The lack of published experiments on determination of stepwise equilibrium constants is striking in view of the prominence given to coordination chemistry and complex ion equilibrium calculations in chemistry courses. One experiment on the overall constant in the silver-ammine system has appeared in this Journal. Student experiments which consider only one predominant species (usually using Job's method) give no idea of the more common complexity met in most systems consisting of metal ions and the ligands NH₃, halide ions, SCN⁻, etc. Knowledge of the stepwise constants is needed to find the distribution of species in the system and to make decisions as to the quantitative applications of the complexes. There is a frequent elementary textbook treatment of the subject which leaves the impression that only one, the highest, complex forms in appreciable amounts. In a 1966 text, example problems are shown incorrectly worked out on this basis. The detailed thought that is given to a laboratory experiment and its calculations should help clarify the subject for the student. Teachers who have not introduced this topic because of its complexity may be inspired to do so after considering the consistent and clarifying mathematical treatment of a variety of complex equilibria by Butler (2).

In general, many experimental and mathematical difficulties are encountered in the determination of formation constants, as examination of the treatise by Rossotti and Rossotti (3) will verify. However, there are a few systems favorable for student investigation. Bjerrum's method for transition metal ion ammines (4) can give extensive data in a short time and lead to approximations to the first four copper-ammine formation constants. The graphical method can give the student a clear grasp of the functional relations involved.

The following adaptation was used with good results by advanced quantitative chemistry students and might serve in any course treating equilibria quantitatively. The experimental work was completed easily in one afternoon by students working in pairs. They had previously prepared standard solutions and were familiar with the pH meter. The ammine systems with Ni(II), Ag(I), Zn(II), Cd(II), and Co(II) might also be assigned to different students or groups. Air oxidation of Co(II) under the conditions required is said to be slow enough not to interfere (4).

The system described here is an aqueous solution of Cu(II), NH₃, NH₄⁺, NO₂⁻, and their possible combinations. The advantageous feature of Bjerrum's method lies in the simple relation of pH to uncoordinated ammonia concentration under the special conditions used. These are: high and constant NH₄NO₃ concentration, 2.00 M, with much lower metal ion and NH₃ concentrations. This keeps the pH below 7, reduces OH⁻ complexing, and provides constant ionic strength so that, from the Ke expression for NH₄⁺,

\[ [\text{NH}_3][\text{H}^+] = [\text{NH}_4^+][\text{H}^+] \]

where \( s \) refers to the values in a known stock solution of NH₃ in 2 M NH₄NO₃, and \( x \) refers to the values in an unknown mixture which is also 2 M in NH₄NO₃. Thus, measurement of pH serves to give the uncoordinated NH₃ concentration in the solutions to which the metal ion has been added. Now \( n \), the average number of NH₃ bound per Cu(II) present, the ligand number, can be calculated. Since \( n \) depends only on NH₃ concentration and the Ke values, stepwise formation constants, a plot of \( n \) versus log NH₃ yields the formation curve which allows estimates of the Ke values (2, 4). A sample calculation and student curve appear below.

The Experiment

Bjerrum mixed known solutions of metal ion and NH₃ to get each point on the curve. A shorter procedure, which may entail some NH₃ evaporation losses if done slowly, is to add known NH₃ solution from a buret, in effect “titrating” the 0.03 M Cu(NO₃)₂ solution, and reading pH at frequent intervals. The 0.2 M NH₃ is standardized with known HCl solution. The Cu(NO₃)₂ is weighed approximately and the total Cu(II) is determined at the end of the experiment, because it is easy then to adjust the pH to about 5.5 with acetic acid, add excess standard EDTA, and back titrate with standard Zn(II) solution to the xylenol orange end point (5). Both solutions are 2.00 M in NH₄NO₃. Temperature should not vary more than one degree, and stirring should be minimized to avoid loss of NH₃. Addition of NH₃ is continued until there are at least six times as much of it as the amount of Cu(II) taken. The later points contain evaporation error. Therefore, these are repeated in reverse adding known volumes of Cu(II) solution to known NH₃ solution. Volumes are chosen to define the curve well in the vicinity of the half integral \( n \) values.

The formation curve obtainable from the experimental data allows estimates of Ke values which are increasingly accurate as the separation of the Ke values increases. Bjerrum has derived elegant graphical methods for difficult cases. For the metal ammines, however, the following method gives results adequate for the data obtainable. The derivation of the required
Table I. Representative Data for Formation Curve.

<table>
<thead>
<tr>
<th>V ml NH₃ added</th>
<th>Total vol.</th>
<th>mmole NH₃ added</th>
<th>pH read</th>
<th>ΔpH</th>
<th>pNH₃</th>
<th>[NH₃]</th>
<th>mmole NH₃ bound</th>
<th>n</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.60</td>
<td>54.00</td>
<td>0.7332</td>
<td>4.72</td>
<td>3.70</td>
<td>4.44</td>
<td>3.63⋅10⁻⁴</td>
<td>0.00196</td>
<td>0.491</td>
</tr>
<tr>
<td>13.00</td>
<td>63.00</td>
<td>2.383</td>
<td>5.56</td>
<td>2.86</td>
<td>3.60</td>
<td>2.51⋅10⁻⁴</td>
<td>0.0158</td>
<td>1.580</td>
</tr>
<tr>
<td>19.00</td>
<td>69.00</td>
<td>3.483</td>
<td>6.04</td>
<td>2.38</td>
<td>3.12</td>
<td>7.60⋅10⁻⁴</td>
<td>0.0524</td>
<td>2.302</td>
</tr>
</tbody>
</table>

The equations is outlined here. For details, see Butler (2).

Letting M stand for Cu(II) and A for NH₃, the formation constants are:

\[ K_1 = \frac{[MA]}{[M][A]} \]
\[ K_2 = \frac{[MA_2]}{[MA][A]} \]
\[ K_3 = \frac{[MA_3]}{[MA_2][A]} \]
\[ K_4 = \frac{[MA_4]}{[MA_3][A]} \]

The total Cu(II) in solution is C:

\[ C = [M] + [MA] + [MA_2] + [MA_3] + [MA_4] \]

The fractions, \( \alpha_n \), of each species present are:

\[ \alpha_0 = \frac{[M]_C}{C} = \frac{1 + K_1[A] + K_2K_3[A]^2 + K_4[A]^3}{1 + K_1[A]} \]
\[ \alpha_1 = \frac{[MA]}{[MA][A]} \]
\[ \alpha_2 = \frac{[MA_2]}{[MA][A]} \]
\[ \alpha_3 = \frac{[MA_3]}{[MA_2][A]} \]
\[ \alpha_4 = \frac{[MA_4]}{[MA_3][A]} \]

Then, \( \tilde{n} \) is:

\[ \tilde{n} = \frac{(NH_3 \text{ bound})/C}{\alpha_0} = \frac{\text{total } A - [A]}{C} = \alpha_1 + 2\alpha_2 + 3\alpha_3 + 4\alpha_4 \]

When little NH₃ has been added, \( \tilde{n} \) less than 0.5, one may approximate \( K_1 \) by substituting the data in the \( K_1 \) expression. Another \( K_1 \) approximation can be taken at \( \tilde{n} = 0.5 \). If \([MA_2]\), etc., are negligible here, then \([M] = [MA]\). From the formation curve, one reads the \([A]\) value at \( \tilde{n} = 0.5 \) and \( K_1 = [A]^{-1} \), at this point. Similarly, one estimates \( K_2, K_3, \) and \( K_4 \) as \([A]^{-1}\) at \( \tilde{n} \) values of 1.5, 2.5, and 3.5.

The first approximations can be tested and improved if needed. The ratio of \([MA_2]/[MA]\) can be found at \( \tilde{n} = 0.5 \) by inserting the \([A]\) value in the \( K_2 \) equation. If \([MA_2]\) does not appear negligible, a further approximation can be tried.

The \( \tilde{n} \) value will be 1.0 when \([M] = [MA_2]\) if \([MA_3]\), etc., are negligible. Here \([A] = (K_1K_2)^{-1/2}\). Substituting in the \( \tilde{n} \) equation, with \( \alpha_3 \) and \( \alpha_4 \) zero, gives,

\[ \tilde{n} = \frac{1 + 2K_1[A]}{(K_1[A])^{-1/2} + 1 + K_1[A]} \]

Since the \( K_3 \) terms are small, the approximate \( K_2 \) value and the \([A]\) at \( \tilde{n} = 0.5 \) can be used to get an improved value for \( K_1 \). This can be put into the \( \tilde{n} \) equation with \( \alpha_3 \) and \( \alpha_4 \) zero, gives,

\[ \tilde{n} = \frac{1 + 2K_1[A]}{(K_1[A])^{-1/2} + 1 + K_1[A]} \]

The student should not be left thinking that many systems share the ease of this approach. He might be asked to consider how to get \( K_n \) values for halide, SCN⁻, CN⁻, etc., systems. It can be that no way seems open to find \( K_n \) and \([A] \), the ligand, as was done here. Often good evidence for the existence of species can be found even when \( K_n \) cannot.

**Typical Results**

Starting with 50.00 ml of Cu(NO₃)₂ found to contain 1.490 mmoles Cu, V ml of 0.1833 M NH₃ were added. (Both solutions 2.00 M in NH₄NO₃.) The pH of the 0.1833 M NH₃ was 8.42, corresponding to the known \( pNH₃ \) of 0.74. Three example points are given in Table 1. One may note that ±0.02 pH uncertainty makes a fairly large uncertainty in \([A]\) but has very little effect on \( \tilde{n} \). The formation curve plotted from student data is shown. The results read from appropriate \( \tilde{n} \) values on the curve as described above are shown in Table 2.

The student should not be left thinking that many systems share the ease of this approach. He might be asked to consider how to get \( K_n \) values for halide, SCN⁻, CN⁻, etc., systems. It can be that no way seems open to find \( K_n \) and \([A] \), the ligand, as was done here. Often good evidence for the existence of species can be found even when \( K_n \) cannot.

**Literature Cited**