INSTRUMENTAL INVESTIGATIONS OF COMPLEX ION EQUILIBRIA

DISSE R TATION

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By

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THE POLAROGRAPHY AND POTEN TIOM ETRY OF MERCURY (II) ION IN SOLUTIONS CONTAINING ETHYLENEDIAMINE AND ETHYLENEDIAMINETETRAACETIC ACID

General Introduction

If a dropping mercury electrode is anodically polarized in a dilute solution of a ligand which forms a complex with mercury, an anodic depolarization wave appears at a potential more negative than that for the anodic dissolution of mercury in non-complexing media.

Cathodic polarographic reduction waves obtained for solutions containing mercury ions and a complexing ligand are likewise displaced toward potentials more negative than the wave for the reduction of the simple aquomercury ion in a non-complexing solution.

It is convenient to consider the equilibrium involved in polarographic reduction in two steps: (1) the dissociation of the complex and (2) the subsequent reduction of the metal ion at the electrode, thus,

\[ \text{Hg}(X)_p^{n^+} \rightleftharpoons \text{Hg}^{n^+} + p(X) \quad (1) \]

\[ \text{Hg}^{n^+} + ne \rightleftharpoons \text{Hg(metal)} \quad (2) \]

The Nernst equation for the potential of the dropping electrode is

\[ \pi_{d.e.} = \pi_0^T + \frac{RT}{nF} \ln C_{\text{Hg}}^0 \quad (3) \]

where \( C_{\text{Hg}}^0 \) is the concentration of mercury ions at the drop surface.

† Presented before the Division of Physical Chemistry, American Chemical Society, April, 1954.
and \( \pi_0^f \) is a constant containing both the formal potential of the Hg\(^{n+}/\text{Hg} \) couple and \( \frac{RT}{nF} \ln a_{\text{Hg}} \) where \( a_{\text{Hg}} \) is the activity of the free mercury at the surface of the drop. The activity coefficients are not shown here and are assumed to be constant for constant ionic strength.

If reaction (1) is sufficiently rapid at the drop surface so that equilibrium with respect to reaction (2) is maintained at the surface of the drop, then

\[
\frac{C_{\text{Hg}}^0}{C_{\text{Hg}X_p}^0} = \frac{C_{\text{Hg}X_p}^0}{(C_X^o)^PK_T} \tag{4}
\]

where the superscript zero denotes the concentrations of the species at the surface of the drop and \( K_T \) is the overall complexity constant for the complex ion.

Substitution of equation (4) into equation (3) yields

\[
\pi_{d.e.} = \pi_0^f - \frac{RT}{nF} \ln (C_X^o)^P + \frac{RT}{nF} \ln C_{\text{HgX_p}}^0 - \frac{RT}{nF} \ln K_T \tag{5}
\]

The current at any point on the wave is a function of the diffusion rate of the reducible material to the electrode. If there is an excess of indifferent electrolyte present, the following expression for thermal diffusion to the drop is valid.

\[
i = k_c(C_{\text{HgX_p}}^0 - C_{\text{HgX_p}}^o) \tag{6}
\]

where \( k_c \) is the product of the diffusion current constant and the capillary characteristic.
When the equilibrium concentration, $C_{HgX}^0$, approaches zero as the diffusion current region is reached, the following expression applies.

$$i_d = k_c \cdot C_{HgX}$$  \hspace{1cm} (7)

Combining (6) and (7) yields

$$C_{HgX}^0 = \frac{(i_d - i)}{k_c}$$  \hspace{1cm} (8)

and substituting (8) into equation (5) for the potential of the dropping electrode yields

$$\pi_{d.e.} = \pi_0^\circ - \frac{RT}{nF} \ln(C_{HgX})^0 + \frac{RT}{nF} \ln \left(\frac{C_{HgX}^0}{k_c \cdot RT / nF \ln K_T}\right)$$  \hspace{1cm} (9)

If the complexing ligand is in sufficient excess

$$C_X^0 \equiv C_X$$  \hspace{1cm} (10)

At 25°C equation (9) becomes

$$\pi_{d.e.} = \pi_0^\circ + 0.0591/n \log(i_d - i) - 0.0591/n \log K_T - 0.0591/n \log C_X$$  \hspace{1cm} (11)

where the term $0.0591/n \log k_c$ is incorporated into $\pi_0^\circ$.

The apparent half-wave potential, i.e., the point where $i = \frac{1}{2}i_d$ is then given by

$$\frac{\pi_1}{2} = \pi_0^\circ + 0.0591/n \log \left(\frac{1}{2}i_d\right) - 0.0591/n \log C_X - 0.0591/n \log K_T$$  \hspace{1cm} (12)

Therefore, the apparent half-wave potential is a function of the mercury ion concentration as well as the complexity constant of the complex and the concentration of ligand. Measurement of the complexity
by the displacement of the half-wave potential is complicated by the fact that in solutions of this type the polarographic waves obtained are composite anodic and cathodic waves containing a large anodic contribution. This anodic contribution cannot be accurately evaluated due to the large excess of ligand and the failure of the anodic wave in the anodic diffusion current region due to such a large excess of ligand. However, a plot of \( \pi_d \), e. versus \( \log(i_d - i) \) for the cathodic portion of the wave should yield a straight line with a slope of 0.0591/n, if the polarographic reduction of the complex is thermodynamically reversible at the dropping electrode.

Since the dropping electrode is in contact with a solution containing mercury ions, it may function as an indicator electrode for the concentration of these ions when it is not polarized. If such is the case, the potential of the dropping electrode with only the charging current flowing is given by the Nernst equation and is

\[
\pi_s = \pi_o^f + 0.0591/n \log [Hg^{n+}] 
\]  

Substituting for \([Hg^{n+}]\) in terms of the complexity constant for the postulated reaction in equation (1) yields

\[
\pi_s = \pi_o^f + (0.0591/n)\log \left( [Hg(X)_p]^{n+} \right) -0.0591/n \log K_T - (0.0591/n)p \log [X] 
\]  

The Complexes of Mercury (II) with Ethylenediamine

For solutions containing mercury (II) ion and excess ethylene-
diamine, equation (14) is

\[ \pi_s = \pi_0 + 0.02961 \log \left[ \frac{[\text{Hg(en)}]^{n+}}{[\text{en}]^n} \right] - 0.0296 \log K_T - 0.0296 \log [\text{en}] \]  

(15)

where en represents ethylenediamine.

If there is a sufficiently large excess of ethylenediamine present, all of the mercury (II) may be considered to be present as the highest complex

\[ \left[ \left[ \text{Hg(en)} \right]^{2+} \right] = C_{\text{Hg}} \]  

(16)

where \( C_{\text{Hg}} \) represents the total concentration of mercury (II) ion present.

Since ethylene diamine is a diacidic base, the equilibrium concentration of ethylenediamine will also be controlled by the consecutive equilibria with hydrogen ion according to the following reactions:

\[ \text{enH}_2^{2+} \rightleftharpoons \text{enH}^+ + \text{H}^+ \]  

(17)

\[ K_1 = \frac{[\text{enH}^+][\text{H}^+]}{[\text{enH}_2^{2+}]} \]  

(18)

\[ \text{enH}^+ \rightleftharpoons \text{en} + \text{H}^+ \]  

(19)

\[ K_2 = \frac{[\text{en}][\text{H}^+]}{[\text{enH}^+]} \]  

(20)

If \( C_{\text{en}} \) represents the total amount of ethylenediamine present in the solution other than that complexed with the mercury (II) ion then,

\[ C_{\text{en}} = \left[ \text{enH}_2^{2+} \right] + \left[ \text{enH}^+ \right] + \left[ \text{en} \right] \]  

(21)

Substituting for \( \left[ \text{enH}_2^{2+} \right] \) and \( \left[ \text{enH}^+ \right] \) from equations (18) and
(20) yields

$$C_{en} = \frac{[\text{en}][H^+]^2}{K_1K_2} + \frac{[\text{en}][H^+]}{K_2} + [\text{en}]$$ (22)

$$C_{en} = \frac{[\text{en}][H^+]^2 + K_1[\text{en}][H^+] + K_1K_2[\text{en}]}{K_1K_2}$$ (23)

Solving for $[\text{en}]$ results in

$$[\text{en}] = \frac{C_{en}K_1K_2}{K_1K_2 + K_1[H^+] + [H^+]^2}$$ (24)

By substitution of equations (16) and (24) into equation (15) yields the following expression for the potential of the dropping mercury electrode,

$$\pi_S = \pi_D^0 + 0.0296 \log C_{\text{Hg}} - 0.0296 \log K_T - 0.0296 \rho \log C_{en} - 0.0296 \log \frac{K_1K_2}{K_1K_2 + K_1[H^+] + [H^+]^2}$$ (25)

If $\pi_S$ is plotted versus log $[\text{en}]$ at constant pH, according to equation (25), a linear plot having a slope of $0.0296 \rho$ should be obtained if the system is thermodynamically reversible.

If the equilibrium concentration of ethylenediamine is decreased, the possibility of the formation of other complexes of mercury (II) ion and ethylenediamine must be considered. Since the most probable complex formed in excess ethylenediamine is the bis-(ethylenediamine)-mercury (II) ion, the complex which must be considered is the mono-(ethylenediamine)-mercury (II) complex.

If $C_{\text{Hg}}$ represents the total concentration of mercury (II) ion, then
\[ C_{\text{Hg}} = [\text{Hg}^{2+}] + [(\text{Hg}(\text{en}))^{2+}] + [(\text{Hg}(\text{en})_{2})^{2+}] \] (26)

\[ [(\text{Hg}(\text{en}))^{2+}] = k_1 [\text{Hg}^{2+}] [\text{en}] \] (27)

where \( k_1 \) is the first formation constant or the complexity constant of the mono complex.

If \( K_T \) is the complexity constant for the bis-(ethylenediamine)-mercury (II) complex, then

\[ C_{\text{Hg}} = [\text{Hg}^{2+}] + k_1 [\text{Hg}^{2+}] [\text{en}] + K_T [\text{Hg}^{2+}] [\text{en}]^2 \] (28)

Solving for \([\text{Hg}^{2+}]\) gives

\[ [\text{Hg}^{2+}] = \frac{C_{\text{Hg}}}{1 + k_1 [\text{en}] + K_T [\text{en}]^2} \] (29)

Then the Nernst equation for the potential of the dropping mercury electrode becomes

\[ \pi_s = \pi^0 + 0.0296 \log C_{\text{Hg}} - 0.0296 \log (1 + k_1 [\text{en}] + K_T [\text{en}]^2) \] (30)

From equation (30), \( k_1 \) may be solved if \( K_T \) is known.

Bjerrum and Nielsen\(^1\) used a similar expression for investigating for the potentiometric determination of the formation constants for the system copper and ethylenediamine.

Complexes of Mercury (II) with Ethylenediaminetetraacetic Acid

The polarograms show that the complex contains only one ethylenediamine tetraacetate ion for each mercury (II) ion. This is reasonable since the ethylenediaminetetraacetate ion is known to be a possible
sexadentate chelating agent. It forms stable complexes with many metal ions, for example, copper (II) ion$^3$ and iron (III) ion$^4$ which contain only one molecule of ethylenediaminetetraacetate ion per metal ion. Thus,

$$\text{Hg}^{2+} + \text{Y}^{4-} \rightleftharpoons \text{HgY}^{2-} \quad (31)$$

The complexity constant for reaction (31) is then

$$K_{\text{HgY}} = \frac{[\text{HgY}^{2-}]}{[\text{Hg}^{2+}] [\text{Y}^{4-}]} \quad (32)$$

Solving equation (32) for $[\text{Hg}^{2+}]$ and substituting in equation (13) where $n = 2$, gives

$$\pi_s = \pi_0^1 + 0.0296 \log [\text{HgY}^{2-}] - 0.0296 \log K_{\text{HgY}} - 0.0296 \log [\text{Y}^{4-}] \quad (33)$$

The value of $[\text{Y}^{4-}]$ at any pH will be determined by the consecutive equilibria with hydrogen ion described by the following equations:

$$\text{H}_4\text{Y} \rightleftharpoons \text{H}_3\text{Y}^- + \text{H}^+ \quad (34)$$
$$\text{H}_3\text{Y}^- \rightleftharpoons \text{H}_2\text{Y}^{2-} + \text{H}^+ \quad (35)$$
$$\text{H}_2\text{Y}^{2-} \rightleftharpoons \text{H}\text{Y}^{3-} + \text{H}^+ \quad (36)$$
$$\text{H}\text{Y}^{3-} \rightleftharpoons \text{H}^+ + \text{Y}^{4-} \quad (37)$$

---


The successive dissociation constants are given by the following equations:

\[
K_1 = \frac{[H^+][H_3Y]}{[H_4Y]} \tag{38}
\]

\[
K_2 = \frac{[H^+][H_2Y^2^-]}{[H_3Y^-]} \tag{39}
\]

\[
K_3 = \frac{[H^+][HY^3^-]}{[H_2Y^2^-]} \tag{40}
\]

\[
K_4 = \frac{[H^+][Y^4^-]}{[HY^3^-]} \tag{41}
\]

If \( C_Y \) represents the concentration of ethylenediaminetetraacetate ion present in all forms other than the mercury (II) complex, then

\[
C_Y = [Y^{4^-}] + [HY^{3^-}] + [H_2Y^{2^-}] + [H_3Y^-] + [H_4Y] \tag{42}
\]

Substituting for the hydrogen-containing species in terms of the dissociation constants and \([Y^{4^-}]\) gives

\[
C_Y = [Y^{4^-}] + \frac{[H^+] [Y^{4^-}]}{K_4} + \frac{[H^+]^2 [Y^{4^-}]}{K_4 K_3 K_4} + \frac{[H^+]^3 [Y^{4^-}]}{K_3 K_2 K_4} + \frac{[H^+]^4 [Y^{4^-}]}{K_1 K_2 K_3 K_4} \tag{43}
\]

Solving for \([Y^{4^-}]\)

\[
[Y^{4^-}] = C_Y \cdot \frac{K_1 K_2 K_3 K_4}{K_1 K_2 K_3 K_4 + K_1 K_2 K_3 [H^+] + K_4 K_2 [H^+]^2 + K_4 [H^+]^3 + [H^+]^4} \tag{44}
\]

According to equation (33) plotting the measured potential \( \pi_s \)

versus \( \log [Y^{4^-}] \) should yield a straight line with a slope of 0.0296 for
the region where reaction (31) is the predominant equilibrium.

Schwarzenbach$^5$ and Biedermann have reported the formation of


hydroxyethylenediaminetetraacetate complexes at relatively high pH values. Then, in regions of high-pH, deviations of the plot of equation (33) indicate the formation of a hydroxy complex, thus

\[ \text{Hg}^{2+} + Y^{4-} + \text{H}_2\text{O} \rightleftharpoons \text{HgOHY}^{3-} + \text{H}^+ \]  

(45)

The usual expression for the equilibrium constant for this particular reaction is

\[
\text{K}_{\text{HgOHY}} = \frac{[\text{HgOHY}^{3-}][\text{H}^+]}{[\text{Hg}^{2+}][Y^{4-}]} 
\]

(46)

The Nernst equation for the potential of the dropping mercury electrode is

\[
\pi_s = \pi_0 + 0.0296 \log C_{\text{Hg}} - 0.0296 \log (\text{K}_{\text{HgOHY}})^3/\text{H}^+ + \text{K}_{\text{HgY}} \\
- 0.0296 \log [Y^{4-}] 
\]

(47)

\text{K}_{\text{HgOHY}} may be calculated from equation (47) if \text{K}_{\text{HgY}} is known.}

\hspace{1cm} \text{Experimental}

The potentiometric and polarographic measurements were made

with the manual polarograph described by Watters.$^6$

\[ (6) \text{J. I. Watters, Rev. Sci. Inst. 22, 851 (1951).} \]
All solutions were outgassed with nitrogen for fifteen minutesprior to the measurements of the potential. The temperature wasmaintained at 25 ± 0.1°C by a constant temperature bath. All pHmeasurements were made with a Beckman Model G pH meter equippedwith a Beckman General Purpose Glass Electrode.

The ethylenediamine were prepared by redistilling the Eastmanproduct, collecting the 25°/o to 75°/o portion of the distillate,dissolving in carbon dioxide free water, and storing in a paraffin-lined bottle which was protected from the atmosphere by guard tubescontaining soda-lime. The water used in the preparation of theethylendiamine stock solution was made free of carbon dioxide byoutgassing with nitrogen. The solution was standardized by titrationwith standard perchloric acid, using brom-cresol green as theindicator.

The capillary used for most of the experimental work delivered1.378 milligrams of mercury per second and had a drop time of5.89 seconds per drop at the potential of the saturated calomel electrode. The capillary characteristic at this potential wasaccordingly \(1.664 \text{ mg}^{2/3} \text{ sec}^{1/2} \text{ for m}^{2/3} \text{ t}^{1/6}\).

A saturated mercurous sulfate electrode was used in conjunctionwith a saturated potassium sulfate salt bridge for the potentialmeasurements. The potential of the sulfate reference electrode wasmeasured versus a saturated calomel electrode after each potential
measurement. Potential measurements were reproducible at a pH of 4.5 using a saturated potassium nitrate salt bridge indicating that complex formation between mercury ions at the electrode surface and sulfate ions did not interfere.

The ethylenediaminetetraacetic acid was the Bersworth reagent grade product and was used after two recrystallizations from hot water. The acid was rather insoluble but the material used was that recovered from the supernatant liquid. The acid was used rather than the disodium salt in order to eliminate interference due to the formation of a complex between the sodium and ethylenediamine-tetraacetate ions.

The mercury (II) nitrate stock solution was prepared by dissolving a weighed amount of redistilled metallic mercury in concentrated nitric acid. The molarity of the solution was verified by titration of a standard sodium chloride solution using sodium nitroprusside as an indicator.  


The solutions containing mercury (II) ion and ethylenediamine were prepared by pipetting known amounts of each into a 100 ml, volumetric flask containing potassium nitrate for the adjustment of the ionic
strength to 0.125. The pH was then adjusted by the addition of either nitric or perchloric acid.

The ethylenediaminetetraacetic acid and mercury (II) ion solutions were prepared by mixing two stock solutions containing the same concentration of mercury (II) ion and ethylenediaminetetraacetic acid, but having a large difference in pH due to different amounts of potassium hydroxide present. By mixing the appropriate ratios, it was possible to obtain the desired pH.

No buffer solutions were used since it was desirable to eliminate as many foreign ions as possible. Ethylenediaminetetraacetic acid itself has sufficient buffering action over a large pH range.

Results and Conclusions

The Ethylenediamine Complexes with Mercury (II)

The anodic polarographic wave obtained for dilute solutions of ethylenediamine was poorly defined and unsuitable for analysis. The deformation of the anodic wave may be due to the formation of both the mono- and bis-(ethylenediamine)mercury (II) complexes at the surface of the electrode. Initially, it is reasonable that the bis-(ethylenediamine)mercury (II) should be formed as mercury from the dropping electrode is oxidized, since there is a large excess of ethylenediamine present at the electrode surface. Then, as the
concentration of mercury (II) ions at the electrode surface is increased by further oxidation, the mono-(ethylenediamine)mercury (II) complex may start to form, resulting in a poorly defined composite anodic wave.

The cathodic polarographic current-voltage curves obtained for solutions containing mercury (II) ion and a constant excess of ethylenediamine are shown in Figure I. The equilibrium concentration of ethylenediamine was varied by the addition of perchloric acid. A slope analysis of the curves according to equation (11) yields 0.034 for 0.0591/n for the three most basic solutions after correction for the iR drop across the polarographic cell. This is close to the theoretical value of 0.0295 for n equals 2, indicating a reversible two-electron reduction. As the solutions became more acidic, the cathodic reduction waves became more drawn out, indicating an irreversible reaction. However, an examination of the anodic to cathodic portions of the polarograms shows that they are continuous across the point of zero current. This indicates that the reaction might be essentially reversible for small currents near conditions of equilibrium with the bulk of the solution, but not under conditions of large current flow. This suggests the possibility of using the dropping mercury electrode as an indicator electrode for the concentration of mercury (II) ion even though the electro-reduction of the complex was irreversible. Table I shows the results of measurements made to
test this supposition. The solutions containing a constant concentration of ethylenediamine, varying concentrations of mercury (II) ion, and enough nitric acid to adjust the pH to approximately that of the solution which produced the most irreversible polarogram. These results indicate that for these solutions the dropping mercury electrode functioned in a reversible manner at equilibrium with the bulk of the solution, since the ratio of the change in potential to the change in log \([\text{Hg}^{2+}]\) is 0.030 compared to the theoretical value of 0.0296 for a reversible two-electron electrode process.

**Table I**

<table>
<thead>
<tr>
<th>(\pi_s) at pH of 4.5</th>
<th>([\text{Hg}^{2+}]) (10^{-4}) M</th>
<th>Log ([\text{Hg}^{2+}])</th>
</tr>
</thead>
<tbody>
<tr>
<td>+0.5016</td>
<td>(2\times 10^{-4}) M</td>
<td>-3.7</td>
</tr>
<tr>
<td>+0.5184</td>
<td>(4\times 10^{-4})</td>
<td>-3.4</td>
</tr>
<tr>
<td>+0.5305</td>
<td>(10\times 10^{-4})</td>
<td>-3.0</td>
</tr>
<tr>
<td>+0.5364</td>
<td>(20\times 20^{-4})</td>
<td>-2.7</td>
</tr>
</tbody>
</table>

Table II shows the results obtained for potentiometric measurements of solutions containing a constant concentration of mercury (II) ion and a constant excess of ethylenediamine as the pH was varied by addition of acid. A plot of log \([\text{en}]\) versus \(\pi_s\) is shown in Figure 2. The reciprocal slope of the straight line is 0.0593, indicating that p
Table II

Ethylenediamine Complexes with Mercury (II) Ion

$1 \times 10^{-3} \text{M} \left[\text{Hg}^{2+}\right], 0.025 \text{M en}, 0.01 \text{M KNO}_3, \text{HNO}_3$ added

<table>
<thead>
<tr>
<th>$\pi_s$ vs. S.C.E.</th>
<th>pH</th>
<th>log [en]</th>
<th>log $K_T$</th>
<th>log $k_1$</th>
</tr>
</thead>
<tbody>
<tr>
<td>-0.0597</td>
<td>12.11</td>
<td>(1)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>-0.0616</td>
<td>11.81</td>
<td>(1)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>-0.0622</td>
<td>11.05</td>
<td>-1.68</td>
<td>22.52</td>
<td></td>
</tr>
<tr>
<td>-0.0530</td>
<td>10.15</td>
<td>-1.88</td>
<td>22.61</td>
<td></td>
</tr>
<tr>
<td>-0.0285</td>
<td>9.50</td>
<td>-2.28</td>
<td>22.58</td>
<td></td>
</tr>
<tr>
<td>+0.0662</td>
<td>7.91</td>
<td>-3.85</td>
<td>22.52</td>
<td></td>
</tr>
<tr>
<td>+0.1318</td>
<td>7.08</td>
<td>-5.00</td>
<td>22.60</td>
<td></td>
</tr>
<tr>
<td>+0.1690</td>
<td>6.60</td>
<td>-5.80</td>
<td>(22.94)$^+$</td>
<td>(17.04)$^\ddagger$</td>
</tr>
<tr>
<td>+0.2425</td>
<td>5.96</td>
<td>-7.02</td>
<td>(22.89)$^+$</td>
<td>(15.63)$^\ddagger$</td>
</tr>
<tr>
<td>+0.2731</td>
<td>5.64</td>
<td>-7.65</td>
<td>(23.11)$^+$</td>
<td>(15.35)$^\ddagger$</td>
</tr>
<tr>
<td>+0.2953</td>
<td>5.43</td>
<td>-8.07</td>
<td></td>
<td>(15.05)$^\ddagger$</td>
</tr>
<tr>
<td>+0.3195</td>
<td>5.24</td>
<td>-8.44</td>
<td>14.58</td>
<td></td>
</tr>
<tr>
<td>+0.3458</td>
<td>4.81</td>
<td>-9.10</td>
<td>14.45</td>
<td></td>
</tr>
<tr>
<td>+0.3523</td>
<td>4.62</td>
<td>-9.68</td>
<td>14.84</td>
<td></td>
</tr>
<tr>
<td>+0.3725</td>
<td>4.31</td>
<td>-10.30</td>
<td>14.78</td>
<td></td>
</tr>
<tr>
<td>+0.4274</td>
<td>3.47</td>
<td>-11.98</td>
<td>14.61</td>
<td></td>
</tr>
<tr>
<td>+0.4488</td>
<td>2.84</td>
<td>-13.24</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Av. 22.57 $\pm$ 0.10  Av. 14.65 $\pm$ 0.20

(1) Low diffusion currents indicate the precipitation of mercury (II) ion.

$^+$ Solved on the basis of no mono complex

$^\ddagger$ Solved on the basis of mono complex with mean $K_T$
in equation (15) is also equal to 2 and that the reaction postulated by equation (1) is

$$\left[\text{Hg(en)}_2\right]^{2+} \rightleftharpoons \text{Hg}^{2+} + 2\text{en}$$

The individual values for $\log K_T$ shown in Table II were calculated from equation (15) using for $\pi_o$ the value of $+0.594$ volts versus the saturated calomel electrode calculated by Matsyka and Kossler\textsuperscript{8} for an ionic strength of 0.1. The concentration of uncomplexed ethylenediamine was calculated using the values of Watters and Loughran\textsuperscript{9} for the acid dissociation constants. These values were $pK_1 = 7.27$ and $pK_2 = 10.03$ for solutions 1 molar in potassium nitrate.

For decreasing equilibrium concentration of ethylenediamine, the points plotted in Figure 2 show deviations from the straight line indicating the formation of the mono-ethylenediamine complex.

Applying equation (30) to the potential data and using the average value of 22.57 for $\log K_T$ yields the results for $\log k_1$ shown in Table II. The average value of $\log k_1$ from the individual measurements is $14.65$ at an ionic strength of 0.125 $\pm$ 0.01.


Figure 2

Figure 3 is a theoretical curve for the change of $\pi_s$ with pH for the conditions of the experiments using the average values of log $k_1$ and log $K_T$. The concentration of mercury (II) ion was 0.001 molar and the concentration of ethylenediamine was 0.025 molar. The experimental points are circled. The only deviation of the experimental data from the theoretical curve occurs in very acid solution where the addition of HCl to the solution revealed the presence of $\text{Hg}_2^{2+}$ by the formation of the precipitate $\text{Hg}_2\text{Cl}_2$. The agreement of the theoretical values and the experimental indicates that the average values of the constants obtained account satisfactorily for the experimental data throughout the pH range of 4 to 11.

The average value of log $K$ is $22.57 \pm 0.10$ and the average value of log $k_1$ is $14.65 \pm 0.20$ at $25^\circ C$ and an ionic strength of $0.125 \pm 0.01$. The diffusion current constant of the bis-(ethylenediamine)-mercury (II) complex is $3.56$ millimolar$^{-1}$ mg$^{2/3}$ sec$^{1/2}$ for solutions 0.001 molar in mercury (II) ion, 0.025 molar in ethylenediamine and 0.10 in potassium nitrate.

L. G. Sillen discussed the difficulties in using a mercury electrode for measuring mercury (II) ion concentration due to the reaction

VOLTAGE VS. S.C.E. AT ZERO CURRENT

Figure 3
\[
\text{Hg}^{2+} + \text{Hg} \rightleftharpoons \text{Hg}_2^{2+}
\]

which has an equilibrium constant of about 81 according to Latimer.\(^{11}\)

---


Sillen reported that in solutions containing complexing agents of the order of complexing ability of the nitrate ion or those forming stable complexes with mercury (I) ion indirect methods for the evaluation of the concentration of mercury (II) ion had to be used. On the basis of the great stability of the mercury (II) complexes with both ethylenediamine and ethylenediaminetetraacetic acid and the relatively greater stability of mercury (II) complexes compared to those of mercury (I), it is evident that none of the latter should be formed.

In this work there was no evidence of interference due to the presence of mercury (I) ion at pH values above 4. In fact, the reverse occurred. The addition of ethylenediamine in appreciable concentrations to a solution containing mercury (I) ion resulted in the immediate blackening of the solution indicating that the mercury (I) complex had disproportionated to free mercury and the mercury (II) complex. In dilute solutions containing mercury (I) ion, mercury (II) ion and ethylenediamine, the potential of a platinum wire electrode drifted rapidly and upon examination showed an altered surface indicating that disproportion had taken place. These experiments indicated that
the complexes of the mercury (I) ion with ethylenediamine were much less stable than the complexes formed between mercury (II) ion and ethylenediamine, and consequently did not interfere with the potential measurements over the pH range of 4 to 11. However, in the extremely acid solutions where the deviations from theoretical occurred the mercury (II) ion present in the solution is virtually uncomplexed and therefore there should be an appreciable quantity of mercury (I) ion present. Consequently, it could no longer be assumed that the mercury was all present in the divalent state.

It might be expected that the value of the formation constant of the mono-(ethylenediamine)mercury (II) ion, $k_1$, would be approximately half that of the total constant $K_T$, as in the case of the ethylenediamine complexes of copper (II) ion which have values of $\log k_1$ and $\log K_T$ of -10.55 and 19.60 respectively\(^{(12)}\) since in both cases a neutral ligand is


added to a doubly charged cation.

The average value of $k_1$ for the mono-(ethylenediamine)mercury (II) complex is considerably larger than half the value of $\log K_T$. This is consistent, however, with the data of Bjerrum\(^{(13)}\) for the formation of

\[(13)\] J. Bjerrum, "Metal Ammine Formation in Aqueous Solutions", P. Haase and Son, Copenhagen, Denmark (1941).
the ammine complexes of the mercury (II) ion. The logarithm of the complexity constant of the diammine mercury (II) ion is 17.5 and the value of the logarithm of the complexity constant of the tetra-ammine mercury (II) ion is 19.25.

The only reference to the constant for the ethylenediamine complex was made in a review by J. Bjerrum who reported a value of

\[
\log K_p \text{ of } 23.42 \text{ for the bis-(ethylenediamine)mercury (II) complex in solutions containing one molar potassium nitrate. No experimental data was given. This value is in fair agreement with the value of } \\
\log K_T \text{ obtained by the dropping mercury electrode.}
\]

An attempt to perform a titration using the method of Bjerrum failed in 1 molar potassium nitrate due to precipitation. The precipitate dissolved in excess ethylenediamine. Presumably, the precipitate formed was the rather insoluble \((\text{Hgen}) \cdot (\text{NO}_3)_2\) reported by Neogi and Mandal.

The Ethylenediaminetetraacetic Acid Complexes with Mercury (II)

In dilute solutions of ethylenediaminetetraacetic acid, well defined anodic polarograms were obtained of the ethylenediaminetetraacetate
complex with mercury (II). In dilute solutions containing both mercury (II) ion and ethylenediaminetetraacetic acid, continuous anodic to cathodic polarographic waves were obtained, which had well defined anodic and cathodic diffusion current regions.

Typical polarograms are shown in Figure 4. Slope analysis of the anodic wave yields the value 0.032 for $\Delta \pi/\Delta \log(i_d-i)$ which is in good agreement with the theoretical value of 0.0296 for a reversible two electron oxidation process. Slope analysis of the composite waves yields a value of 0.033 for $\Delta \pi/\Delta \log \frac{i_d(c) - i}{i - i_d(a)}$ where the subscripts c and a indicate cathodic and anodic respectively. This indicates the highly reversible nature of both processes.

The composite polarographic wave for a solution containing twice as much ethylenediaminetetraacetic acid as mercury (II) ion, 0.001 M and 0.0005 M respectively, had nearly equal anodic and cathodic diffusion currents, indicating that mercury (II) ion complexes with only one ethylenediaminetetraacetate ion at the pH of the measurement.

To determine the value of the equilibrium constant of reaction (31), solutions containing a large excess of ethylenediaminetetraacetic acid and a low concentration of mercury (II) ion were used. This permitted a control of pH without the presence of foreign buffer solutions which might complicate the equilibrium. Since the polarographic waves of such solutions would have an excessively large anodic
Figure 4
contribution, the half-wave potential would not be easily determined. Consequently, the potentials of the dropping electrode in equilibrium with the bulk of the solution were measured. Theoretically, this measurement should be made with a current flow equal to the charging current that is at the point of intersection of the cathodic polarographic wave with the residual current polarographic wave. Investigation of the difference between the spontaneous potential and the equilibrium potential showed no significant difference in these quantities for the solutions measured. This is demonstrated by the rather steep slope of the reduction wave across the point of zero current.

The concentration of the uncomplexed ethylenediaminetetraacetate ion, \([\text{Y}^4^-]\), was calculated from equation (44) after subtraction of the amount of ethylenediaminetetraacetate ion present in the complex from the total amount present in the solution. The acid dissociation constants of the ethylenediaminetetraacetic acid were determined by Schwarzenbach and Ackerman\(^{15a}\) who reported the following values of the negative logarithms of the constants at an ionic strength of 0.1:

\[
\begin{align*}
pK_1 &= 2.00, \\
pK_2 &= 2.67, \\
\end{align*}
\]

Table III shows the potential data obtained for solutions 0.001 molar in mercury (II) ion, 0.050 molar in ethylenediaminetetraacetic acid,
<table>
<thead>
<tr>
<th>$\pi_s$ vs. S.C.E.</th>
<th>pH</th>
<th>$\log [Y^{4-}]$</th>
<th>$\log K_{HgOHY}$</th>
<th>$\log K_{HgY}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>-0.1681</td>
<td>12.22</td>
<td>-1.32</td>
<td>(11.82)</td>
<td></td>
</tr>
<tr>
<td>-0.1549</td>
<td>11.48</td>
<td>-1.34</td>
<td>12.16</td>
<td></td>
</tr>
<tr>
<td>-0.1450</td>
<td>11.20</td>
<td>-1.36</td>
<td>12.13</td>
<td></td>
</tr>
<tr>
<td>-0.1269</td>
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<td>-1.48</td>
<td>12.21</td>
<td></td>
</tr>
<tr>
<td>-0.1148</td>
<td>10.18</td>
<td>-1.65</td>
<td>12.40</td>
<td></td>
</tr>
<tr>
<td>-0.1068</td>
<td>9.86</td>
<td>-1.86</td>
<td>12.58</td>
<td></td>
</tr>
<tr>
<td>-0.0910</td>
<td>9.53</td>
<td>-2.11</td>
<td>(12.68)$^+$</td>
<td>(22.04)$^{++}$</td>
</tr>
<tr>
<td>-0.0596</td>
<td>8.76</td>
<td>-2.82</td>
<td>(13.06)$^+$</td>
<td>(21.82)$^{++}$</td>
</tr>
<tr>
<td>+0.0158</td>
<td>6.99</td>
<td>-4.64</td>
<td></td>
<td>21.17</td>
</tr>
<tr>
<td>+0.0348</td>
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<td></td>
</tr>
<tr>
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<td>20.93</td>
<td></td>
</tr>
<tr>
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<td>-7.66</td>
<td>20.98</td>
<td></td>
</tr>
<tr>
<td>+0.1357</td>
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<td>-8.59</td>
<td>21.07</td>
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</tr>
<tr>
<td>+0.1541</td>
<td>4.22</td>
<td>-9.31</td>
<td>21.17</td>
<td></td>
</tr>
<tr>
<td>+0.1803</td>
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</tr>
<tr>
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<td>21.18</td>
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</tr>
<tr>
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<td>3.41</td>
<td>-10.98</td>
<td>(21.68)</td>
<td></td>
</tr>
<tr>
<td>+0.2179</td>
<td>3.10</td>
<td>-11.67</td>
<td>(21.38)</td>
<td></td>
</tr>
</tbody>
</table>

Av. 12.30 $\pm$ 0.20 Av. 21.12 $\pm$ 0.20

$^+$ Solved on basis of mean $K_{HgY}$

$^{++}$ Solved on basis of mean $K_{HgOHY}$
and an ionic strength adjusted to approximately 0.3 by additions of potassium hydroxide and potassium nitrate.

Figure 5 is a plot of equation (33). It is linear over most of the pH range, but shows deviations from theoretical at low and high pH values, indicating the formation of hydroxy and acidic complexes observed by Schwarzenbach and his coworkers for several other metal ions.

Calculations for the value of $K_{HgOHY}$, the formation constant of the hydroxy-ethylenediaminetetraaceto-mercurate (II) ion, were made according to equation (47), using the average value of log $K_{HgY}$. The individual values of log $K_{HgY}$ were calculated from equation (33), using the value of +0.0594 volts versus the saturated calomel electrode for $E^\circ$. The results of these calculations are shown in Table III.

No calculations for the complexity constant of the HgHY$^-$ complex could be made due to precipitation of the tetraacetic acid in solutions of pH less than 4.

The mercury (II)-ethylenediaminetetraacetate ion system was previously studied by Matyska and Kossler by a thorough analysis of the anodic depolarization waves produced with dilute solutions of ethylenediaminetetraacetic acid and changing pH. They identified three complexes, HgHY$^-$, HgY$^{2-}$ and HgOHY$^{3-}$, and reported these values for the equilibrium constants: log $K_{HgY} = 15.7$, log $K_{HgHY} = 9.0$ and log $K_{HgOHY} = 6.8$ which are significantly different from the
Figure 5

VOLTAGE VERSUS S.C.E. AT ZERO CURRENT
values reported here. Examination of their data indicates a possible error in the value which they assign the reference electrode used for the measurements. They reported a value for the Hg-Hg$_2$SO$_4$ reference electrode of +0.417 volts versus the normal hydrogen electrode, the deviation from the theoretical value of +0.65 volts being ascribed to impurities in the metallic mercury.

The average value of the log $K_{HgY}$ is $21.13 \pm 0.20$ and the average value of log $K_{HgOHY} = 12.30 \pm 0.30$ for solutions with an ionic strength of approximately 0.3 and a temperature of 25°C. The value for log $K_{HgY}$ may be compared with the value 22.15 for a mean ionic strength of 0.066 reported by Goffart, Michel and Duyckaerts\textsuperscript{16} when the present investigation was nearing completion. They used an analogous potentiometric method except the potential was taken at the point of intersection of the polarographic wave with the charging current curve.

The relative values of the two constants, $K_{HgY}$ and $K_{HgOHY}$ found in the present study agree with the relative values of these constants reported by Matyska and Kossler\textsuperscript{,}. This consideration leads to a value of log $K_{HgHY}$ of 14.5 on the basis of the data of Matyska and Kossler by correcting the potential of their reference electrode.

In 0.025 molar ethylenediaminetetraacetic acid and 0.001 molar mercury (II) ion, the diffusion current constant of the HgY complex is 3.09 microamperes\(^{-1}\) millimolar\(^{-1}\) mg\(^{2/3}\) sec\(^1/6\) for the pH range of 6 to 9.

SPECTROPHOTOMETRIC INVESTIGATIONS OF THE MIXED COMPLEXES FORMED BETWEEN COPPER (II) ION, AMMONIA AND BIDENTATE ANIONS

General Introduction

In a previous investigation by Aarnc\(^{17}\) the existence of a mixed complex of copper ion with both ammonia and pyrophosphate ion was indicated by the application of Job's method to spectrophotometric data. However, his experiments did not permit an evaluation of the equilibrium constants for the formation of the mixed complex. The present investigation was undertaken for the purpose of evaluating these equilibrium constants\(^{18},^{19}\). The method of study was then used to investigate the mixed complex of copper (II) ion with ammonia and oxalate ions. A related mixed complex of the copper (II) ion with
ethylenediamine and pyrophosphate was investigated by Loughran\textsuperscript{20,21}.

(20) E. D. Loughran, M. S. Thesis, The Ohio State University, 1953.

Several other methods were also used and these will be considered in detail.

The Stability of the Parent Complexes

The extinction curves and complexity constants for the pyrophosphate complexes of copper (II) ion have been obtained by Watters and Aaron\textsuperscript{22}.


while Bjerrum\textsuperscript{13,23} calculated the stepwise formation constants and extinction curves for the various copper (II) ammine complexes. Bjerrum and Nielsen\textsuperscript{1} correlated these results with those obtained for the ethylenediamine complex. Vosburgh and Cooper\textsuperscript{24} included copper ammines in their study of the method of continuous variations.


The copper (II) oxalate complex has been investigated potentio-
metrically by Britton and Jarrett\(^{25}\) who obtained a value of 8.29 for


the logarithm of the second complexity constant, in 0.01 M potassium
oxalate. It was investigated polarographically by Meites\(^{26}\) who obtained


a corresponding value of 10.32 in 1 M potassium oxalate. In the present
study the value 9.70 was taken for the logarithm of the complexity
constant of the oxalate complex at 25°C and unit ionic strength. This
value was reported by DeWitt and Watters.\(^{27}\)


Nomenclature and Definitions

In the investigation of complexes, particularly since Bjerrum\(^{13}\)
published his monograph on ammine complexes, it has been recognized
that the molecules or ions associated with the metal ion called ligands,
may be successively added to the central metal ion, thus

\[
M + A \rightleftharpoons MA
\]

and the corresponding formation constant is

\[
k_1 = \frac{[MA]}{[M][A]}
\]
In this dissertation, brackets indicate concentration in the general equations and the charges of ions are omitted for simplicity. The following steps and the corresponding consecutive formation constants are

\[ MA + A \rightleftharpoons MA_2; \quad \frac{[MA_2]}{[MA][A]} = k_2 \] (3)
\[ MA_2 + A \rightleftharpoons MA_3; \quad \frac{[MA_3]}{[MA][A]} = k_3 \] (4)
\[ MA_{i-1} + A \rightleftharpoons MA_i; \quad \frac{[MA_i]}{[MA_{i-1}][A]} = k_i \] (5)

A somewhat different system is useful in certain mathematical procedures. In this system the equilibrium for each intermediate with the parent central ion is considered and the constants are named consecutive complexity constants, thus

\[ M + A \rightleftharpoons MA; \quad \frac{[MA]}{[M][A]} = K_1 = k_1 \] (6)
\[ M + 2A \rightleftharpoons MA_2; \quad \frac{[MA_2]}{[M][A]^2} = K_2 = k_1k_2 \] (7)
\[ M + iA \rightleftharpoons MA_i; \quad \frac{[MA_i]}{[M][A]^i} = K_i = k_1k_2\cdots k_i \] (8)

The complexity constant for the highest complex is called the overall or total complexity constant.

Consider the following equilibria and their corresponding complexity constants

\[ M + aA \rightleftharpoons MA_a; \quad K_A = \frac{[MA_a]}{[M][A]^a} \] (9)
For the same metal ion in equilibrium with a different ligand, the equations are:

\[ M + bB \rightleftharpoons MB_b ; \quad K_B = \frac{[MB_b]}{[M][B]^b} \]  

(10)

It may be postulated that certain mixed complexes may form if the second ligand B is added to a solution containing MA\textsubscript{a} in an excess of A. Thus,

\[ MA_a + pB \rightleftharpoons MA_cB_p + (a-c)A ; \quad K_p = \frac{[MA_cB_p][A]^{a-c}}{[MA_a][B]^p} \]  

(11)

The corresponding equations for the addition of ligand A to solution of MB\textsubscript{b} in the presence of excess B,

\[ MB_b + tA \rightleftharpoons MB_uA_t + (b-u)B ; \quad K_q = \frac{[MB_uA_t][B]^{b-u}}{[MB_b][A]^t} \]  

(12)

If only one mixed complex forms then the compounds MA\textsubscript{c}B\textsubscript{p} and MB\textsubscript{u}A\textsubscript{t} are identical.

Equations for the equilibrium of the mixed complex with its parents may be written as follows:

\[ M + cA + pB \rightleftharpoons MA_cB_p ; \quad K_m = \frac{[MA_cB_p]}{[M][A]^c[B]^p} \]  

(13)

It can readily be shown that

\[ K_p = \frac{K_m}{K_A} \quad \text{and} \quad K_q = \frac{K_m}{K_B} \]  

(14)

In the present study the equations are somewhat simplified since only two bidentate pyrophosphates\textsuperscript{22} or pxalates\textsuperscript{25} associate with each copper ion. It was postulated that two ammonia molecules could replace one of these anions, thus
\[
\text{MB}_2 + 2A \rightleftharpoons \text{MBA}_2 + B^2 \quad K_F = \frac{[\text{MA}_2\text{B}][\text{B}]}{[\text{MB}_2][\text{A}]^2} \quad (15)
\]

where B refers to the bidentate ligands and A refers to the displacing ammonia molecule.

In the spectrophotometric measurements \(\log_{10} \frac{I_0}{I}\) is defined as the extinction. In the equation \(\log_{10} \frac{I_0}{I} = e c l\), \(e\) is the molar extinction coefficient if the concentration is given in moles per liter of solution and the cell length is given in centimeters.

**Calculation of Free Ligand Concentration**

In order to properly evaluate the amount of free ligand present in the solution, the total concentration of ligand and the amount of ligand involved in complex formation must be known. Spectrophotometrically, the amount of ligand involved in the formation of the various complexes is readily estimated. From the convergence of the extinction curves, the molecular extinction coefficient, \(e_m\), may be estimated for a wavelength \(\lambda\). Since the bidentate ligand is kept in excess, and the formation constants are of a sufficiently large magnitude, it may be assumed that all the metal ion is present initially as the MB\(_2\) complex. From the following expression

\[
f_m = \frac{(e_{\text{obs}} - e_B)}{(e_m - e_B)} \quad (16)
\]

\(f_m\), the fraction of the metal ion present as the mixed complex can be calculated. \(e_{\text{obs}}\) is the measured extinction, \(e_B\) is the extinction of the MB\(_2\) complex, and \(e_m\) is the extinction of the mixed complex.
If the concentration of metal ion is kept constant throughout the series of measurements, measured extinction values may be used for all quantities and the calculations are simplified.

The fraction of the metal ion present as the di-bidentate complex is then given by

\[ f_B = 1 - f_m \]  \hspace{1cm} (17)

For the reaction indicated by equation (15) the amount of uncomplexed B is given by

\[ [B] = C_B - 2f_B C_m - (1-f_B) C_m \]  \hspace{1cm} (18)

or

\[ [B] = C_B - (1+f_B) C_m \]  \hspace{1cm} (19)

where \( C_B \) is the total concentration of B present and \( C_m \) is the total concentration of metal ion present.

Since the bidentate molecules to be investigated are also acids, the association of the uncomplexed bidentate anions with hydrogen ions must also be considered. This consideration leads to the following equations for the pyrophosphate ion and the oxalate ion respectively,

\[ [P_2O_7^{4-}] = [C_p-(1+f_p)C_{cu}] \cdot \frac{K_3K_4}{K_3K_4 + K_3^{-aH^+} + aH^+} \]  \hspace{1cm} (20)

where \( K_3 \) and \( K_4 \) are the third and fourth successive dissociation constants of pyrophosphoric acid, \(^{22}\) having the values \( 10^{-5.61} \) and \( 10^{-7.68} \).

\[ [C_2O_4^{2-}] = C_{ox} - (1+f_{ox}) C_{cu} \]  \hspace{1cm} (21)
The acidity constants of oxalic acid have the values $10^{-1.14}$ and $10^{-3.85}$. Thus, oxalic acid is a sufficiently strong acid so that it is quantitatively dissociated over the pH range to be investigated.

The calculation of the concentration of the free displacing ligand, $A$, is made in an analogous manner and subject to the same considerations with respect to reaction with hydrogen ions. In the present investigation the displacing ligand is the ammonia molecule. The following equation is readily shown to yield the concentration of free ammonia,

$$\left[\text{NH}_3\right] = \left(C_n - \frac{2f_m}{C_{\text{Cu}}} \right) \cdot \frac{K_n}{K_n + a_{\text{H}^+}^+} \quad (22)$$

where $C_n$ indicates the total concentration of ammonia in all forms and $K_n$ is the constant for the dissociation of a hydrogen ion from $\text{NH}_4^+$. The value of $K_n$ to be used is $10^{-9.37}$ which was obtained experimentally and also by interpolation of the data of Bjerrum between the temperatures 22 and 30°C.

The Slope Intercept Method

The fundamental technique was introduced by Hildebrand and Benesi in a study of simple (1:1) complexes between iodine and

benzene or its derivatives. Siddall and Vosburgh\textsuperscript{30} used the technique


in studying the hydrolysis of ferric ion. Refinements in which the higher (1:2) complex and absorption by the reactants is also considered appear in papers by McConnell and Davidson\textsuperscript{31}, Landauer and McConnell\textsuperscript{32},

\textit{(31) Harden McConnell and N. Davidson, J. Am. Chem. Soc., 72, 3168 (1950).}

and Lawrey and McConnell.\textsuperscript{33}

\textit{(33) D. M. G. Lawrey and H. McConnell, J. Am. Chem. Soc., 74, 6175 (1950).}

If the equilibrium postulated by equation (15) obtains, in the presence of excess B, the increase in extinction should be due to the formation of the mixed complex since all of the metal ion is initially present as the MB\textsubscript{2} complex ion. Let \( \bar{e} \) represent the observed mean molar extinction coefficient of solutions containing M and an excess of the two ligands, A and B. At a given wavelength, the total extinction is

\[
\log_{10} I_0/I = \bar{e} [MB_2] + \bar{e} [MA_2B] = e_B [MB_2] + e_m [MA_2B] \tag{23}
\]

where \( e_B \) is the observed extinction for a solution containing the same
amount of metal ion and B as the other solutions but containing
no A, and \( e_m \) is the extinction of a solution of the mixed complex
the same concentration of metal ion.

For the reaction

\[
M + 2B \rightleftharpoons MB_2
\]  \hspace{1cm} (24)

the complexity constant may be written

\[
K_B = \frac{[MB_2]}{[M][B]^2}
\]  \hspace{1cm} (25)

For the reaction

\[
M + B + 2A \rightleftharpoons MA_2B
\]  \hspace{1cm} (26)

the complexity constant may be written

\[
K_m = \frac{[MA_2B]}{[M][A]^2 [B]}
\]  \hspace{1cm} (27)

Substituting for \([MA_2B]\) and \([MB_2]\) in equation (23), the values obtained from equations (27) and (25) respectively, equation (23)
becomes

\[
\bar{e} K_B [M] [B]^2 + \bar{e} K_m [M][A]^2 [B] = e_B K_B [M][B]^2 +
\]

\[
e_m K_m [M][A]^2 [B]
\]  \hspace{1cm} (28)

The equilibrium constant for the reaction postulated by
equation (15) may be expressed by

\[
K_r = \frac{[MA_2B][B]}{[MB_2][A]^2} = \frac{K_m}{K_B}
\]  \hspace{1cm} (29)

Dividing equation (28) by \( K_B \), \([M]\) and substituting \( K_r \) for its
equivalent from equation (29), the expression then becomes
Solving equation (30) for $\bar{e}$ and dividing by $[B]$ yields

$$\bar{e} = \frac{e_m K_r [A]^2 + e_B [B]}{K_r [A]^2 + [B]}$$  \hspace{1cm} (31)$$

Subtracting $e_B$ from both members of equation (31) gives

$$\bar{e} - e_B = \frac{e_m K_r [A]^2 + e_B K_r [A]^2}{K_r [A]^2 + [B]}$$  \hspace{1cm} (32)$$

Taking the reciprocal of equation (32) yields

$$\frac{1}{\bar{e} - e_B} = \frac{1}{e_m - e_B} + \frac{[B]}{(e_m - e_B) K_r [A]^2}$$  \hspace{1cm} (33)$$

Multiplying equation (33) by $[A]^2/[B]$ yields

$$\frac{[A]^2/[B]}{(\bar{e} - e_B)} = \frac{1}{(e_m - e_B) K_r} + \frac{1}{(e_m - e_B)} \frac{[A]^2}{[B]}$$  \hspace{1cm} (34)$$

Equation (34) is a linear equation with a slope equal to $1/(e_m - e_B)$ and an intercept equal to $1/(e_m - e_B) K_r$ provided that the postulated equilibrium is the correct one. In the regions where the postulated equilibrium does not hold the points will deviate from a straight line. $K_r$ is determined by dividing the slope by the intercept. The extinction coefficient of the mixed complex may be evaluated from the value of the reciprocal slope and $e_B$.

If the concentration of metal ion is kept constant throughout the series then $\bar{e}$ in equation (34) may be replaced by $\bar{E}$, the observed extinction; $e_B$ by $E_B$, the measured extinction of the metal ion bidentate
complex, and $E_m$ the extinction of the mixed complex may replace $e_m$.

Thus equation (34) is transformed in

$$\frac{[A]^2/[B]}{(E - E_B)} = \frac{1}{(E_m - E_B)K_r} + \frac{1}{(E_m - E_B)} \frac{[A]^2}{[B]}$$

(34a)

The extinction coefficient, $e_m$, is then obtained by dividing $E_m$ by the concentration of metal ion.

Where there is a continuous displacement of the ligand $B$ by $A$ and conversion to the other parent complex, $MA_4$, takes place, the slope-intercept method may be applied to the solution of the equilibrium constant from both parent complexes. The equations for the reaction

$$MA_4 + B \rightleftharpoons MA_2B + 2A$$

(35)

are completely analogous to those derived for the other case.

Other Methods

The following methods were also applied to the investigation of the mixed complex of copper (II) ion with oxalate ion and ammonia to ascertain whether they possessed a unique advantage. Consequently the equations will be developed for this particular system.

The Method of Lewis

This method of spectrophotometric analysis of complex ion equilibria was proposed and used by Lewis$^{34}$ then by Newton and

(34) W. B. Lewis, Thesis, University of California at Los Angeles, 1942.
Arcand\textsuperscript{35} and Whiteker and Davidson\textsuperscript{36}. This is the first application of this method to the study of equilibria involving mixed complexes.

Let $\bar{e}$ be the observed mean molar extinction coefficient, then

$$E = \log_{10} \frac{I_0}{I} = \bar{e} \quad C_{\text{Cu}} = e_{\text{ox}} \left[ \text{Cu(C}_2\text{O}_4\text{)}^2^- \right] + e_m \left[ \left[ \text{Cu(NH}_3\text{)}_2\text{(C}_2\text{O}_4\text{)} \right]^0 \right]$$

(36)

assuming that for the solutions chosen all of the copper (II) ion will be essentially in either the dioxalatocuprate (II) complex or a mixture of the mixed complex and the dioxalatocuprate (II) complex. Then,

$$\bar{e} \left[ \left[ \text{Cu(NH}_3\text{)}_2\text{(C}_2\text{O}_4\text{)} \right]^0 \right] + \bar{e} \left[ \text{Cu(C}_2\text{O}_4\text{)}^2^- \right] = e_{\text{ox}} \left[ \text{Cu(C}_2\text{O}_4\text{)}^2^- \right] + e_m \left[ \left[ \text{Cu(NH}_3\text{)}_2\text{(C}_2\text{O}_4\text{)} \right]^0 \right]$$

(37)

Solving equation (37) for $\bar{e}$ gives

$$\bar{e} \left[ \left[ \text{Cu(NH}_3\text{)}_2\text{(C}_2\text{O}_4\text{)} \right]^0 \right] = e_m \left[ \left[ \text{Cu(NH}_3\text{)}_2\text{(C}_2\text{O}_4\text{)} \right]^0 \right] - (\bar{e} - e_{\text{ox}}) \left[ \text{Cu(C}_2\text{O}_4\text{)}^2^- \right]$$

(38)

If equation (38) is divided by $\left[ \left[ \text{Cu(NH}_3\text{)}_2\text{(C}_2\text{O}_4\text{)} \right]^0 \right]$ then

$$\bar{e} = e_m - (\bar{e} - e_{\text{ox}}) \frac{\left[ \text{Cu(C}_2\text{O}_4\text{)}^2^- \right]}{\left[ \left[ \text{Cu(NH}_3\text{)}_2\text{(C}_2\text{O}_4\text{)} \right]^0 \right]}$$

(39)

The ratio $\left[ \text{Cu(C}_2\text{O}_4\text{)}^2^- \right] / \left[ \left[ \text{Cu(NH}_3\text{)}_2\text{(C}_2\text{O}_4\text{)} \right]^0 \right]$ may be expressed by the total complexity constants of the following reactions:
\[
\begin{align*}
\text{Cu}^{2+} + 2\text{C}_2\text{O}_4^{2-} & \rightleftharpoons \text{Cu}([\text{C}_2\text{O}_4]_2)^{2-} ;
K_{\text{ox}} = \frac{\left[\text{Cu}([\text{C}_2\text{O}_4]_2)^{2-}\right]}{\left[\text{Cu}^{2+}\right]\left[\text{C}_2\text{O}_4^{2-}\right]^2} \quad (40) \\
\text{Cu}^{2+} + 2\text{NH}_3 + \text{C}_2\text{O}_4^{2-} & \rightleftharpoons \text{Cu}([\text{NH}_3]_2([\text{C}_2\text{O}_4])\]^{0} \\
K_m = \frac{\left[[\text{Cu}([\text{NH}_3]_2([\text{C}_2\text{O}_4])\]^{0}\right]}{\left[\text{Cu}^{2+}\right][\text{NH}_3]^{2}\left[\text{C}_2\text{O}_4^{2-}\right]^2} \quad (41)
\end{align*}
\]

From these considerations

\[
\frac{\left[\text{Cu}([\text{C}_2\text{O}_4]_2)^{2-}\right]}{\left[[\text{Cu}([\text{NH}_3]_2([\text{C}_2\text{O}_4])\]^{0}\right]} = \frac{K_{\text{ox}} \left[\text{C}_2\text{O}_4^{2-}\right]}{K_m [\text{NH}_3]^{2}} \quad (42)
\]

If the term \( K \) is defined by

\[
K_T = \frac{K_m}{K_{\text{ox}}} \quad (43)
\]

equation (39) may be rewritten to become

\[
\overline{e} = e_m - (\overline{e} - e_{\text{ox}}) \left[\text{C}_2\text{O}_4^{2-}\right]/K_T [\text{NH}_3]^{2} \quad (44)
\]

This is the equation of a straight line if the observed molar extinction coefficient \( \overline{e} \), is plotted versus the term \( \left[\text{C}_2\text{O}_4^{2-}\right]/[\text{NH}_3]^{2} \).

The reciprocal slope of the straight line is \( K_T \) and the intercept will be \( e_m \), the extinction coefficient of the mixed complex.

If the metal ion concentration is kept constant, then extinction values may be used and equation (44) becomes

\[
\overline{E} = E_m - (\overline{E} - E_{\text{ox}}) \left[\text{C}_2\text{O}_4^{2-}\right]/K_T [\text{NH}_3]^{2} \quad (44a)
\]

\( e_m \), the extinction coefficient of the mixed complex may then be found by dividing \( E_m \) by the concentration of copper (II) ion.
The Method of Leden

Ido Leden developed a technique for the mathematical evaluation of the consecutive equilibria present in a solution of a metal ion and complexing ligand. This method has been applied to spectrophotometric data by Gruen and Katz.

Even though the method is not essentially one involving spectrophotometric data, the application of this technique of analysis is of interest since if there were a discernible stepwise formation of the mixed complex, it would be possible to obtain an evaluation of both stepwise constants. If the formation of the mixed complex is assumed to proceed in two steps, the following equations may be written:

\[ \text{Cu}^{2+} + \text{NH}_3 + \text{C}_2\text{O}_4^{2-} \rightleftharpoons [\text{Cu(NH}_3)(\text{C}_2\text{O}_4)]^0 \] (45)

\[ \text{Cu}^{2+} + 2\text{NH}_3 + 2\text{C}_2\text{O}_4^{2-} \rightleftharpoons [\text{Cu(NH}_3)_2(\text{C}_2\text{O}_4)]^0 \] (46)

For reactions (45) and (46), the following equilibrium constants may be written:

\[ K_{m1} = \frac{[[\text{Cu(NH}_3)(\text{C}_2\text{O}_4)]^0]}{[\text{Cu}^{2+}][\text{NH}_3][\text{C}_2\text{O}_4^{2-}]} \] (47)

\[ K_{m2} = \frac{[[\text{Cu(NH}_3)_2(\text{C}_2\text{O}_4)]^0]}{[\text{Cu}^{2+}][\text{NH}_3]^2[\text{C}_2\text{O}_4^{2-}]} \] (48)

Since the complex solutions contain an excess of complexing
ligands, the total amount of copper (II) ion present may be set equal to the sum of the concentrations of the complex ion species.

$$\left[\text{Cu}^{2+}\right]_T = \left[\text{Cu}^2\left(\text{C}_2\text{O}_4\right)_2\right]^{-2} + \left[\left[\text{Cu}\left(\text{NH}_3\right)(\text{C}_2\text{O}_4)\right]_0\right] + \left[\left[\text{Cu}\left(\text{NH}_3\right)_2\left(\text{C}_2\text{O}_4\right)\right]_0\right]$$

(49)

If $$\left[\text{Cu}^2\left(\text{C}_2\text{O}_4\right)_2\right]^{-2}$$ is subtracted from both members of equation (49), then

$$\left[\text{Cu}^{2+}\right]_T - \left[\text{Cu}^2\left(\text{C}_2\text{O}_4\right)_2\right]^{-2} = \left[\left[\text{Cu}\left(\text{NH}_3\right)(\text{C}_2\text{O}_4)\right]_0\right] + \left[\left[\text{Cu}\left(\text{NH}_3\right)_2\left(\text{C}_2\text{O}_4\right)\right]_0\right]$$

(50)

Substituting equations (47) and (48) into equation (50) gives

$$\left[\text{Cu}^{2+}\right]_T - \left[\text{Cu}^2\left(\text{C}_2\text{O}_4\right)_2\right]^{-2} = K_{m1} \left[\text{Cu}^{2+}\right] \left[\text{NH}_3\right] \left[\text{C}_2\text{O}_4^{-2}\right] + K_{m2} \left[\text{Cu}^{2+}\right] \left[\text{NH}_3\right]^2 \left[\text{C}_2\text{O}_4^{-2}\right]$$

(51)

If equation (51) is then divided by $$\left[\text{Cu}^2\left(\text{C}_2\text{O}_4\right)_2\right]^{-2} = K_{oX} \left[\text{Cu}^{2+}\right] \left[\text{C}_2\text{O}_4^{-2}\right]^2$$ this expression results

$$\frac{\left[\text{Cu}^{2+}\right]_T - \left[\text{Cu}^2\left(\text{C}_2\text{O}_4\right)_2\right]^{-2}}{\left[\text{Cu}^2\left(\text{C}_2\text{O}_4\right)_2\right]^{-2}} = K_{r1} \left[\text{NH}_3\right] + K_{r2} \left[\text{NH}_3\right]^2$$

(52)

where $$K_{r1}$$ and $$K_{r2}$$ are the respective mixed complex formation constants divided by $$K_{oX}$$, the formation constant of the dioxalatocuprate (II) complex.

Multiplying equation (52) by $$\left[\text{C}_2\text{O}_4^{-2}\right]/\left[\text{NH}_3\right]$$ yields

$$\left(\frac{\left[\text{Cu}^{2+}\right]_T - \left[\text{Cu}^2\left(\text{C}_2\text{O}_4\right)_2\right]^{-2}}{\left[\text{Cu}^2\left(\text{C}_2\text{O}_4\right)_2\right]^{-2}}\right) \left[\text{C}_2\text{O}_4^{-2}\right] = K_{r1} + K_{r2} \left[\text{NH}_3\right]$$

(53)
Let
\[ F_{\text{ox}} = \frac{\left[ \text{Cu}^{2+} \right]_T - \left[ \text{Cu}(\text{C}_2\text{O}_4)_2^{2-} \right]}{\left[ \text{Cu}(\text{C}_2\text{O}_4)_2^{2-} \right] \left[ \text{NH}_3 \right]} \]  
(54)

Then
\[ F_{\text{ox}} = K_{r_1} + K_{r_2} \left[ \text{NH}_3 \right] \]  
(55)

Equation (55) is the equation of a straight line if \( F_{\text{ox}} \) is plotted versus \( [\text{NH}_3] \). The value of the slope will be \( K_{r_2} \) and the intercept will be equal to \( K_{r_1} \). If no detectable intermediate is formed the plot should pass through the origin.

The Method of Bjerrum

Mixed complexes may also be studied by the application of the technique first developed by Bjerrum\(^{13}\) if the concentration of one ligand entering into the complex ion can be determined accurately by some means such as the measurement of pH with the glass electrode. In the case of the mixed complex formed by copper (II) ion with oxalate ion and ammonia it is possible to measure the concentration of free ammonia by this means.

If a solution contains copper (II) ion and excess oxalate, it may be assumed that all the copper is present as the dioxalatocuprate (II) ion. Then, in accordance with the nomenclature of Bjerrum, \( \bar{n} \) may be defined for this particular case as the average number of ammonia molecules that are bound to copper (II) ions in the complex. This quantity may be defined mathematically as follows:
\[
\bar{n} = \frac{C_N - [\text{NH}_3]}{C_{Cu}}
\]

Where \(C_N\) is the total concentration of ammonia present in all forms and \(C_{Cu}\) is the total concentration of copper (II) ion present in the solution.

\[
C_{Cu} = \left[\text{Cu}^{2+}\right] \left[\text{C}_2\text{O}_4^{2-}\right] + \left[\text{Cu}^2+(\text{NH}_3)_2(\text{C}_2\text{O}_4)\right]^0
\]

(57)

From equations (40) and (41)

\[
C_{Cu} = K_{ox} \left[\text{Cu}^{2+}\right] \left[\text{C}_2\text{O}_4^{2-}\right]^2 + K_m \left[\text{Cu}^{2+}\right] \left[\text{NH}_3\right]^2 \left[\text{C}_2\text{O}_4^{2-}\right]
\]

(58)

\[
C_N - [\text{NH}_3] = 2 \left[\text{Cu}^2+(\text{NH}_3)_2(\text{C}_2\text{O}_4)\right]^0
\]

(59)

Substituting (58), (41) and (59) in equation (56) and dividing by \([\text{Cu}^{2+}]\) yields:

\[
\bar{n} = \frac{2K_m \left[\text{NH}_3\right]^2 \left[\text{C}_2\text{O}_4^{2-}\right]}{K_m \left[\text{NH}_3\right]^2 \left[\text{C}_2\text{O}_4^{2-}\right]^2 + K_{ox} \left[\text{C}_2\text{O}_4^{2-}\right]^2}
\]

(60)

Dividing equation (60) by \(K_{ox}\) and \([\text{C}_2\text{O}_4^{2-}]\) gives

\[
\bar{n} = \frac{2K_r \left[\text{NH}_3\right]^2}{K_r \left[\text{NH}_3\right]^2 + \left[\text{C}_2\text{O}_4^{2-}\right]}
\]

(61)

Therefore

\[
K_r = \frac{\left[\text{C}_2\text{O}_4^{2-}\right]}{(2 - \bar{n}) \cdot \left[\text{NH}_3\right]^2}
\]

(62)

The customary practice in interpreting data obtained in this manner is to plot \(\bar{n}\) versus \(p[\text{NH}_3]\) where \(p[\text{NH}_3] = -\log[\text{NH}_3]\).

By reading directly from the graph, it is possible to obtain the total
formation constant to a first approximation by taking the value of 
$p\left[\text{NH}_3\right]$ at the point where $\bar{n} = 1$. It is quite easily shown that
for this particular case, when $\bar{n} = 1$, $\log K_r = \log[C_2O_4^{2-}] + 2p\left[\text{NH}_3\right]$. However, since this method is to be applied to titration
data, it is necessary to have an accurate value of $[C_2O_4^{2-}]$ which
changed during the course of the titration. The corrected value of
the oxalate concentration is obtained by substitution of the measured
values of $\bar{n}$ into the following expressions:

$$[C_2O_4^{2-}] = C_{ox} - \left[(4-\bar{n})/2\right] \cdot C_{Cu}$$

(63)

where $C_{ox}$ is the total amount of oxalate present.

The log $K$ values may then be accurately and conveniently
calculated from any $\bar{n}$ value and the corresponding value of
$p\left[\text{NH}_3\right]$.

The Equilibrium with Tetraammine-copper (II) ion

From the extinction coefficients for the mixed complex and
the dioxalatocuprate (II) ion and the tetraammine-copper (II) ion,
it is possible to calculate the concentrations of all species present
using determinants and the extinction at three wavelengths.

For the reaction

$$[\text{Cu(NH}_3)_2(C_2O_4)^0] + 2\text{NH}_3 \rightleftharpoons \text{Cu(NH}_3)_4^{2+} + C_2O_4^{2-}$$

(64)
the equilibrium constant may be written.

\[ K_Q = \frac{[\text{Cu(NH}_3\text{)}_4^{2+}] [\text{G}_2\text{O}_4^{2-}]}{[[\text{Cu(NH}_3\text{)}_2(\text{G}_2\text{O}_4)]^0] [\text{NH}_3]} \]  \hspace{1cm} (65)

The formation constant of the tetraammine complex is given by

\[ K_{N_4} = \frac{[\text{Cu(NH}_3\text{)}_4^{2+}]}{[\text{Cu}^{2+}] [\text{NH}_3]^4} \]  \hspace{1cm} (66)

Therefore, from equations (65) and (66)

\[ K_Q = \frac{K_{N_4}}{K_m} \]  \hspace{1cm} (67)

The value of \( K_{N_4} \) has been determined by Bjerrum\textsuperscript{13} and therefore the value of \( K_m \) can be determined.
Experimental

All of the spectrophotometric measurements were made using a Beckman Model DU spectrophotometer with a thermostatted cell compartment. The temperature was maintained at $25 \pm 0.1^\circ C$. The measurements of pH were made using a Beckman Model G pH meter with a Beckman General Purpose Glass Electrode. The pH meter was standardized with a 0.05 molar borax solution ($\text{pH at } 25^\circ C = 9.18$) immediately prior to any series of measurements and checked after the series. All pH measurements were made at $25 \pm 0.1^\circ C$.

The solution used for the spectrophotometric portions of the work were prepared in the following way: the required amount of ammonium nitrate was weighed directly into a 100 ml. volumetric flask. Twenty milliliters of the standard potassium oxalate or sodium pyrophosphate solution were added by pipette and ten, twenty, or twenty-five milliliters of the standard copper solution were added by pipette, depending upon the concentration of copper (II) ion desired. The necessary amount of ammonium hydroxide was added from a buret with the buret tip inserted down the neck of the flask to prevent both the loss of ammonia due to volatilization and reaction with the carbon dioxide of the air. The solutions were then diluted to volume with distilled water and brought to temperature by means of a constant temperature bath.
The ammonium hydroxide was prepared from a freshly opened bottle of ammonium hydroxide and diluted with carbon dioxide free water. The stock solution was stored in a paraffin-lined bottle protected from the atmosphere by guard tubes containing soda lime. The buret was attached to the bottle containing the standard ammonium hydroxide by a siphon tube and likewise was protected from carbon dioxide contamination by a guard tube containing soda lime.

The stock solution of ammonium hydroxide was standardized by titration with standard perchloric acid, using brom-cresol green as the indicator. The solution was standardized just before each series of experiments.

The potassium oxalate solution was standardized by titration with standard potassium permanganate solution and stored in a brown bottle. The salt was C.P. grade.

The stock solution of pyrophosphate ion was prepared by weighing the Na₄P₂O₇ + 10 H₂O Mallinckrodt Analytical Reagent grade. The salt was repeatedly standardized against standard HCl solution using brom-cresol green as the indicator.

The stock solution of the copper (II) ion was prepared from both the C.P. grade copper nitrate and copper sulfate salts. It was standardized electrolytically and check spectrophotometrically as the ethylenediamine complex.
The volumetric apparatus was calibrated by the manufacturer. Pyrex cells were used for the spectrophotometric measurements and were calibrated for the wavelength range over which they were used.

The titrations were performed in an electrolytic beaker which was closed from the air. The titration beaker was flushed out with nitrogen prior to the addition of the solutions. The titrating solution was the standard ammonium hydroxide and the solution titrated was fifty milliliters of a solution of 0.025 M copper nitrate, 0.05 M in ammonium nitrate and 0.1011 M in potassium oxalate. Attempts to add sodium or potassium nitrate in order to raise the ionic strength to unity met with failure due to precipitation, presumably of double copper oxalates. The solution was originally brought to temperature but temperature control was not maintained during the course of the titration. Magnetic stirring was used with a constant stirring speed maintained and a constant time interval kept between each addition of titrant and each reading of the pH meter. The pH meter was standardized just before the titration and was checked after the titration to determine if any drift had occurred.

The solutions having various \( [\text{Cu}^{2+}] : [\text{C}_2\text{O}_4^{2-}] : [\text{NH}_3] \) ratios for the spectrophotometric measurements contained 0.01 M or 0.02 M copper nitrate, 0.1011 M in potassium oxalate, 0.9 M in ammonium nitrate, and various concentrations of ammonia. One series 0.025
molar copper nitrate, 0.05 molar ammonium nitrate and 0.1011 molar potassium oxalate was used in order to obtain spectrophotometric data for approximately the same conditions as the titrations discussed above. The solutions were prepared in 100 ml. volumetric flasks.

The solutions having various \([\text{Cu}^{2+}] : [\text{P}_{2}\text{O}_{7}^{4-}] : [\text{NH}_3]\) ratios for the spectrophotometric measurements contained 0.025 M copper sulfate, 0.050 M tetra-sodium pyrophosphate, and 1 M ammonium nitrate. A second series of solutions was used which was identical with the first with the exception of the ammonium nitrate. One molar potassium nitrate was used instead of the more acidic ammonium nitrate to prevent the loss of pyrophosphate ions from the complex by combination with hydrogen ions. The solutions were prepared in 100 ml. volumetric flasks.

That chemical equilibrium was obtained instantaneously in all of the experiments was evident from the fact that the extinction was independent of the order of addition of the three components, copper (II) ion, pyrophosphate ion or oxalate ion and ammonia and from the fact that it did not change for several days. This behavior is typical for most of the complexes of copper (II) ion investigated in this laboratory.
Results and Conclusions

The Copper (II) Ion, Pyrophosphate Ion and Ammonia System

The addition of ammonia to solutions containing copper (II) ions and pyrophosphate ions produced extinctions which were different from those of either the ammine or pyrophosphate complexes or their mixtures. The change in extinction was investigated by Aaron\textsuperscript{17} using the Job method of continuous variation under a variety of conditions and he reported that the existence of the complex

$$[\text{Cu(NH}_3\text{)}_2\text{(P}_2\text{O}_7\text{)}]^2^-.$$  

A series of extinction curves for solutions containing 0.025 molar copper (II) ion, 0.05 molar pyrophosphate ion and 1 molar ammonium nitrate with varying concentration of ammonium hydroxide is shown in Figure 6 and Figure 7. Curve 1 was obtained for a solution with no ammonia added. Curve 9 was obtained for a solution which contained excess ammonia but no pyrophosphate ion. If the addition of ammonia to solutions containing $[\text{Cu(P}_2\text{O}_7\text{)}_2]^6^-$ had produced a simple mixture of $[\text{Cu(P}_2\text{O}_7\text{)}_2]^6^-$ and $[\text{Cu(NH}_3\text{)}_4]^2^+$, the family of curves should have been isosbestic at the wavelength of intersection of curves 1 and 9, 713 m$\mu$. Instead, all solutions up to 0.15 molar in ammonium hydroxide had extinction curves which were isosbestic with curve 1 at 763 m$\mu$, indicating equilibrium between $[\text{Cu(P}_2\text{O}_7\text{)}_2]^6^-$ and one new specie.
Figure 6
On the basis of the qualitative information provided by Aaron the following equilibrium may be postulated.

\[
[Cu(P_2O_7^{2-})]^{6-} + 2NH_3 \rightleftharpoons [Cu(NH_3)_2(P_2O_7)^{4-}] + P_2O_7^{4-} \quad (68)
\]

The general case for the slope-intercept equation then may be transformed to apply to the data by setting \( A = NH_3 \), \( B = P_2O_7^{4-} \). Therefore the equation is then

\[
\frac{[NH_3]^2}{[P_2O_7^{4-}]} = \frac{1}{(e - e_p)(e_{m} - e_p)K_r} + \frac{1}{(e_{m}-e_p)[P_2O_7^{4-}]} \quad (69)
\]

where \( e_p \) is the molar extinction of the dipyrophosphatocuprate (II) ion and \( K_r \) is the ratio of the complexity constant of the mixed complex, \( K_m \), to the complexity constant of the dipyrophosphatocuprate (II) complex, \( K_p \).

In Figure 8, the linearity of all points for solutions passing through the isosbestic at 763 m\( \lambda \) confirms the postulated equilibrium. The slope, \( 4.08 \times 10^{-2} \) molar cm. \( ^{-1} \), yielded \( 10^{1.21} \) as the value of \( K_r \) when divided by the intercept, \( 2.5 \times 10^{-3} \) molar cm. The sum of the reciprocal slope and \( e_p \), having the value \( 18.6 \) molar\( ^{-1} \) cm\( ^{-1} \) yielded the value \( 43.1 \) molar\( ^{-1} \) cm\( ^{-1} \) for \( e_m \) in close agreement with the limiting value estimated from curve 8, Figure 6. Substituting the value of \( K_r \) and the corrected value \( 10^{13.01} \) for the complexity constant for the dipyrophosphatocuprate (II) complex yields the value of \( 10^{14.22} \) for \( K_m \), the complexity constant of the mixed complex.
The equilibrium constant, \( K_m \), was also calculated from individual data. The calculation of the constant from individual results yielded a mean value of \( 10^{14.27} \) in excellent agreement with the value obtained by the slope-intercept method.

In order to investigate the stepwise addition of the ammonia molecules, solutions containing a \([Cu^{2+}] : [P_{2}O_{7}^{4-}] : [NH_3] \) ratio of 1:1 were used in conjunction with the less acidic potassium nitrate in order to prevent loss of \( P_{2}O_{7}^{4-} \) by association with hydrogen ion. However, precipitation occurred in those solutions which had a \([Cu^{2+}] : [P_{2}O_{7}^{4-}] : [NH_3] \) ratio of less than 1:1:2 in added ammonia, eliminating the possibility of determining the equilibrium constant for the addition of the first ammonia molecule. Nevertheless the following equations for the stepwise addition of ammonia may be written.

\[
[Cu(P_{2}O_{7})]^{2-} + NH_3 \rightleftharpoons [Cu(NH_3)(P_{2}O_{7})]^{2-} \quad (70)
\]

\[
k_m_1 = \frac{[Cu(NH_3)(P_{2}O_{7})]^{2-}}{[Cu(P_{2}O_{7})^{2-}][NH_3]} \quad (71)
\]

\[
[Cu(NH_3)(P_{2}O_{7})]^{2-} + NH_3 \rightleftharpoons [Cu(NH_3)_2(P_{2}O_{7})]^{2-} \quad (72)
\]

\[
k_m_2 = \frac{[Cu(NH_3)_2(P_{2}O_{7})]^{2-}}{[Cu(NH_3)(P_{2}O_{7})]^{2-}[^{2}][NH_3]} \quad (73)
\]

The combination of the experimental value of \( 10^{14.22} \) for \( K_m \) the total complexity constant, with \( k_{f_1} \), the formation constant for the
The monopyrophosphatocuprate (II) complex, having the value of $10^{4.24,22}$ yields a value of $10^{4.98}$ for the product of $k_m^1$, $k_m^2$ which is close to $10^{5.05}$, the product of the corresponding third and fourth formation constants of copper ammine under the same conditions. The latter constants have the values $10^{2.93}$ and $10^{2.12}$, respectively. On this basis $k_m^1$ and $k_m^2$ may be expected to have similar values.

Using the assumption that all of the copper (II) ion present in the solutions exists as either \([\text{Cu(NH}_3\text{)(P}_2\text{O}_7]^2}\) or \([\text{Cu(NH}_3\text{)}_2\text{(P}_2\text{O}_7]^2}\) or mixtures of the two, yields the following slope-intercept equation

$$\frac{1}{(e_m - e)} = \frac{1}{e_m - e_m^1} + \frac{k_m^2 [\text{NH}_3]}{(e_m - e_m^1)}$$

(74)

where $e_m$ is the previously determined value of the mixed complex and $e_m^1$ is the extinction coefficient of the complex containing only one ammonia.

For the solutions having 1 M KNO₃ as the supporting electrolyte, there was an isosbestic at 770 m\(\mu\). As the \([\text{Cu}^{2+}] : [\text{P}_2\text{O}_7^{4-}] : [\text{NH}_3]\) ratio was varied from 1:1:2 to 1:1:8, the resulting extinctions approached the limit for the \([\text{Cu(NH}_3\text{)}_2\text{(P}_2\text{O}_7]^2}\) as shown in Table IV.

The amount of free ammonia was calculated in a manner analogous to that previously described. For this calculation the value of $e_m^1$ was assumed to be 26.4 molar\(^{-1}\) cm\(^{-1}\), which is the mean of $e_m$ and $e_p$, the molar extinction coefficient of the monopyrophosphatocuprate (II) ion. The calculations were repeated using the accurate
Table IV

Effect of Varying the $[\text{Cu}^{2+}] : [\text{P}_2\text{O}_7^{4-}] : [\text{NH}_3]$ Ratio

<table>
<thead>
<tr>
<th>$C_{\text{Cu}}$</th>
<th>$C_{\text{P}_2\text{O}_7^{4-}}$</th>
<th>$C_{\text{NH}_3}$</th>
<th>pH</th>
<th>$E_{\text{percm. 650 nm}}$</th>
<th>log $K_m$</th>
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<tbody>
<tr>
<td>0.025</td>
<td>0.025</td>
<td>0.050</td>
<td>9.90</td>
<td>0.820</td>
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<tr>
<td>0.025</td>
<td>0.025</td>
<td>0.075</td>
<td>10.32</td>
<td>0.918</td>
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<tr>
<td>0.025</td>
<td>0.025</td>
<td>0.100</td>
<td>10.55</td>
<td>0.962</td>
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</tr>
<tr>
<td>0.025</td>
<td>0.025</td>
<td>0.125</td>
<td>10.66</td>
<td>1.003</td>
<td></td>
</tr>
<tr>
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<td>0.150</td>
<td>10.78</td>
<td>1.025</td>
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</tr>
<tr>
<td>0.025</td>
<td>0.025</td>
<td>0.250</td>
<td>10.99</td>
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<tr>
<td>0.025</td>
<td>0.050</td>
<td>0.025</td>
<td>7.39</td>
<td>0.685</td>
<td>14.29</td>
</tr>
<tr>
<td>0.025</td>
<td>0.050</td>
<td>0.050</td>
<td>7.78</td>
<td>0.820</td>
<td>14.27</td>
</tr>
<tr>
<td>0.025</td>
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<td>0.075</td>
<td>7.97</td>
<td>0.926</td>
<td>14.38</td>
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<td>0.025</td>
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<td>0.100</td>
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<td>1.01</td>
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<td>0.025</td>
<td>7.60</td>
<td>0.650</td>
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<td>0.050</td>
<td>7.89</td>
<td>0.775</td>
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<td>0.075</td>
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<td>8.30</td>
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<td>0.100</td>
<td>8.46</td>
<td>0.940</td>
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Table IV (contd.)

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<tr>
<th>C_{Cu}</th>
<th>C_{P_2O_7^{4-}}</th>
<th>C_{NH_3}</th>
<th>pH</th>
<th>E per cm 650 m(\mu)</th>
<th>log K_m</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.025</td>
<td>0.100</td>
<td>0.125</td>
<td>8.52</td>
<td>0.990</td>
<td>14.44</td>
</tr>
<tr>
<td>0.002</td>
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<td>0.0654</td>
<td>8.12</td>
<td>0.082</td>
<td>14.41</td>
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<tr>
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<td>0.020</td>
<td>0.098</td>
<td>8.37</td>
<td>0.086</td>
<td>14.47</td>
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</table>

The first six solutions contained 1 M KNO_3. The remainder contained 1 M NH_4NO_3.
value of 25.8 molar\(^{-1}\) cm\(^{-1}\), obtained from the slope-intercept data. The extinction measurements were made at 650 m\(\mu\), where the maximum in extinction occurs. The value 43.2 molar\(^{-1}\) cm\(^{-1}\) for \(e_m\) was obtained from the previous slope-intercept calculations.

The linearity of the plot of the slope intercept equation confirmed the postulated stepwise equilibrium. The slope of 2.89 molar cm\(^{-1}\) and intercept of 0.0575 molar cm\(^{-1}\) yielded a value of \(10^{1.70}\) for \(k_{m_2}\) which compares favorably with the value for the corresponding ammine.

The reciprocal of the intercept, 17.4 molar\(^{-1}\) cm\(^{-1}\), was subtracted from the value 43.2 molar\(^{-1}\) cm\(^{-1}\) calculated for \(e_m\) to yield the value 25.8 molar\(^{-1}\) cm\(^{-1}\) for \(e_m\) at 650 m\(\mu\).

The effect of the addition of more ammonium hydroxide is shown by the extinction curves in Figure 7. The solutions used were identical with those for Figure 6, the only difference being in the amount of ammonium hydroxide added. These curves shift from the \([\text{Cu(NH}_3]_4\]^2^+\) curve toward longer wavelengths and are no longer isosbestic with the family of curves for mixtures of \([\text{Cu(P}_2\text{O}_7)_2]^-\) and \([\text{Cu(NH}_3]_2\text{(P}_2\text{O}_7)]^-\) indicating the presence of other complex species. The lack of an isosbestic indicates the complicated nature of the equilibrium involved.

Bjerrum has shown that there is a shift toward longer wavelengths for solutions containing copper (II) ion and an ammonia
concentration in excess of 0.2 molar. He noticed the same effect when ammonia was added to solutions of diethylenediamine and the tetrapyridine complexes of copper (II) ion. This shift was ascribed to the tendency of copper (II) ion to add a molecule of ammonia in the fifth position. The shift exhibited by the curves in Figure 7 may be due to the formation of $[\text{Cu(NH}_3]\text{H}_3(\text{P}_2\text{O}_7)]^{2-}$. No calculations were made to confirm this since the effect is not large and at least four species are involved in the equilibrium.

The Copper (II) Ion, Oxalate Ion and Ammonia System

A typical family of extinction curves obtained for solutions containing 0.02 M copper (II) ion, 0.1011 M potassium oxalate, and 0.9 M ammonium nitrate with increasing concentrations of ammonium hydroxide is shown in Figures 9 and 10. These extinction curves exhibit two isosbestic points: one at 740 m$\mu$ for curves 3 to 9, the other at 665 m$\mu$ for curves 10, 11 and 12.

The slope-intercept method was applied initially to extinction data obtained at 650 m$\mu$ since this appeared to be the wavelength of maximum extinction for the mixed complex. The value of the extinction coefficient of the mixed complex, $e_m$, was estimated from the convergence of the extinction curves and the concentrations of the free ligands present calculated from equations (21) and (22) in conjunction with pH measurements.
Figure 9
The experimental data and the values calculated for a plot of equation (34) where \( A = \text{NH}_3 \), \( B = \text{C}_2\text{O}_4^{2-} \) and \( e_B \) is then the extinction coefficient of the dioxalatocuprate (II) ion are shown in Table V. The plot of equation (34a) from the data in Table V is shown in Figure 11 and is a straight line with scattering appearing only at high concentrations of added ammonium hydroxide where the dioxalatocuprate (II) complex is almost completely converted to the mixed complex. The value of \( e_m \) found from the reciprocal slope of the line in Figure 11 was 44.5 molar\(^{-1}\) cm\(^{-1}\) where the value estimated from the extinction curves was 45.3 molar\(^{-1}\) cm\(^{-1}\). This is satisfactory agreement since the errors in the extinction measurements are rather large at the high extinction values of these solutions. The value of log \( K_R \) was found to be 3.11 at 25°C from solutions 0.02 molar in copper (II) ion, 0.10 molar in potassium oxalate and 0.9 molar in ammonium nitrate.

The values obtained for the concentrations of free ammonia and free oxalate ion from the extinction measurements at 650 m\(\mu\) were applied to extinction data at 620 m\(\mu\) and 600 m\(\mu\) to obtain the extinction coefficients of the mixed complex at those wavelengths and the value of \( K_R \) by means of the slope-intercept method. The value of log \( K_R \) at 620 m\(\mu\) was 3.12. The value of log \( K_R \) at 600 m\(\mu\) was 3.09.

The concentrations of the mixed complex and the dioxalatocuprate (II) ion were recalculated by simultaneous equations from extinction measurements at two wavelengths and the extinction
Table V

Slope-Intercept Data at 650 mA

<table>
<thead>
<tr>
<th>E</th>
<th>$\bar{E}$</th>
<th>$\bar{e}$</th>
<th>$f_m$</th>
<th>$f_{ox}$</th>
<th>$[C_2O_4^{2-}]$</th>
<th>pH</th>
<th>$[NH_3] \times 10^3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.582</td>
<td>29.1</td>
<td>0.157</td>
<td>0.843</td>
<td>0.0642</td>
<td>6.87</td>
<td>2.86</td>
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</tr>
<tr>
<td>0.652</td>
<td>32.6</td>
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<td>0.660</td>
<td>0.0679</td>
<td>7.14</td>
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</tr>
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<td>0.714</td>
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<td>0.497</td>
<td>0.0711</td>
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<td>7.57</td>
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</tr>
<tr>
<td>0.761</td>
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<td>0.626</td>
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<td>0.0736</td>
<td>7.43</td>
<td>10.52</td>
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<tr>
<td>0.824</td>
<td>41.2</td>
<td>0.791</td>
<td>0.209</td>
<td>0.0769</td>
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<tr>
<td>0.850</td>
<td>42.5</td>
<td>0.859</td>
<td>0.141</td>
<td>0.0782</td>
<td>7.87</td>
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<tr>
<td>0.885</td>
<td>44.25</td>
<td>0.950</td>
<td>0.050</td>
<td>0.0800</td>
<td>8.10</td>
<td>48.42</td>
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</tr>
</tbody>
</table>

$$\frac{[NH_3]^2}{[C_2O_4^{2-}]} \times 10^4$$

<table>
<thead>
<tr>
<th>Value</th>
<th>1.274</th>
<th>2.12</th>
<th>106</th>
</tr>
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<tr>
<td>4.200</td>
<td>3.23</td>
<td>161.5</td>
<td></td>
</tr>
<tr>
<td>8.06</td>
<td>4.20</td>
<td>210</td>
<td></td>
</tr>
<tr>
<td>15.00</td>
<td>6.28</td>
<td>314</td>
<td></td>
</tr>
<tr>
<td>34.80</td>
<td>11.52</td>
<td>576</td>
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<tr>
<td>109.0</td>
<td>33.23</td>
<td>1661.5</td>
<td></td>
</tr>
<tr>
<td>293.0</td>
<td>80.72</td>
<td>4036.0</td>
<td></td>
</tr>
</tbody>
</table>

The solutions were 0.02 molar in copper (II) ion, 0.1011 molar in potassium oxalate, and 0.90 molar in ammonium nitrate. The value of $e_m$ used was 0.906 or 45.3 molar$^{-1}$ cm$^{-1}$. The measured value of $e_{ox}$ was 0.522 or 26.1 molar$^{-1}$ cm$^{-1}$. 
Figure 11

\[ 10^4 \times \frac{[\text{NH}_3]^2}{[\text{C}_2\text{O}_4^{2-}]} \times (\bar{E} - E_{\text{ox}}) \]

\[ 10^5 \times \frac{[\text{NH}_3]^2}{[\text{C}_2\text{O}_4^{2-}]} \]

Figure 11
coefficients for the mixed complex at these wavelengths that were obtained from slope-intercept plots. More consistent results were obtained for the concentrations of all species present when the wavelengths chosen were 650 m$\mu$ and 680 m$\mu$ than for any other pair of wavelengths due to the greater reliability of the values of $e_m$ at these wavelengths. From these data, the individual values of $K_r$ were calculated for each solution measured. Table VI shows a summary of the individual values calculated for log $K_r$.

Deviations occur in the calculated value of $K_r$ after the concentration of added ammonium hydroxide reaches 0.06 molar. This is not unreasonable since the critical term $\frac{[\text{Cu(NH}_3)_2(\text{C}_2\text{O}_4)^0]}{[\text{Cu(\text{C}_2\text{O}_4})_2]^2^-}$. At high concentrations of the mixed complex, this term becomes subject to large error due to the appreciable error in the determination of $[\text{Cu(\text{C}_2\text{O}_4})_2]^2^-$ by spectrophotometric means.

A second series of solutions prepared in the same manner as previously but containing 0.01 molar copper (II) ion upon application of the slope-intercept method to the spectrophotometric results gave a value of 3.02 for log $K_r$ and 46.0 molar $^{-1}$ cm$^{-1}$ for the value of $e_m$ at 650 m$\mu$. The value of $e_m$ estimated from the absorption curves was 46.2 molar$^{-1}$ cm$^{-1}$.

The linearity of all plots of equation (34a) and the consistency of the values obtained for log $K_r$ from both the slope-intercept plots for several wavelengths and the individual data indicate that the
Table VI

$K_r$ from Individual Data

Calculated at 650 m$\mu$ and 600 m$\mu$

<table>
<thead>
<tr>
<th>$[\text{Cu(NH}_3)_2(\text{C}_2\text{O}_4)^+]$</th>
<th>$[\text{Cu}^2+ (\text{C}_2\text{O}_4^2-)]$</th>
<th>$[\text{C}_2\text{O}_4^2-]$</th>
<th>$[\text{NH}_3]^2 \times 10^5$</th>
<th>$\log K_r$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0030</td>
<td>0.0172</td>
<td>0.0637</td>
<td>0.818</td>
<td>3.13</td>
</tr>
<tr>
<td>0.0067</td>
<td>0.0133</td>
<td>0.0678</td>
<td>2.852</td>
<td>3.08</td>
</tr>
<tr>
<td>0.0102</td>
<td>0.0097</td>
<td>0.0715</td>
<td>5.73</td>
<td>3.12</td>
</tr>
<tr>
<td>0.0131</td>
<td>0.0065</td>
<td>0.0750</td>
<td>11.07</td>
<td>3.13</td>
</tr>
<tr>
<td>0.0164</td>
<td>0.0034</td>
<td>0.0783</td>
<td>26.73</td>
<td>3.18</td>
</tr>
<tr>
<td>0.0170</td>
<td>0.0032</td>
<td>0.0779</td>
<td>85.56</td>
<td>2.70</td>
</tr>
<tr>
<td>0.0192</td>
<td>0.0006</td>
<td>0.0007</td>
<td>234.4</td>
<td>3.04</td>
</tr>
</tbody>
</table>

Calculated at 650 m$\mu$ and 680 m$\mu$

<table>
<thead>
<tr>
<th>$[\text{Cu(NH}_3)_2(\text{C}_2\text{O}_4)^+]$</th>
<th>$[\text{Cu}^2+ (\text{C}_2\text{O}_4^2-)]$</th>
<th>$[\text{C}_2\text{O}_4^2-]$</th>
<th>$[\text{NH}_3]^2 \times 10^5$</th>
<th>$\log K_r$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0036</td>
<td>0.0161</td>
<td>0.0653</td>
<td>0.818</td>
<td>3.25</td>
</tr>
<tr>
<td>0.0059</td>
<td>0.0147</td>
<td>0.0658</td>
<td>2.873</td>
<td>2.96</td>
</tr>
<tr>
<td>0.0100</td>
<td>0.0101</td>
<td>0.0688</td>
<td>5.73</td>
<td>3.08</td>
</tr>
<tr>
<td>0.0129</td>
<td>0.0068</td>
<td>0.0746</td>
<td>11.56</td>
<td>3.09</td>
</tr>
<tr>
<td>0.0158</td>
<td>0.0042</td>
<td>0.0769</td>
<td>26.73</td>
<td>3.03</td>
</tr>
<tr>
<td>0.0170</td>
<td>0.0031</td>
<td>0.0779</td>
<td>85.61</td>
<td>2.70</td>
</tr>
<tr>
<td>0.0193</td>
<td>0.0007</td>
<td>0.0804</td>
<td>212.4</td>
<td>3.02</td>
</tr>
</tbody>
</table>

Solutions were 0.02 molar in copper (II) ion, 0.1011 molar in potassium oxalate, and 0.90 molar in ammonium nitrate.

The average of $\log K_r$ is 3.035.
equilibrium postulated by equation (15) is the prevailing one in these solutions.

Application of the Lewis method to the data obtained for the series of solutions containing 0.01 molar copper (II) ion, at 650 m\(\lambda\) showed a high degree of scattering for a plot of equation (44a). Presumably this was due to the fact that the difference between the extinction coefficient of the mixed complex and the dioxalato-cuprate (II) complex at 650 m\(\lambda\) is not sufficiently large. To increase the term \((E - E_{ox})\) in equation (44a) the copper (II) ion concentration was increased. With this change the results shown in Table VII and Figure 12 were obtained.

The values used for the concentration of ammonia and uncomplexed oxalate were similar to those calculated for the slope-intercept determination made at 650 m\(\lambda\). The value of \(e_m\) obtained by extrapolation of the linear portion of the curve in Figure 12 is 44.9 molar\(^{-1}\) cm\(^{-1}\) where the value estimated from the extinction curves is 45.3 molar\(^{-1}\) cm\(^{-1}\). Points in the regions of low concentrations of added ammonium hydroxide show scattering and in order to obtain a reasonable straight line too much weight must be placed upon the data obtained at higher concentrations of ammonium hydroxide where the errors may be quite large. However, the value of log \(K_F\) obtained from this plot was 3.02. Thus, the Lewis method was less effective than the Hildebrand method.
Table VII

Data for the Lewis Method

<table>
<thead>
<tr>
<th>$E$</th>
<th>$\left[\text{C}_2\text{O}_4^{2-}\right]/\left[\text{NH}_3\right]^2$</th>
<th>$\left[\text{C}_2\text{O}_4^{2-}\right]/\left[\text{NH}_3\right]^2$</th>
<th>$\left(\bar{E} - E_{\text{ox}}\right)$</th>
<th>$\bar{E}$</th>
<th>$(\bar{E} - E_{\text{ox}}) \left[\text{C}_2\text{O}_4^{2-}\right]/\left[\text{NH}_3\right]^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.582</td>
<td>7850.</td>
<td>471.</td>
<td>29.1</td>
<td>23,550</td>
<td></td>
</tr>
<tr>
<td>0.652</td>
<td>2380</td>
<td>309.</td>
<td>32.6</td>
<td>15,450</td>
<td></td>
</tr>
<tr>
<td>0.714</td>
<td>1240</td>
<td>238.</td>
<td>35.7</td>
<td>11,900</td>
<td></td>
</tr>
<tr>
<td>0.761</td>
<td>665</td>
<td>159.</td>
<td>38.05</td>
<td>7,950</td>
<td></td>
</tr>
<tr>
<td>0.824</td>
<td>288</td>
<td>87.0</td>
<td>41.2</td>
<td>4,350</td>
<td></td>
</tr>
<tr>
<td>0.850</td>
<td>91.4</td>
<td>30.0</td>
<td>42.5</td>
<td>1,500</td>
<td></td>
</tr>
<tr>
<td>0.885</td>
<td>34.1</td>
<td>12.4</td>
<td>44.25</td>
<td>620</td>
<td></td>
</tr>
</tbody>
</table>
Figure 12

\[ \frac{[\text{HN}][\text{C}_2\text{O}_4^2\text{z}]}{[\text{C}_2\text{O}_4^2\text{z}]} \times (e - e^0) \]
The application of such a function as that derived from the method of Leden to the spectrophotometric data was possible only for the series of solutions 0.02 molar in copper (II) ion. Even then, after the solutions were 0.05 molar in added ammonium hydroxide, there was very bad scattering of the experimental points. The plot of equation (55) for the data contained in Table VIII is shown in Figure 13. For the linear portion of the curve shown in Figure 13, the value of $3.14$ was found for $\log K_r$.

The fact that the linear portion of the curve shown in Figure 13 may be extrapolated to the origin is evidence that the only mixed complex formed in these solutions in any appreciable quantity is the diammino-oxalatocuprate (II) complex.

An examination of the function, $F_{OX}$, shows that the critical term is the ratio $\left[\frac{[\text{Cu(NH}_3)_2(\text{C}_2\text{O}_4)]^0}{[\text{Cu(C}_2\text{O}_4)_2]^2}\right]$ and the function is accurate only for intermediate ratios.

Using extinction data obtained for solutions 0.12 molar, 0.16 molar and 0.20 molar in added ammonium hydroxide and solving $K_Q$ from equation (65) gave the results appearing in Table IX. The concentrations of the complex species were calculated from simultaneous equations at two wavelengths using the known values of the extinction coefficients of the tetraammine copper (II) ion at these wavelengths and the estimated values of $e_m$ for these wavelengths.
Table VIII

Calculations for the Leden Function

<table>
<thead>
<tr>
<th></th>
<th>([\text{Cu} (\text{NH}_3)_2 (\text{C}_2\text{O}_4)_2]^{2+})</th>
<th>([\text{Cu} (\text{C}_2\text{O}_4)_2]^{2+})</th>
<th>([\text{C}_2\text{O}_4^{2-}] / [\text{NH}_3])</th>
<th>(F_{\text{ox}})</th>
<th>([\text{NH}_3]) x 10^3</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0030</td>
<td>0.0172</td>
<td>22.27</td>
<td>3.884</td>
<td>2.86</td>
<td></td>
</tr>
<tr>
<td>0.0067</td>
<td>0.0133</td>
<td>12.70</td>
<td>6.397</td>
<td>5.34</td>
<td></td>
</tr>
<tr>
<td>0.0102</td>
<td>0.0097</td>
<td>9.445</td>
<td>9.931</td>
<td>7.57</td>
<td></td>
</tr>
<tr>
<td>0.0131</td>
<td>0.0065</td>
<td>7.129</td>
<td>14.37</td>
<td>10.52</td>
<td></td>
</tr>
<tr>
<td>0.0164</td>
<td>0.0032</td>
<td>4.788</td>
<td>24.54</td>
<td>16.35</td>
<td></td>
</tr>
<tr>
<td>0.0170</td>
<td>0.0031</td>
<td>2.663</td>
<td>14.60</td>
<td>29.25</td>
<td></td>
</tr>
<tr>
<td>0.0192</td>
<td>0.0006</td>
<td>1.667</td>
<td>53.34</td>
<td>48.42</td>
<td></td>
</tr>
</tbody>
</table>

The concentrations of the complex species are those calculated from extinction measurements made at the wavelengths 650 m\(\mu\) and 600 m\(\mu\).
Figure 13
Table IX

Calculation of $K_Q$ from Extinction Measurement

<table>
<thead>
<tr>
<th>$[\text{NH}_4\text{OH}]$</th>
<th>$\bar{e}_{620} \text{ m}\mu$</th>
<th>$\bar{e}_{580} \text{ m}\mu$</th>
<th>$[\text{Cu(NH}_3)_4^{4+}]$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.120</td>
<td>0.848</td>
<td>0.615</td>
<td>0.0019</td>
</tr>
<tr>
<td>0.160</td>
<td>0.885</td>
<td>0.678</td>
<td>0.0040</td>
</tr>
<tr>
<td>0.200</td>
<td>0.920</td>
<td>0.732</td>
<td>0.0057</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>$[\text{Cu(NH}_3)_2(\text{C}_2\text{O}_4)]^0$</th>
<th>pH</th>
<th>$[\text{NH}_3]$</th>
<th>$K_Q$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0184</td>
<td>8.36</td>
<td>0.087</td>
<td>1.153</td>
</tr>
<tr>
<td>0.0167</td>
<td>8.55</td>
<td>0.132</td>
<td>1.146</td>
</tr>
<tr>
<td>0.0155</td>
<td>8.67</td>
<td>0.166</td>
<td>1.140</td>
</tr>
</tbody>
</table>

The solutions measured were 0.020 molar in copper (II) ion, 0.1011 molar in potassium oxalate, and 0.90 molar in ammonium nitrate.
The average value of $K_Q$ was found to be 1.146 and the average value of $\log K_m$ then is 12.51 using the Bjerrum value of 12.57 for $\log K_{N_4^*}$. The value of $\log K_m$ calculated in this way is low relative to any of the values calculated from the spectrophotometrically determined value of $\log K_r$. This is to be expected since it is easily shown from calculations based on the Bjerrum's value $K_8 = 2.8$ for the fifth formation constant of the pentaamminocopper (II) ion that in these solutions several percent of the copper ion exists as the pentaamminocopper ion.

Figure 14 shows a plot of titration experiments applying the method of Bjerrum to the titration data. In the vicinity of $\bar{n} = 2$ there is an observable inflection point but no levelling off since tetraammine copper (II) starts to form.

Calculations of $\log K_r$ are shown in Table X. The average value obtained from the titration experiments is $\log K_r = 3.22$. This may be compared with the value 3.18 obtained by slope-intercept treatment of spectrophotometric data for similar solutions. The latter series of solutions were 0.025 molar in copper (II) ion, 0.1011 molar in potassium oxalate and 0.05 molar in ammonium nitrate with ammonia varied.

Due to the possibility of drift in titration data individual solutions were prepared for every experimental point. This also provided better control of the ionic strength and the temperature.
Figure 14
Table X

Calculation of $K_r$ from Titration Data

<table>
<thead>
<tr>
<th>$\bar{n}$</th>
<th>$[\text{NH}_3] \times 10^3$</th>
<th>$[\text{C}_2\text{O}_4^{2-}]$</th>
<th>log $K_r$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.508</td>
<td>3.25</td>
<td>0.0565</td>
<td>3.55</td>
</tr>
<tr>
<td>1.010</td>
<td>6.54</td>
<td>0.0617</td>
<td>3.16</td>
</tr>
<tr>
<td>1.612</td>
<td>13.65</td>
<td>0.0675</td>
<td>2.93</td>
</tr>
<tr>
<td>0.516</td>
<td>3.25</td>
<td>0.0566</td>
<td>3.46</td>
</tr>
<tr>
<td>1.027</td>
<td>6.54</td>
<td>0.0619</td>
<td>3.17</td>
</tr>
<tr>
<td>1.602</td>
<td>11.69</td>
<td>0.0676</td>
<td>3.07</td>
</tr>
</tbody>
</table>

The average value of log $K_r$ is 3.22.
The spectrophotometric curves for all series showed no isosbestic for the first several solutions of each series. One possible explanation is that other complexes may form with only traces of ammonia.

The average value of log $K_T$ by all graphical evaluations of the spectrophotometric data is 3.10. This yields a value of 12.80 for log $K_m$ using the value of 9.70 for log $K_{ox}$ as calculated by DeWitt and Watters. 27

The consistency of the data and the consistency of the value of log $K_T$ determined both by titration and spectrophotometric methods indicate that the equilibria postulated by equations (15) and (64) are the ones predominating in the solutions measured.

Meites 26 previously studied this system polarographically and was able to determine from the shift in halfwave potential with ammonia concentration that two molecules of ammonia were removed from the mixed complex upon reduction of the copper (II) ion to copper (I). However, he was unable to determine any formulae or calculate any equilibrium constants due to the presence of a two-step electro-reduction process containing one thermodynamically irreversible step, the copper (I) to the amalgam.

Of the spectrophotometric methods for evaluating complex ion equilibria, the most consistent and most generally applicable appears to be the slope-intercept method.
Table XI

Determination of the Acid Dissociation Constant of the Ammonium Ion at 25°C

<table>
<thead>
<tr>
<th>$[\text{C}_2\text{O}_4^{2-}]$</th>
<th>$[\text{NH}_4^+]$</th>
<th>$[\text{NH}_4\text{OH}]$</th>
<th>pH</th>
<th>$pK_N$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1011</td>
<td>0.050</td>
<td>0.0100</td>
<td>8.73</td>
<td>9.43</td>
</tr>
<tr>
<td>0.1011</td>
<td>0.050</td>
<td>0.0200</td>
<td>9.05</td>
<td>9.45</td>
</tr>
<tr>
<td>0.1011</td>
<td>0.050</td>
<td>0.0501</td>
<td>9.44</td>
<td>9.44</td>
</tr>
</tbody>
</table>

The average value of $pK_N$ is 9.44, which was used to calculate $p[\text{NH}_3]$ in Figure 14 from Titration Data.
AUTobiography

I, John Grove Mason, was born in Louisville, Kentucky on December 4, 1929. I received my secondary education in the public schools of Louisville, Kentucky and Kansas City, Missouri, graduating from Louisville Male High School in June, 1946. I received my B.S. in Chemistry from the University of Louisville, Louisville, Kentucky, in June, 1950 and entered The Ohio State University Graduate School in October of that year. From October 1950 until June 1952 I was a research assistant for the C. F. Kettering Foundation Project No. 367 and worked on Pre-biological Photosynthesis. Subsequently I was employed by the Department of Chemistry as alternately a teaching assistant and a research assistant. I was inducted into the Army of the United States on October 25, 1954 and completed the dissertation while on leave in January, 1955.