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A NEW OPTICAL
PRINCIPLE FOR THE INVESTIGATION
OF STEP EQUILIBRIA

BY

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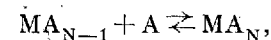
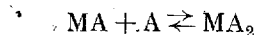
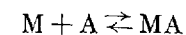


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The term "step equilibria" is applied to reciprocal reactions of the type



where an ion (or a molecule) M is in chemical equilibrium with a series of compounds (complexes) $MA_1, MA_2 \dots MA_N$ formed from M (the central group) by addition of one or several ligands A (molecules or ions). Step reactions of this type play an important rôle in complex chemistry. They are best investigated by methods which make it possible to determine the equilibrium concentrations of the free ligand or of one of the central group compounds involved. From this point of view the author has previously¹ maintained that determinations of the light absorption are rarely suited for the establishment of the equilibrium constants of the step system, and that they are better applicable when it is a question of proving the correctness of a set of constants obtained from the determination of one of the individual concentrations involved. This point of view is not entirely adequate, however, and, as it is the main purpose of the present paper to show, it is quite possible to determine the free ligand concentration, and hence the equilibrium constants of the system, solely by means of measurements of the light absorption. An accurate determination, however, is only possible if the following conditions are satisfied: (1) The ligand's own absorption must be infinitesimal in relation to that of the complexes, and (2)

the measurements must be carried out in a salt medium at a high and constant concentration of a neutral salt, so that (a) the law of mass action applies in its classical form, and (b) Beer's law applies to the individual complexes.

The theory of step equilibria is dealt with in detail in the above cited paper by the author, and only some of its main features will be recalled in the present paper. In accordance with the nomenclature of the paper in question we shall here introduce the following quantities and designations:

$[A]$ = concentration of free ligand.

$[MA_n]$ = concentration of the molecule type MA_n .

N = maximum value of n .

$C_M = \sum_0^N [MA_n]$, total concentration of central group.

$C_A = [A] + \sum_0^N n [MA_n]$, total ligand concentration.

$\bar{n} = \frac{C_A - [A]}{C_M} = \frac{\sum_0^N n [MA_n]}{\sum_0^N [MA_n]}$, the formation function of the system = the average number of ligands bound per central group.

$\alpha_n = \frac{[MA_n]}{C_M}$, the degree of formation of the compound MA_n or the fraction of the total central group concentration present as the compound MA_n .

$k_n = \frac{[MA_n]}{[MA_{n-1}][A]}$, consecutive complexity constant corresponding to the equilibrium $MA_{n-1} + A \rightleftharpoons MA_n$.

$K_n = k_1 k_2 \cdots k_n = \frac{[MA_n]}{[M][A]^n}$, gross complexity constant corresponding to the equilibrium $M + nA \rightleftharpoons MA_n$.

If the gross complexity constant is introduced into the summation expression for the formation function, we get, after eliminating the free central group concentration:

$$\bar{n} = \frac{\sum_0^N n K_n [A]^n}{\sum_0^N K_n [A]^n} = \frac{K_1 [A] + 2 K_2 [A]^2 + \cdots + N K_N [A]^N}{1 + K_1 [A] + K_2 [A]^2 + \cdots + K_N [A]^N}, \quad (1)$$

K_0 being = 1. From this expression it follows that the formation function depends on the concentration of free ligand only, and is independent of the central group concentration. Of course, this is not something here derived for the first time, but no one seems to have noticed that this rule makes it possible to establish the equilibrium constants of the step system by investigating the properties of the system which in an unequivocal manner permit us to ascertain a change in the formation function $\bar{n}$, or, what amounts to the same thing, enable us to decide whether 2 solutions, with different total concentrations, have the same percentage distribution of the complexes. Solutions meeting this requirement will in the following be called "corresponding solutions." It follows from (1) that corresponding solutions also have the same concentration of free ligand. Hence it is possible to establish the following set of equations for the calculation of the formation function and the unknown ligand concentration:

$$\bar{n} = \frac{C'_A - [A]}{C'_M} = \frac{C''_A - [A]}{C''_M}. \quad (2)$$

The total concentrations indicated refer to the composition of the two corresponding solutions. Of methods suitable for deciding whether two solutions are corresponding, several may be considered, but the only one of practical significance is that based on the measurements of light absorption. The present paper shows how it is possible with the aid of the new principle and the measurement of light absorption to establish the formation curve for the cupric ammonia system in good agreement with the results of the many other methods by which this system has previously been investigated. It is further shown how a coloured system (the copper ammonia system) may be employed as indicator system in the investigation of analogous colourless systems (the zinc ammonia system). Finally, an attempt is made at using the method for an investigation of the complex formation in concentrated solutions of cupric chloride.

The measurements may be carried out either by means of a colorimeter, as a kind of colorimetric titration, or by means of a spectrophotometer. These procedures are described in chapters one and two which also include the examples of the practical application. The third and last chapter discusses the possibilities of using optical measurements for a direct determination of the number of compounds in the chemical equilibrium. This determination is but rarely possible. It is always possible, however, if the formation curve is known, to calculate the equilibrium constants of the system and thus obtain information regarding the number of complexes present and their mutual proportions.

1. Determination of the Formation Curve by Means of Colorimetric Titration.

In the case of most complexes Beer's law is usually valid with good approximation, and if the investigation deals especially with conditions in aqueous solution at a high and constant concentration of a neutral salt we may with great accuracy consider the molar extinction coefficients ϵ_n of the complexes present as being perfectly constant. The molar extinction coefficient ϵ of the system, inasmuch as we confine ourselves to systems where only the complexes absorb, is connected with the molar extinction coefficients and the degrees of formation of the individual complexes by the equation

$$\epsilon = \sum_0^N \alpha_n \epsilon_n = \alpha_0 \epsilon_0 + \alpha_1 \epsilon_1 + \alpha_2 \epsilon_2 \cdots + \alpha_N \epsilon_N. \quad (3)$$

In contrast to the extinction coefficients of the complexes ϵ is a variable which depends on the composition of the solution, but if we limit ourselves to corresponding solutions it is immediately apparent from (3) that ϵ , too, is constant. In other words, for step equilibria of the type in question Beer's law must be satisfied at constant concentration of the free ligand. This rule may without application of the equations (2) be used in the determination of free ligand, the procedure being as follows: The colorimeter employed has two vertical cylindrical tubes with plate glass bottoms, the only requirement being that the cross section of one of the tubes (the dilution

tube) has the same area throughout. A suitable amount of the coloured solution to be investigated is poured into both tubes (in the case of complete symmetry the same amount in each) so that the solutions when observed in the colorimeter look identical. The actual measurements now are carried out as a kind of titration to the same tone of colour. A suitable amount of the solvent is added from a burette to one of the tubes, this causing a change not only in the intensity, but also in the tone of colour. The effect of the dilution then is neutralized by adding from another burette so much of a ligand solution of known concentration that the solutions when observed in the colorimeter once more give the same colour impression. If, to achieve this, x ml of solvent and y ml of ligand solution with concentration a are added, the concentration of free ligand in the complex solution in question must be given by the expression

$$[A] = \frac{a \cdot y}{(x + y)}. \quad (4)$$

The formation function or the average number of ligands per central atom is calculated as

$$\bar{n} = \frac{C_A - [A]}{C_M}. \quad (5)$$

Should it be found impossible, by dilution and subsequent addition of ligand to a coloured complex solution, to make the two solutions in the colorimeter assume the same colour tone and colour intensity, this can only mean that the complex formation does not proceed according to the usual scheme and that the solutions presumably contain multinuclear complexes. On the other hand, if the method functions it is a sign that we have to do with step equilibria of the simple type. The method cannot be applied to all coloured step systems, but only to systems of a suitable complexity and colour intensity. If the complexity is too great, the complexes will not dissociate noticeably upon dilution, and if too small ($C_A \propto [A]$) it will be impossible to calculate $\bar{n}$ according to (5).

a. Experimentally. A Wolff colorimeter was used for the measurements, with the modification that the usual measuring

tubes for this colorimeter (the height of the liquid column being changed by drawing water through a side tap at the bottom of the tube) were replaced by tubes from a König-Martens spectrophotometer. The tubes for this apparatus had almost the same cross-sectional area throughout their entire length, and further had a sufficiently large diameter (3 cm) to ensure a plane surface; in return, they required a relatively large amount of liquid (7 ml per 1 cm of layer). The 25 cm tube was used as dilution tube and the 5 cm tube as the tube with the constant solution. Both tubes were used with only one of the plate glass covers screwed on, thus being open at the top. In some instances correction was made for the difference in the height of the liquid column by placing the 12 cm tube, filled with an amount of solvent corresponding to the dilution, on top of the 5 cm tube; in order to get the same number of reflections of the light, a glass was at the same time placed on top of the dilution tube. With the reasonably dust-free solutions used, however, this correction played a rôle only with the highest dilutions. In the case of low colour intensity it might be practical to interpose a colour filter in the path of the rays. Thus by using a green colour filter, transparent for light in the wave range 495—573 m μ , placed immediately below the ocular, it was possible to measure only weakly coloured solutions like 6 in table 1 with about the same accuracy as the other solutions.

b. Determination of the formation curve for the cupric ammonia system in 2 N ammonium nitrate. The results of the measurements are recorded in table 1. The concentrations¹ of free ammonia in the 6th column are mean values calculated according to (4) on the basis of titrations of solutions having the total copper and total ammonia concentrations stated. The diluent was a 2 N ammonium nitrate solution, and the ligand solution (all according to the concentration of free ammonia in the solution investigated) was a 0.02 or a 0.1 N aqueous ammonia which likewise was 2 N with respect to ammonium nitrate. For orientation the table gives the number of mls which to begin with were introduced into the absorption

¹ When nothing else is said, all concentrations in this paper are moles per liter.

Table 1. Investigation of some cupric ammonia solutions in 2 N ammonium nitrate by the colorimetric method.

No.	C _{Cu}	C _{NH₃}	Initial volume	Final volume	[NH ₃] _{exp.}	log [NH ₃]	$\bar{n}_{exp.}$
1...	0.02016	0.0518	10	71	0.0016 $\pm$ 0.0003	-2.80 $\pm$ 0.09	2.49 $\pm$ 0.02
2...	0.02016	0.0830	5	69	0.0064 $\pm$ 0.0015	-2.19 $\pm$ 0.10	3.80 $\pm$ 0.08
3...	0.1012	0.310	4	70	0.0029 $\pm$ 0.0005	-2.54 $\pm$ 0.08	3.03 $\pm$ 0.01
4...	0.1015	0.3725	5	64	0.0058 $\pm$ 0.0015	-2.24 $\pm$ 0.12	3.61 $\pm$ 0.02
5...	0.1015	0.413	3	55	0.020 $\pm$ 0.005	-1.70 $\pm$ 0.11	3.87 $\pm$ 0.05
6...	0.00159	0.00506	20	51	0.0009 $\pm$ 0.0002	-3.05 $\pm$ 0.10	2.62 $\pm$ 0.13
7...	0.0248	0.1016	5	17	0.006 $\pm$ 0.002	-2.22 $\pm$ 0.15	3.85 $\pm$ 0.08

tubes (the initial volume), and the total volume in the dilution tube at the conclusion of the titration (the final volume). Before the final volume was reached, 3 or 4 adjustments to the same colour tone had usually been made. The recorded uncertainty of the concentrations of free ammonia found should not be taken too literally, but as an estimate of the accuracy with which it was possible to reproduce a determination. The table also shows how the uncertainty of the ammonia determination influences the $\bar{n}$ -values calculated according to (5). Fig. 1 (upper part) shows a graphical representation of the colorimetrically determined values of $\bar{n}$ and log [NH₃] with accompanying range of uncertainty. The fully drawn curves represent the formation curves for the cupric ammonia system in 2 N ammonium nitrate at 18° and 22°, on the basis of ammonia tension¹ and glass electrode² measurements. In the colorimetric measurements the temperature is about 18°. The figure directly shows that on the whole the colorimetric method, within the supposed experimental uncertainty, gives the correct result.

c. Use of the cupric ammonia system as an indicator system. The colorimetric method can be used not only in the case of coloured systems, but also for investigating colourless systems when a suitable indicator system is added to the solutions in question. To illustrate this application, an investigation was made of a couple of ammoniacal zinc salt solutions with

¹ Untersuch. über Kupferammoniakverb. I, D. Kgl. Danske Vidensk. Selskab, Math.-fys. Medd. XI, No. 5 (1931), p. 16.

² Metal Ammine Formation in Aqueous Solution, p. 125.

Table 2. The use of the cupric ammonia system as indicator system in the investigation of two ammoniacal zinc salt solutions in 2 N ammonium nitrate solution.

No.	C_{Cu}	C_{Zn}	C_{NH_3}	Initial volume	Final volume
1...	0.00993	0.01987	0.1111	10	55
2...	0.00159	0.00498	0.01004	20	84
No.	$[NH_3]_{exp.}$	$\log [NH_3]$	$\bar{n}_{Cu}$	$\bar{n}_{Znexp.}$	
1...	0.0065	2.19	3.47	3.53	
2...	0.0013	2.89	2.67	0.90	
No.	$[NH_3]_{calc.}$	$\log [NH_3]$	$\bar{n}_{Cu}$	$\bar{n}_{Zncalc.}$	
1...	0.0089	2.05	3.59	3.35	
2...	0.00148	2.83	2.75	0.84	

a suitable content of cupric salt. In these determinations the green filter was interposed.

The upper part of table 2 gives the total concentrations of the solutions measured as well as the initial and final volumes in the two titrations. The middle section gives the experimentally determined data for the concentration of free ammonia, and the formation function for the zinc system calculated from this concentration with the use of our knowledge of the formation curve for the cupric ammonia system. The bottom part of the table finally gives the same quantities calculated on the basis of the total concentrations with the use of our knowledge of the formation curves for both the cupric and the zinc system.¹ The temperature at the measurements is about 18°, and accordingly the formation curves corresponding to 18° are used in these calculations. The values found and those calculated are in very good agreement, and the experiments show directly the pronounced steepness of the formation curve for the zinc ammonia system.

d. Some experiments with strong cupric chloride solutions. An attempt was also made at using the colorimetric method to obtain some information on the formation of complexes in strong solutions of cupric chloride. The green solutions were diluted, whereby the colour changed in the direction of

¹ As regards the formation curve of the zinc system, see Metal Ammine Formation in Aqueous Solution, p. 158.

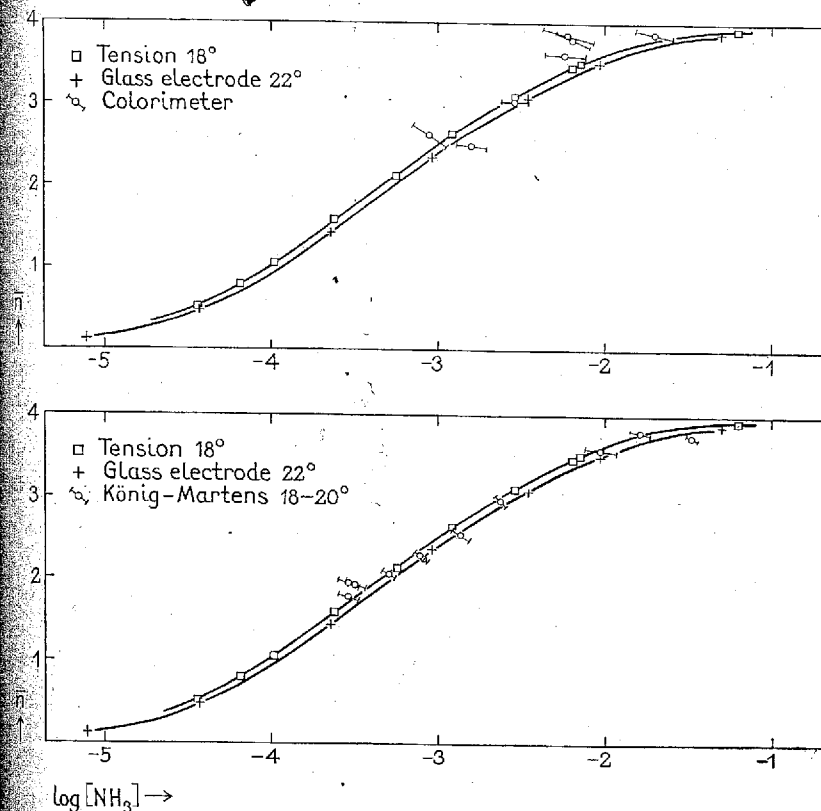


Fig. 1. Optical determination of the formation curve for the cupric ammonia system in 2 N ammonium nitrate. For the significance of the indicated uncertainty of the colorimetrically determined points (upper part of the figure) and the spectrophotometrically determined points (lower part of the figure), see the text.

blue, and the original colour then was reestablished by the addition of strong solutions of chlorides. The eye is especially sensitive to green, and the adjustment itself could be made with considerable accuracy. Nevertheless, this method gives only qualitative information regarding the complex formation, since the large copper concentrations make it impossible to work under conditions of the medium being but approximately constant. It is always possible to strike the same colour tone within the limits of experimental accuracy. This shows that, in the main, only mononuclear complexes are present, but the concentrations of free chlorine ion found are on the other hand strongly depen-

Table 3. Experiments with two strong cupric chloride solutions.

I. $C_{\text{CuCl}_2} = 4.06$ (dark green)

	Concentrations of free chloride found	Mean	$\bar{n}$
NH_4Cl	5.0	5.0	0.77
CaCl_2	4.3, 4.6, 4.4	4.4	0.92
LiCl	3.9, 3.9	3.9	1.04
HCl	3.2, 3.2	3.2	1.21

II. $C_{\text{CuCl}_2} = 1.62$ (bluish green)

NH_4Cl	2.8, 2.6, 2.6	2.67	0.35
KCl	2.7, 2.6	2.65	0.36
CaCl_2	2.6, 2.5, 2.5	2.53	0.44
LiCl	2.4, 2.2	2.3	0.58
HCl	2.2, 2.1	2.15	0.67

dent on the question which chloride is used for the determination. Table 3 presents a summary of the titrations carried out in 2 strong cupric chloride solutions with hydrochloric acid, calcium chloride and various alkali chlorides.

The concentrations of free chloride show the chloride normality of the salt which at the colorimetric titration was found to correspond to the particular copper solution. The result is comparatively independent of the change of volume of the copper solution during the titration. The formation function $\bar{n}$ is calculated, according to (5), from the mean value of the chloride normality for each salt. The table shows directly how largely the complex formation is dependent on the kind of chloride used in the determination. In the order NH_4Cl , KCl , CaCl_2 , LiCl and HCl , we find an increasing tendency to produce complex formation, and it is worth noting that the mean activity coefficients of the salts in question rise in the same consecutive order (see table 4).

Table 4. Mean activity coefficients (at 25°) for the chlorides used at the chlorine ion normalities 2 and 4.

	NH_4Cl	KCl	CaCl_2	LiCl	HCl
2N.....	0.57	0.58	0.72	0.95	1.02
4N.....	0.59	0.58	1.57	1.56	1.76

The figures are from Landolt-Börnstein's tables.

2. Spectrophotometric Determination of the Formation Curve.

By means of a König-Martens spectrophotometer the formation curve may be determined with considerably greater accuracy than by the simple colorimetric arrangement. It is here necessary to work with a few given thicknesses of layer, and the procedure therefore is of necessity different from that of the colorimetric titration. The principle of the method may be characterized as an attempt at finding solutions which without being identical in total concentrations still have the same molar extinction coefficient at all wave lengths. If we consider two corresponding solutions of this kind and call the total concentrations of central group and ligand C_M^0 , C_A^0 and C_M , C_A , respectively, we have in accordance with expression (2):

$$\bar{n} = \frac{C_A^0 - [A]}{C_M^0} = \frac{C_A - [A]}{C_M}$$

Solving this set of equations with respect to the formation function and the concentration of free ligand we find

$$\bar{n} = \frac{C_A^0 - C_A}{C_M^0 - C_M} \quad (6)$$

$$[A] = \frac{C_M^0 C_A - C_M C_A^0}{C_M^0 - C_M} \quad (7)$$

a. The formation curve for the cupric ammonia system. The application of (6) and (7) may be elucidated in connection with some measurements of the cupric ammonia system in 2N ammonium nitrate. At a wave length of 590 m μ , where the absorption continuously increased with the ammonia concentration, measurements were made, for a constant copper concentration ($C_{\text{Cu}}^0 = 0.01972$), of the molar extinction coefficient (ϵ_{590}) with a series of different ammonia concentrations. The results are recorded graphically in fig. 2. By means of such an adjustment curve it is possible to arrive at corresponding solutions. If we measure ϵ_{590} for an arbitrary solution having a copper

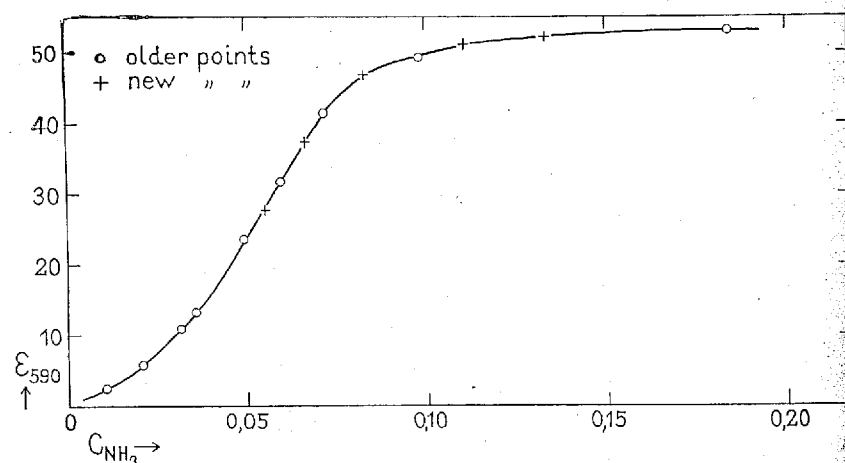


Fig. 2. Adjustment curve giving the connection between the molar extinction coefficient at the wave length $590\text{ m}\mu$ and the total ammonia concentration for cupric ammonia solutions with a total copper concentration of 0.01972 molar.

concentration (C_{Cu}) different from 0.01972 , the adjustment curve will directly give the ammonia concentration ($C_{\text{NH}_3}^0$) corresponding to the copper concentration 0.01972 , so that the gross composition of two corresponding solutions is known. The concentration of free ammonia and the average number of ammonia molecules bound may then be calculated directly by means of the expressions (6) and (7).

The measurements forming the basis for the adjustment curve were mainly taken from an earlier paper¹ and supplemented by new measurements. In the new measurements the copper concentration was not exactly 0.01972 , but the total ammonia concentration corresponding to this concentration was calculated with the aid of (6), the formation function being known in this special case. The supplementary measurements for the adjustment curve are recorded in table 5 a. It will be seen from the adjustment curve that there is exceptionally good agreement between the earlier and the new measurements (points $\circ$ and $+$, respectively).

The actual measurements for the determination of the formation curve are recorded in table 5 b. The first part of this table gives the gross composition of the solution investigated.

¹ Untersuch. über Kupferammoniakverb. II, D. Kgl. Danske Vidensk. Selskab. Math.-fys. Medd. XI, No. 10 (1932), p. 47.

Table 5. Measurements by means of the König-Martens spectrophotometer of the cupric ammonia system in $2\text{ N NH}_4\text{NO}_3$ at $18-20^\circ$.

a. Supplementary measurements for the adjustment curve.

C_{Cu}	C_{NH_3}	$\bar{n}$	C_{NH_3} (corresponding to $C_{\text{Cu}} 0.01972$)	ϵ_{590}
0.02016	0.1352	3.96	0.1335	52.2
0.02016	0.1126	3.92	0.1109	51.1
0.01972	0.0830	3.65	0.0830	46.7
0.02016	0.0678	3.25	0.0664	37.2
0.02016	0.0564	2.80	0.0552	27.75

b. Actual measurements.

No.	C_{Cu}	C_{NH_3}	ϵ_{590}	$C_{\text{NH}_3}^0$ (graph.) ($C_{\text{Cu}} 0.01972$)
1...	0.1015	0.413	50.7	0.107
2...	0.1015	0.401	48.35	0.0910
3...	0.1015	0.3725	45.7	0.0800
4...	0.00253	0.00982	32.5	0.0605
5...	0.00253	0.00776	25.0	0.0512
6...	0.001018	0.003106	20.35	0.0452
7...	0.001018	0.003106	20.9	0.0459
8...	0.001018	0.002587	17.12	0.0408
9...	0.001018	0.002270	15.1	0.0381
10...	0.001018	0.002250	15.3	0.0383
11...	0.001018	0.002080	13.0	0.0350

No.	$\bar{n}$	$[\text{NH}_3]$	$-\log [\text{NH}_3]$	$\frac{\Delta \bar{n}}{\bar{n}} / \frac{\Delta C_{\text{NH}_3}^0}{C_{\text{NH}_3}^0}$	$\frac{\Delta [\text{NH}_3]}{[\text{NH}_3]} / \frac{\Delta C_{\text{NH}_3}^0}{C_{\text{NH}_3}^0}$
1...	3.74	0.0332	1.479	0.35	4.0
2...	3.79	0.0162	1.790	0.29	7.0
3...	3.58	0.00947	2.024	0.27	10.5
4...	2.95	0.00236	2.627	1.19	3.8
5...	2.53	0.00137	2.863	1.18	5.5
6...	2.25	0.000816	3.088	1.07	3.0
7...	2.29	0.000777	3.109	1.07	3.2
8...	2.044	0.000507	3.294	1.07	4.4
9...	1.916	0.000320	3.495	1.07	6.5
10...	1.928	0.000287	3.542	1.06	6.6
11...	1.761	0.000288	3.541	1.06	7.3

the molar extinction coefficient measured, and, finally, the corresponding ammonia concentration $C_{\text{NH}_3}^0$, determined graphically by means of this quantity and the adjustment curve. In the measurements of the least absorbing solutions with copper concentrations of the order of magnitude 0.001 it was necessary to use the 12 cm and 25 cm tubes in order to measure sufficiently large extinctions. With such long tubes the dispersion of light by the particles of dust gives rise to a comparatively large error (cf. p. 8). This source of error was reduced as much as possible by continuously measuring the solution in question against a freshly prepared solution with the same ammonia and ammonium concentrations, but with no cupric salt added. The addition of cupric salt was carried out by pipetting from a carefully filtered stock solution of cupric nitrate. The approximately one molar ammonia stock solution, in order to secure a completely CO_2 -free and almost dust-free solution, was prepared with ammonia from a steel cylinder after passing through a long tube with pieces of potassium hydroxide and then a cotton filter before being led into water.

The continuation of table 5 b gives the formation function and the concentration of free ammonia as calculated from the formulae (6) and (7). The figures in the last two columns finally show the magnitude of the relative uncertainty of these two quantities in proportion to the relative uncertainty of the experimentally determined $C_{\text{NH}_3}^0$ -concentration, with the tacit understanding that the uncertainty of this concentration is solely responsible for the uncertainty of the calculated formation function and the concentration of free ammonia. The calculation is carried out by means of the expressions

$$\frac{\Delta \bar{n}}{\bar{n}} = \left| \frac{C_{\text{NH}_3}^0}{(C_{\text{Cu}}^0 - C_{\text{Cu}}) \bar{n}} \right| \text{ and } \frac{\Delta [\text{NH}_3]}{[\text{NH}_3]} = \left| \frac{C_{\text{NH}_3}^0}{\left(\frac{C_{\text{Cu}}^0}{C_{\text{Cu}}} - 1 \right) [\text{NH}_3]} \right| \quad (8)$$

which under the above assumption are easily derived from (6) and (7). The experimental material is graphically reproduced in fig. 1, lower part. As in the upper part of fig. 1, the fully drawn curves are the formation curves for the copper ammonia

system in the same medium at 18° and 22° on the basis of the earlier ammonia tension and glass electrode measurements. The range of uncertainty attending the spectrophotometrically determined points is traced so as to show how an uncertainty of 2 per cent. in the graphically determined $C_{\text{NH}_3}^0$ -concentration affects the formation curve. The extinction coefficients are presumably determined with an accuracy of about 1 per cent., but this entails a somewhat higher uncertainty in the graphically determined $C_{\text{NH}_3}^0$ -concentration, especially on the upper part of the adjustment curve, where the extinction coefficient changes comparatively little with the ammonia concentration. The uncertain temperature recording (room temperature) further contributes towards an increase of the inaccuracy of the spectrophotometrically determined points, but as a whole fig. 1 shows that the estimated uncertainty is of the right order of magnitude.

b. On the field of application of the method. The formulae (8) give us some information as to the conditions the most favourable to the application of the new method. It will be seen, for example, that if $C_{\text{Cu}} > C_{\text{Cu}}^0$ (solutions 1 to 3 in table 5), nothing special is gained, as regards the determination of

the concentration of free ammonia, by making the ratio $\frac{C_{\text{Cu}}^0}{C_{\text{Cu}}} <$ about $\frac{1}{5}$, while in the opposite case (solutions Nos. 4 and 11), provided it is possible for other reasons, it is of distinct advantage to make the ratio $\frac{C_{\text{Cu}}^0}{C_{\text{Cu}}}$ large. For the ammonia determination

it is first of all necessary to work with solutions so dilute that the concentration of free ammonia is not too small in proportion to the smallest of the total ammonia concentrations. Hence there is a limit to the applicability of the method, depending, besides on the complexity, also on the magnitude of the absorption of the complexes. Thus it is not only because of a too large complexity, but also because of the light absorption of the particular complexes being rather small, that the first stretch of the formation curve for the copper ammonia system cannot be determined by the new method. With respect to the determination of the formation function there is conversely a limit to the application of the method in the case of slight complexity, or, expressed

differently, when the concentration of free ammonia and the total ammonia concentrations are of the same order of magnitude. We may try to remedy this by using large concentrations. On the last stretch of the formation curve, where the complexity is not particularly great, the $\bar{n}$ -determination has been assured by means of large total concentrations, but this is not without consequences for the determination of the concentration of free ammonia (see solution 3 in table 5). The fact is that if we wish to determine the formation function with a high degree of certainty, the determination of the concentration of free ligand will become correspondingly more uncertain, and vice versa.

It will be understood from the above that the method is not always applicable, but that it has an optimum depending on the magnitude of the complexity constants and the light absorption. Finally, we shall call attention to a fact which is of significance in some cases. For a step system where the ligand is a base and which is investigated in a medium containing a large concentration of the corresponding acid, the absolutely correct expression for the formation function is

$$\bar{n} = \frac{C_A - [A] + [H^+]}{C_M} \quad (9)$$

Hence, with the method described, it is not actually the concentration of free ligand itself that is determined, but the ligand concentration minus the hydrogen ion concentration of the solution. In the copper ammonia system this circumstance does not give rise to any noticeable correction, but in other cases, *e. g.* in the copper pyridine system, it may be a question of rather large corrections. It should be added that in the case of the last mentioned system conditions are so favourable that the whole formation curve may be determined by the spectrophotometric method. Measurements of this kind were carried out at 3 different wave lengths, and gave the same result within the range of experimental accuracy; they will be described in a separate paper. We shall only mention here that when applying the spectrophotometric method to a system unknown beforehand it is necessary to make the investigation at several wave lengths. Otherwise we cannot be certain that we have to do with a simple step equilibrium so that the basis for the method is in order.

3. On the Possibility of Optical Identification of the Individual Compounds in the Equilibrium.

If in a step system the ratio between the consecutive constants is sufficiently large (more than 4 times the statistical ratio¹), the wave-like appearance of the formation curve will show directly the number of intermediate compounds in the equilibrium. In complex step systems the consecutive constants usually follow so closely upon one another that the individual steps have disappeared completely for the benefit of a single S-shaped curve, as in the formation curve for the copper ammonia system investigated here. Thus we do not get a direct proof of the existence of the intermediate complexes, but have to draw our conclusions on the basis of the calculated complexity constants. It may be asked whether there is any possibility of identifying the individual compounds in the equilibrium by optical means. In a comprehensive paper OTTO RUFF² has dealt with this question. His calculations, which are quite general in form, show with reference to the case in question that for a step system having a coloured central group, colourless ligand and N coloured complexes, a curve representing the extinction coefficient ϵ at a certain wave length plotted against the total ligand concentration at constant total concentration of central group will have $N-1$ maxima and minima at the most. If instead of the plotting employed by RUFF we use a diagram with ϵ being plotted against the formation function $\bar{n}$ it is easily seen that according to the above the number of maxima and minima in such an $\epsilon, \bar{n}$ -diagram cannot exceed the number of the intermediate compounds. As to the positions of the maxima and minima nothing can be said with absolute certainty, but in general they will be close to the whole value of the formation function corresponding to the composition of the complex in question, and the closer the more pronounced the particular maxima and minima. Fig. 3, as an example, shows the molar extinction coefficient ϵ for the cupric ammonia system at wave length $676 \text{ m}\mu$ plotted against the formation function. The particular curve has a maximum for $\bar{n}$ approximately 3 and a minimum for $\bar{n}$ approximately 4, and

¹ See Metal Ammine Formation in Aqueous Solutions, pp. 31 and 35.
² OTTO RUFF, Zeitschr. physik. Chem. **76** (1911) 21.

thus it is possible on a purely optical basis to deduce the existence of 2 out of the 4 complexes intermediate between the cupric ion and the pentammine ion. The existence of the tetrammine ion follows directly from the shape of the formation curve, and further it follows from the slope of the curve that at least one of the remaining complexes exists. Thus there is not very much in the line of extra information to be gained from knowledge of the light absorption of the system, and on the whole it may be said that this method rarely gives direct information regarding the number of complexes in the equilibrium. To get a maximum or minimum corresponding to each complex the extinction coefficient of consecutive compounds must be alternately large and small, and of course we rarely find a wave length where this is the case, or we may find several wave lengths so as to have in all a maximum or minimum corresponding to the existence of each complex and located in accordance herewith. The possibility of establishing the presence of complexes is not always dependent on maxima or minima, however. If the ratio between the consecutive constants is very large, the extinction curve will abruptly change its slope at each whole $\bar{n}$ -value corresponding to the existence of a complex. Reference is made to fig. 3 where the dotted broken line shows the course of the curve when the ratio between the consecutive constants is infinitely large.

The material used for fig. 3 is taken from »Untersuchungen über Kupferammoniakverbindungen II«¹, except for the data recorded in table 6.

A small quantity of nitric acid has been added to solution No. 1 in order to suppress the ammine formation completely so

Table 6.

The extinction coefficient at 676 m μ for some cupric solutions (very poor in ammonia) in 2N NH₄NO₃ at approximately 20°

No.	C _{Cu}	C _{HNO₃}	C _{NH₃}	[H ⁺]	[NH ₃]	$\bar{n}$	ϵ_{676}
1...	0.0505	0.01995	0	0.01995	0.000000024	0	4.88
2...	0.0505	—	0.00409	0.000104	0.0000046	0.083	5.80
3...	0.0505	—	0.01018	0.000040	0.0000120	0.202	6.89

¹ D. Kgl. Danske Vidensk. Selskab, Math.-fys. Medd. XI, No. 10 (1932), p. 46

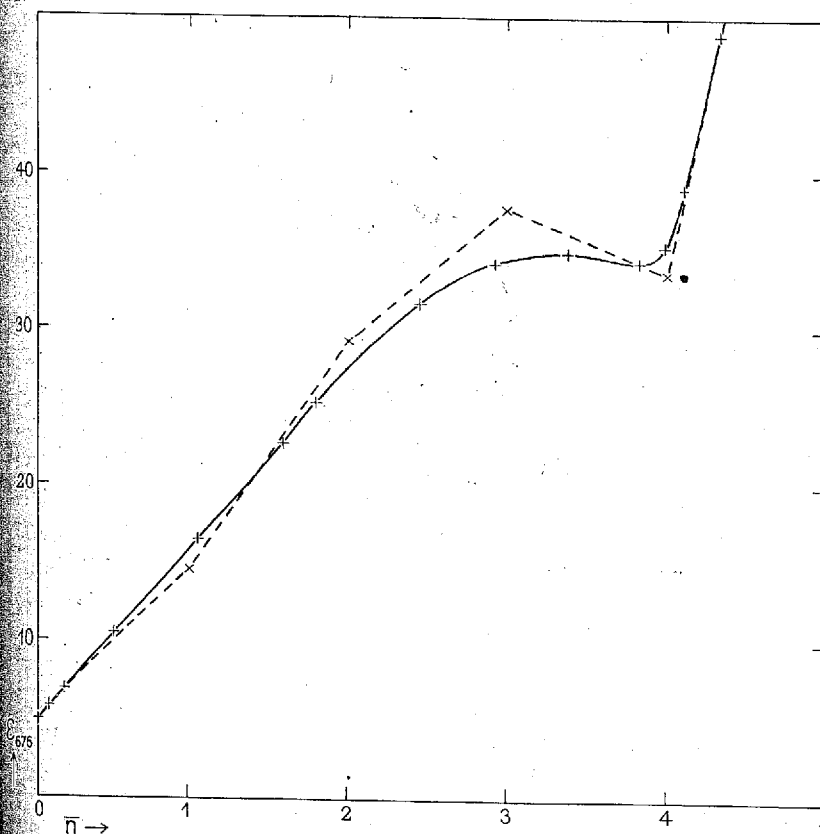


Fig. 3. The connection between the extinction coefficient and the formation function for the cupric ammonia system at wave length 676 m μ . The dotted broken line connects the extinction coefficients corresponding to the pure complexes.

that the extinction coefficient measured directly gives the absorption of the aquo-cupric ion¹. In the case of the other solutions the formation function is calculated with the aid of (9). The recorded concentrations of hydrogen ion and free ammonia are in the usual way determined by means of the glass electrode². The concentrations of free ammonia found in the case of solutions Nos. 2 and 3 are almost proportional to the corresponding values of the formation function, and this actually proves that

¹ Cf. loc. cit. p. 56.

² See Metal Ammine Formation in Aqueous Solution, p. 123 ff.

in the boundary region investigated there is only a monammine complex besides the aquo-cupric ion. Under this assumption $\log k_1$ for solution No. 2 is calculated as 4.29, and for solution No. 3 as 4.32, while the previously cited formula¹

$$\log k_1 = 3.99 + 0.080 C_{\text{NH}_4\text{NO}_3} + 0.013 (30^\circ - t^\circ)$$

gives 4.28 in 2 N ammonium nitrate at 20°. From our knowledge of the extinction coefficient of the solutions in the boundary region it is possible to calculate directly the extinction coefficient for the monammine complex. Using solution No. 2, ϵ_1 is calculated to be 15.9, and from solution No. 3 14.9, in very nice agreement with the previously calculated value 14.6. This value, together with the calculated extinction coefficients for the other cupric ammine ions², is used in tracing the broken line in fig. 3.

The above discussion should not lead to the assumption that it is especially important to have a direct graphical proof of the existence of the complexes occurring in the equilibrium. This is so far from being the case, as not only the existence, but also the distribution of the particular complexes can be calculated with certainty solely on the basis of our knowledge of the formation curve. Finally, it is interesting to note, that the formation curve itself in many instances may be established by purely optical methods, as it is the object of the present paper to show.

The author wishes to thank Professor, Dr. NIELS BJERRUM for permission to use a König-Martens spectrophotometer and a Wolff colorimeter from the Chemical Laboratory of the Royal Veterinary and Agricultural College.

¹ Loc. cit. p. 127.

² Untersuch. über Kupferammoniakverb. II, p. 52.

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