HCl, 0.5 M KCl, 0.005% gelatin, and
(a) $1 \times 10^{-3} \text{ M}$ tu, (b) $2 \times 10^{-3} \text{ M}$ tu,
(c) $3 \times 10^{-3} \text{ M}$ tu.
Polarograms of 2.0 M HCl, 0.5 M KCl, 0.02% gelatin containing (a) no CuCl₂ and no FDS•2HCl; (b) 5.0 x 10⁻⁴ M CuCl₂; (c) 5.0 x 10⁻⁴ M CuCl₂ and 2.5 x 10⁻³ M FDS•2HCl; (d) 5 x 10⁻¹ M CuCl₂ and 5.0 x 10⁻³ M FDS•2HCl.
Therefore

\[ \alpha n = - \frac{0.05915 \Delta \log \frac{i}{i_d-1}}{\Delta E_{d.e.}} \]

The results of applying this equation to the waves for solutions containing copper ions and copper-FTS·2HCl ions are given in Table VI.
Table VI

<table>
<thead>
<tr>
<th></th>
<th>(a)</th>
<th>(b)</th>
<th>(c)</th>
</tr>
</thead>
<tbody>
<tr>
<td>FIRST WAVE</td>
<td>1.00</td>
<td>1.21</td>
<td>1.12</td>
</tr>
<tr>
<td>SECOND WAVE</td>
<td>1.03</td>
<td>1.19</td>
<td></td>
</tr>
<tr>
<td>THIRD WAVE</td>
<td>0.81</td>
<td>0.91</td>
<td>0.73</td>
</tr>
</tbody>
</table>

Values of $\alpha n$ for solutions containing 2.0 M HCl, 0.5 M KCl, 0.02% gelatin, and (a) $5 \times 10^{-4}$ M CuCl$_2$, (b) $5 \times 10^{-4}$ M CuCl$_2$, 2.5 $\times 10^{-3}$ M FDS$\cdot$2HCl, (c) $5 \times 10^{-4}$ M CuCl$_2$, 5 $\times 10^{-3}$ M FDS$\cdot$2HCl.
DISCUSSION
Infrared Spectra

The force constant is a measure of the stiffness of a bond. The more the double bond character of a single bond, the greater is the force constant. The frequency of a vibration is proportional to the square root of the force constant. Hence, as double bond character increases, the frequency increases.

It is known from X-ray crystallography that Cu(I) bonds through sulfur rather than nitrogen in CuS₂Cl (10). The electronic structure of thiourea may be represented by a resonance hybrid of three structures as shown in Figure II on page 15. Since coordination occurs through sulfur, the contribution of structure A will decrease. This should result in a decrease of the C-S stretching frequency (24).

As can be seen from Table I on page 21 distinctive shifts are noted. The 1460 cm⁻¹ peak of thiourea is shifted to larger values in the other four compounds indicating greater double bond character between C and N. The 730 cm⁻¹ peak in thiourea decreases in frequency indicating less C to S double bond character. The 1410 cm⁻¹ band of thiourea should not be shifted in FDS·2HCl since this band is not shifted in metal complexes of thiourea where metal to sulfur bonding occurs (12).

The 1600 cm⁻¹ band of thiourea has been attributed to NH₂ bending vibrations (10) (12). This seems reasonable since this band is shifted to 1650 cm⁻¹ in FDS·2HCl as would be expected.
since greater double bond character between C and N exists. This 1650 cm$^{-1}$ peak is shifted to lower values in copper complexes of FDS•2HCl indicating that complexation occurs at nitrogen.

In the Materials section of this thesis the Cu(I)-FDS•2HCl complex was found to have the formula Cu$_2$(FDS•2HCl)Cl$_2$ on the basis of electrodeposition studies. If complexation occurs at the nitrogen as shown from infrared analysis, a structure consistent with this formula is shown in Figure VIII.

Polarography of FDS•2HCl

The FDS•2HCl Wave. The value of $\alpha n$ has been shown to be equal to 0.82. Theoretically $\alpha$ may vary from nearly zero to nearly one (21e). For most irreversible systems $\alpha$ is equal to 0.5. For a reversible wave $\alpha$ equals one.

Preisler and Berger (6) report that the following reaction occurs at a platinum electrode in acid solution.

$$\text{FDS•2H}^+ + 2e^- \rightleftharpoons 2 \text{tu}$$

If we allow $n$ to equal two in our system, $\alpha$ would equal 0.41. This is an acceptable value for $\alpha$.

The height of the polarographic wave for the reduction of FDS•2HCl is comparable with the height of the total wave of CuCl$_2$ of the same concentration. This might indicate that the number of electrons involved in both overall reductions is the same. This would not, however, limit the possibility of a rate-determining
Figure VIII

\[ \text{STRUCTURE OF} \]

\[ \text{Cu}_2(\text{FDS} \cdot 2\text{HCl})\text{Cl}_2 \]
step to occur near the foot of the irreversible FDS•2HCl wave.

Such a mechanism might be postulated at those voltages near the foot of the FDS•2HCl wave

\[ O + n_a e \rightarrow I \quad \text{(rate-determining)} \]

\[ I + (n - n_a)e \rightarrow R \quad \text{(fast)} \]

where \( n_a \) is equal to one. The rate of the reaction is controlled by the rate at which \( O \) is reduced. The maximum current obtained when \( O \) is reduced would still depend on \( n \) rather than \( n_a \). If \( n_a \) were set equal to one, \( \alpha \) would equal 0.82 which is still within the limits of potential values for \( \alpha \).

From the results of the polarography of FDS•2HCl, the value for \( k_f^0, h \) was determined to be 0.204 cm/sec. According to Heyrovský and Kuta (19b) if \( k_f^0, h \) exceeds 2 x 10^{-2} cm/sec, a reversible wave results. They state that no information can be obtained on the kinetics of the electrode process at higher values of \( k_f^0, h \).

A value of 0.399 was obtained for \( k_{f, h} D^{-1/2} \) at the half-wave potential for FDS•2HCl. Delahay (20c) states that the current is virtually diffusion controlled when \( k_{f, h} D^{-1/2} \) is larger than 5 sec^{-1/2} and rate controlled when \( k_{f, h} D^{-1/2} \) is smaller than 0.05 sec^{-1/2}. By this criterion the FDS•2HCl might be considered quasireversible (21f).

On the basis of studies of the effect of the height of the column of mercury on the half-wave potential, it has been established that the FDS•2HCl wave is diffusion controlled when the
current approaches the maximum value on the FDS•2HCl wave.

From the arguments just presented, it would seem that the FDS•2HCl wave might be explained as follows. Prior to the half-wave potential the wave is irreversible and rate-controlled—the slow step being a one electron addition followed by a fast step in which the second electron is added. Near the half-wave potential the wave becomes quasireversible. After the half-wave potential the wave becomes diffusion controlled as in a reversible wave.

Polarography of CuCl₂-Thiourea

According to the work of Slashcheva, Usanovich, and Sumarokova (3) as cupric chloride is added to thiourea in aqueous solution Cu₂tu₆⁺⁺ is formed up to the equivalence point according to the equation

\[ 8 \text{tu} + 2 \text{Cu}^+ + 4 \text{Cl}^- \rightarrow \text{Cu}_2\text{tu}_6^{+2} + \text{FDS} \cdot 2\text{H}^+ + 4 \text{Cl}^- \]

After the equivalence point a further reaction occurs represented by

\[ \text{Cu}_2\text{tu}_6^{+2} + 2 \text{Cu}^+ + 6 \text{Cl}^- \rightarrow 2 \left[ \text{Cu}\text{tuCl} \right]_2 + \text{FDS} \cdot 2\text{H}^+ + 2 \text{Cl}^- \]

They confirm the existence of \([\text{Cu}_2\text{tu}_6]\text{Cl}_2\) from analysis for copper content and molecular weight determination by freezing point lowering in aqueous solution. After the second equivalence point only excess CuCl₂ exists.

In Table IV on page 31 are listed the half-wave potentials of
solutions made by the addition of thiourea to CuCl₂ in 2.0 M HCl and 0.5 M KCl. The half-wave potential of the second wave is seen to remain constant at -0.33 volts between the Cu⁺² to thiourea mole ratios of 1:4 and 1:2 indicating the presence of the same Cu(I) complex between these two points in agreement with Slashcheva et al.

Although ğer for the first wave does diminish as would be predicted since Cu(II) is unstable in the presence of thiourea (1), $E_2$ for the first wave becomes noticeably more negative as the concentration of thiourea increases. This gradual displacement to more negative potentials is attributed to complexation of Cu(II) with FDS•2HCl. Since the work of Slashcheva et al. was not done in solutions at low pH, it is reasonable too that no Cu(II)-FDS•2HCl complex was found. Formamidine disulfide dihydrochloride is unstable in solutions of pH higher than 4.3. Decomposition accompanied by the liberation of sulfur occurs (6).

The total wave height of both copper waves does not vary as the concentration of thiourea is increased. As the concentration of Cu(II) decreases, the concentration of other reducible species increases in the second wave. At concentrations of thiourea of $2 \times 10^{-3}$ M and above, precipitation occurred within 10 to 20 minutes. This precipitate was assumed to be $[\text{Cu}_2\text{tu}_6]\text{Cl}_2$ as shown by Slashcheva et al. It would seem that three waves should be observed when copper (II) and thiourea are put into solution since there are three different reducible species—copper(II), copper(I), and FDS•2HCl. Only two
waves are observed. From the $\alpha n$ values reported in Table V, it is seen that $\alpha n$ for the first wave remains constant at about 1.8. Since $\alpha n$ for the reduction of copper(II) to copper(I) can at most be equal to one, both copper(II) and FDS•2HCl must be reduced in the same step.

The second wave has an $\alpha n$ value of about 0.5. This wave becomes irreversible when copper(I) becomes complexed with thiourea. This is in contrast to what has been reported by Lane et al. (26). Perhaps the height of the second wave is due to a catalytic effect.

Polarography of CuCl₂-FDS•2HCl

As the concentration of FDS•2HCl is increased in a solution containing $5 \times 10^{-4}$ M CuCl₂, 2.0 M HCl, 0.5 M KCl, the half-wave potentials of all three waves become more negative as indicated in Table IV on page 31. That these waves become more negative is a consequence of complex formation.

It would be advantageous if specific reductions were assigned to each wave. That wave assigned to the reduction of FDS•2HCl should increase in height with increasing concentration of FDS•2HCl. Either the first or second wave would be logically chosen since the third wave will be attributed to the reduction of Cu(I) to its amalgam. The half-wave potentials of the first and second waves are too positive to be assigned to the reduction of Cu(I). The second wave does increase in height while the height
of the first wave varies very little. In addition, the half-wave potential of FDS•2HCl uncomplexed with copper is more negative than the half-wave potential for the reduction of Cu(II) to Cu(I) when no FDS•2HCl is present. The second wave is therefore assigned to the reduction of FDS•2HCl to thiourea. The first wave is chosen as representing the reduction of Cu(II) complexed with FDS•2HCl to Cu(I).

As can be seen from Figure VII on page 35 the limiting currents of both the second and third waves increase with increasing FDS•2HCl concentration. The increase in height of the second wave is attributed to the increase in concentration of FDS•2HCl as has already been stated. The increase in height of the third wave can be understood if, as has already been stated, Cu(II) is unstable in the presence of thiourea. If thiourea is present at the D.M.E. surface as would be the case since the second wave represents the reduction of FDS•2HCl to thiourea, the thiourea can react with cupric ions to produce cuprous ions spontaneously thereby increasing the Cu(I) concentration at the D.M.E. to a much higher concentration than in the bulk of the solution. This would cause an increased wave height for the third wave. Because the height of the first wave is not reduced with increasing concentration of FDS•2HCl, thiourea must not be present at the surface of the D.M.E. at such voltages.

As can be seen from Table VI on page 37 the value of αn
for the FDS•2HCl wave does not approach two as would be expected if FDS•2HCl is reduced reversibly to thiourea. The addition of CuCl₂ to FDS•2HCl does not increase the reversibility of the FDS•2HCl wave.
APPENDIX
An electrode reaction is said to be reversible if, experimentally, the process cannot be distinguished from an infinitely fast reaction. A reaction which may be reversible by one experimental method of measurement, may not be reversible by another technique. Polarographic data for processes fast enough to appear reversible yield much thermodynamic data. Polarographic data for totally irreversible processes elucidate the kinetics of the rate-determining step in a totally irreversible process. The definitions of reversible and irreversible processes are qualitative.

The polarographic current of a totally irreversible reduction wave does not begin to increase until a potential more negative than the formal potential of the couple is reached. The current $i$ which flows at some potential $E$ for a totally irreversible process would be equal to $i_d$ if the electrode reaction were reversible. The function $F(X)$ is equal to the ratio $\frac{i}{i_d}$ as defined by Koutecký (25).

Koutecký (25) gave values for the function $F(X)$, where $X$ and the variable $\lambda$ are defined by the equation

$$\lambda = \sqrt{\frac{7}{12}} X = k_f h t^{1/2} \frac{D_0^{1/2}}{1/2}$$

(A-1)

where $t$ is the drop time, $D_0$ is the diffusion coefficient of the electroactive substance, and $k_f h$ is the potential-dependent heterogeneous rate constant for an irreversible reaction described by
\[ k_{f,h} = k_{f,h}^0 \exp \left[ -\alpha nF(E + 0.2\text{V}) / RT \right] \]

\[ \log k_{f,h} = \log k_{f,h}^0 - \frac{\alpha nF(E + 0.2\text{V})}{RT} \]  \hspace{2cm} (A-2)

where \( \alpha \) is the transfer coefficient, \( n \) is the number of electrons in the reduction half-reaction occurring at the dropping mercury electrode (D.M.E.), \( F \) is the number of coulombs per Faraday, \( R \) is the gas constant (in volt-coulombs per degree), and \( T \) is the absolute temperature; \( k_{f,h}^0 \) is the value of the rate constant for the electrode reaction when the electrode potential \( E \) equals the reference value \(-0.2\text{V}\) vs. S.C.E., where the potential \( E \) is referred to the saturated calomel electrode (S.C.E.).

On the basis of values of \( F(X) \) and \( \lambda \) given by Koutecký it is found that \( \log \lambda \) varies linearly with \( \log \left( \frac{F(X)}{1-F(X)} \right) \) (25). Explicitly

\[ \log \lambda = -0.1300 + 0.9163 \log \frac{F(X)}{1-F(X)} \]  \hspace{2cm} (A-3)

But

\[ 0.1300 = \log 1.349 \]

\[ \frac{F(X)}{1-F(X)} = \frac{i}{i-d-1} \text{ since } F(X) = \frac{i}{i_d} \]

for totally irreversible waves.

\[ \log \lambda = -\log 1.349 + 0.9163 \log \frac{i}{i_d-1} \]  \hspace{2cm} (A-4)

Substituting equation \((A-4)\) into equation \((A-4)\)

\[ \log k_{f,h} \frac{t^{1/2}}{D_0^{1/2}} = -\log 1.349 + 0.9163 \log \frac{i}{i_d-1} \]
\[
\log 1.319 \frac{k_f h}{D_0^{1/2}}^{1/2} = 0.9163 \log \frac{i}{i_{d-i}}
\]

\[
\log k_f h + \log 1.319 \frac{k_f h}{D_0^{1/2}}^{1/2} = 0.9163 \log \frac{i}{i_{d-i}} \quad (A-5)
\]

Substituting equation (A-2) into equation (A-5)

\[
\log k_f^0 = \frac{\alpha n F (E + 0.2412)}{RT} + \log 1.319 \frac{k_f h}{D_0^{1/2}}^{1/2}
\]

\[
= 0.9163 \log \frac{i}{i_{d-i}}
\]

\[
- \frac{\alpha n F (E + 0.2412)}{RT} = - \log 1.319 \frac{k_f h}{D_0^{1/2}}^{1/2} + 0.9163 \log \frac{i}{i_{d-i}}
\]

\[
E + 0.2412 = \frac{RT}{\alpha n F} \log 1.319 \frac{k_f h}{D_0^{1/2}}^{1/2} - \frac{RT}{\alpha n F} \log \frac{i}{i_{d-i}}
\]

\[
= 0.9163 \log \frac{i}{i_{d-i}} \quad (A-6)
\]

At 25°C

\[
E_{d.e.} + 0.2412 =
\]

\[
\frac{0.05915}{\alpha n} \log \frac{1.319 \frac{k_f h}{D_0^{1/2}}^{1/2}}{D_0^{1/2}} - \frac{0.05915}{\alpha n} \log \frac{i}{i_{d-i}} \quad (A-7)
\]

which may be written

\[
E_{d.e.} = E_{1/2} - \frac{0.05915}{\alpha n} \log \frac{i}{i_{d-i}} \quad (A-8)
\]

where

\[
E_{1/2} = -0.2412 + \frac{0.05915}{\alpha n} \log \frac{1.319 \frac{k_f h}{D_0^{1/2}}^{1/2}}{D_0^{1/2}} \quad (A-9)
\]


8. B. Rathke, Ber., 17, 297 (1884).


