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MATEMATISK-FYSISKE MEDDELELSER, BIND XXII, NR. 18

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# STUDIES ON ACIDO COMPLEX FORMATION. I.

OPTICAL INVESTIGATIONS OF CUPRIC  
CHLORIDE IN MIXTURES WITH  
OTHER CHLORIDES

BY

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1946

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## 1. Introduction.

The complex formation in solutions of metal salts has only in a few cases been investigated in such a way that the available measurements give sure information on the composition and stability of the complex ions in question. It is the aim of the present series of investigations on acido complex formation to provide a more comprehensive material of quantitatively investigated systems, and thereby to find general rules for the complex formation. Simultaneously, the author considers it important to attempt an improvement of the methods used for the investigation of complex systems.

In systems of comparatively great complexity it is possible to carry through the investigations at a high and constant concentration of a highly dissociated neutral salt and at low concentrations of the complex-forming substances. Thus, the classical law of mass action can be applied, and the consecutive complexity constants can be established by methods similar to those used by the author in his studies on metal ammine formation.<sup>1</sup> In systems of very slight complexity it is unfeasible to perform the investigations in a constant salt medium, since the complex formation itself involves the application of high and greatly varying anion concentrations. This renders quantitative information much more difficult, but, nevertheless, an examination can be made also in the range of very high concentrations, if the experimental method used permits a direct determination of the concentration of at least one of the complexes involved. A

<sup>1</sup> Untersuchungen über Kupferammoniakverbindungen I, II und III: D. Kgl. Danske Vidensk. Selskab, Mat.-fys. Medd. **11**, No. 5 (1931), **11**, No. 10 (1932), **12**, No. 15 (1934). Metal Ammine Formation in Aqueous Solution. —Theory of the Reversible Step Reactions. Doctoral thesis, Copenhagen 1941 (Publ. by P. Haase & Son). Metal Ammine Formation in Aqueous Solution V: D. Kgl. Danske Vidensk. Selskab, Mat.-fys. Medd. **22**, No. 7 (1945).

closer account of this problem is given in the present paper, which deals with the complex formation in cupric chloride solutions, particularly in mixtures of cupric chloride and easily soluble chlorides (hydrochloric acid, lithium-, magnesium-, and calcium chloride); the complex formation was studied by means of light absorption measurements. The complexity of the cupric chloride system is only very low (cf. Table 1, where the order of magnitude of the first complexity constant of some metal chloride systems is recorded) and, therefore, it is remarkable that, under certain approximative assumptions as to conditions of activity, a determination of the whole curve of the complex formation is possible, *viz.* from the tetraquo cupric ion to the tetrachloro complex. Moreover, the concentration of the different complexes in the various chloride solutions can be accounted for semiquantitatively.

Table 1. First complexity constant in some metal chloride systems.

$$k_1 = \frac{[\text{MeCl}^{+v-1}]}{[\text{Me}^{+v}][\text{Cl}^-]}$$

Metal ion	$k_1$	
$\text{Cu}^{++}$ . . . . .	$\lesssim 1$	The present paper.
$\text{Fe}^{++}$ . . . . .	$\sim 2$	OLERUP, Dissertation, Lund 1944.
$\text{Fe}^{+++}$ . . . . .	$\sim 5$	»                   »                   »
$\text{Pb}^{++}$ . . . . .	$\sim 25$	GÜNTEMBERG, Dissertation, Copenhagen 1938.
$\text{Cd}^{++}$ . . . . .	$\sim 100$	LEDEN, Dissertation, Lund 1943.
$\text{Hg}^{++}$ . . . . .	$\sim 3 \cdot 10^7$	MORSE, Z. physik. Chem. <b>41</b> (1902) 727.

## 2. Discussion of Previous Investigations.

### a. Light Absorption of the Cupric Chloride System.

As is wellknown, the colour of cupric chloride solutions changes from blue to green with increasing concentration and, after addition of easily soluble chlorides to high concentration, it may turn almost purely yellow. Fig. 1 shows how this appears in the absorption spectrum of the solutions. The logarithm of the molar extinction coefficient  $\varepsilon$  calculated from the total copper concentration of the solutions (the absorption of the chlorine ion

being very small for wave-lengths  $> 200 \text{ m}\mu$ ) is plotted as ordinates, and the wave number in  $\text{cm}^{-1}$  as abscissae; for orientation purposes, the wave-length in  $\text{m}\mu$  is also plotted. The measurements represented in Fig. 1 are mainly taken from a

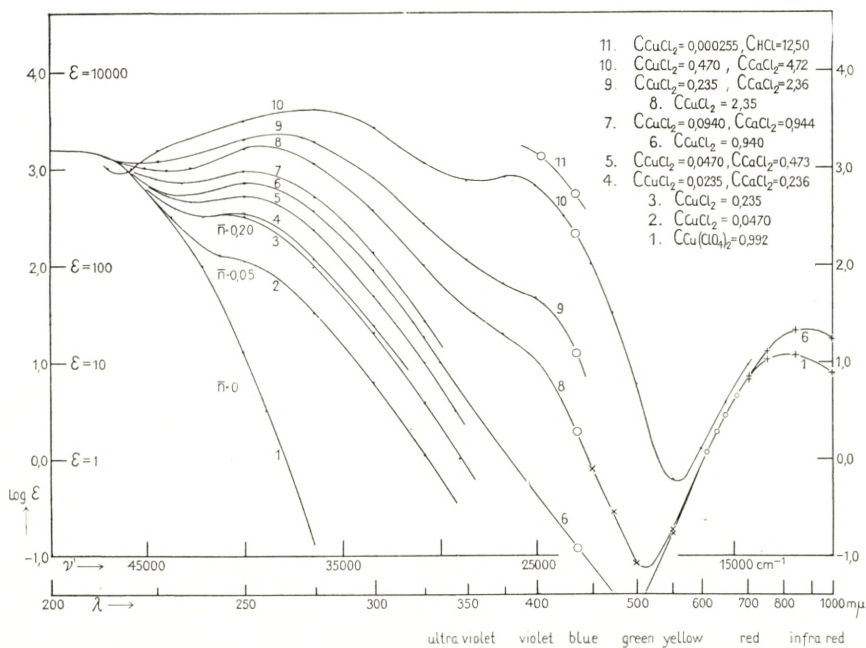


Fig. 1. Extinction curves of a number of cupric chloride solutions with and without calcium chloride (or hydrochloric acid). —  $\epsilon$  = the molar extinction coefficient,  $\nu'$  the wave number in  $\text{cm}^{-1}$ , and  $\lambda$  the wave-length in  $\text{m}\mu$ .

paper by DOEHLEMANN and FROMHERZ.<sup>1</sup> Thus, the absorption curves in the ultraviolet (corresponding to the solutions Nos. 1—10) were drawn on the basis of these authors' photographic measurements with a sector photometer. DOEHLEMANN and FROMHERZ continued the curve for solution No. 10 through the visible spectrum by measurements with a König-Martens spectrophotometer. The other curves have been continued on the basis of measurements by VAN DER GON<sup>2</sup> (marked with  $\times$ ) and the present author<sup>3</sup> ( $\circ$ ), and in the infrared on the basis of measurements by MECKE and LEY<sup>4</sup> ( $+$ ).

<sup>1</sup> DOEHLEMANN and FROMHERZ, Z. physik. Chem. A **171** (1934) 371.

<sup>2</sup> VAN DER GON, Arch. Néerlandaises des Sciences Exactes [3] A **7** (1924) 140.

<sup>3</sup> Kupferammoniakverb. II, p. 55, and Table 3 in the present paper.

<sup>4</sup> MECKE and LEY, Z. physik. Chem. **111** (1924) 391.

From Fig. 1 it appears that the complex formation in dilute cupric chloride solutions manifests itself in the ultraviolet absorption long before the absorption in the visible and the infrared spectrum is noticeably changed. DOEHLEMANN and FROMHERZ assume that the absorption band at about  $250\text{ m}\mu$ , which appears even at small chlorine ion concentrations, must be ascribed to the tetra- or trichloro complex, and that the displacement of the band in the direction of higher wave-lengths with higher chlorine ion concentrations may be attributed to the formation of polynuclear chloro complexes. This assumption is quite improbable and directly at variance with the fact that the extinction curves of the mixtures with a low copper concentration conform well to the corresponding extinction curves of the pure cupric chloride solutions. This observation indicates that there are on the whole mononuclear complexes only and, furthermore, this fact is of interest because it makes an estimation of the complexity of the system possible. In the following sections the problem will be considered in greater detail.

#### b. Estimation of the Formation Function on the Basis of DOEHLEMANN and FROMHERZ'S Measurements.

For some of the mixtures represented in Fig. 1 it is possible by interpolation to choose a cupric chloride solution of such a concentration that its molar extinction coefficient is the same as that of the mixed solution throughout the investigated part of the spectrum. This means that we have two solutions with the same complex distribution and the same concentration of free ligand, although their total concentrations are different. Such solutions have been termed corresponding by the author,<sup>1</sup> and they are important because from their total concentrations we may calculate both the mean number of bound ligands per metal atom, the so-called formation function  $\bar{n}$ , and the concentration of free ligand. Since a detailed discussion of this problem may be found in the mentioned work by the author, the method will only be outlined here.<sup>2</sup>

<sup>1</sup> D. Kgl. Danske Vidensk. Selskab, Mat.-fys. Medd. **21**, No. 4 (1944).

<sup>2</sup> The method, which is of fundamental importance for the calculation of step equilibria on the basis of optical measurements, has been applied, inde-

The formation function  $\bar{n}$  is given by the expression

$$\bar{n} = \frac{C_{\text{Cl}^-} - [\text{Cl}^-]}{C_{\text{Cu}}} \quad (1)$$

$C_{\text{Cl}^-}$  and  $C_{\text{Cu}}$  denote the total concentrations of chlorine ion and cupric copper, respectively, and  $[\text{Cl}^-]$  the concentration of free chlorine ion. In two corresponding solutions the formation functions are identical, and if this is expressed in an equation, we easily find

$$\bar{n} = \frac{C_{\text{Cl}^-}^0 - C_{\text{Cl}^-}}{C_{\text{Cu}}^0 - C_{\text{Cu}}} \quad (2)$$

$$[\text{Cl}^-] = \frac{C_{\text{Cu}}^0 C_{\text{Cl}^-} - C_{\text{Cu}} C_{\text{Cl}^-}^0}{C_{\text{Cu}}^0 - C_{\text{Cu}}} \quad (3)$$

The total concentrations without indices refer *e. g.* to the mixed solutions, and the indexed concentrations to corresponding pure cupric solutions. Thus,

$$C_{\text{Cl}^-}^0 = 2 C_{\text{Cu}^{++}}^0 = 2 C_{\text{CuCl}_2}^0.$$

Table 2. Formation function and concentration of free chlorine ion calculated according to the theory of corresponding solutions from the measurements of DOEHLEMANN and FROMHERZ.

No.	$C_{\text{Cu}^{++}}$	$C_{\text{Cl}^-}$	$C_{\text{CuCl}_2}^0$ 275 m $\mu$	$C_{\text{CuCl}_2}^0$ 300 m $\mu$	$C_{\text{CuCl}_2}^0$ 325 m $\mu$
4.....	0.0235	0.519	0.288	0.282	—
5.....	0.0470	1.038	0.563	0.575	0.616
7.....	0.0940	2.076	1.260	1.260	1.175

No.	$[\text{Cl}^-]$	$\bar{n}$	$\epsilon_{275}$	$\epsilon_{300}$	$\epsilon_{325}$
4.....	0.515	$0.19 \pm 0.03$	114	23.6	—
5.....	1.03	$0.25 \pm 0.06$	224	47.5	10.0
7.....	2.04	$0.34 \pm 0.05$	490	133	26.1

pendently of the present author, by Olerup in his thesis (Järnkloridernas Komplexitet, Lund 1944, p. 65) to the particular case that one of the corresponding solutions is so dilute that the concentration of free ligand becomes identical with the total ligand concentration.

Table 2 shows the result of a calculation of the formation function for mixtures Nos. 4, 5, and 7. The calculation has been made for three wave-lengths by interpolation on curves, where  $\log \varepsilon$  of the measured pure cupric chloride solutions has been plotted against the logarithm of their concentration. The table comprises the interpolated values for  $C_{\text{CuCl}_2}^0$  and the mean values of the formation function and of the concentration of free chlorine ion, calculated by means of (2) and (3). For the solutions examined, not quite the same corresponding cupric chloride concentration is determined at each of the wave-lengths used. The influence of this uncertainty on the formation function appears in the table as a mean uncertainty of the calculated values. The application of formulae (2) and (3) is underlaying the assumption that the classical law of mass action is valid. This condition is presumably fulfilled for the most dilute solutions of Fig. 1, where the ionic strengths of the corresponding cupric chloride and calcium chloride solutions do not deviate essentially from one another, however, in this range the calculation of  $\bar{n}$  depends particularly on the accuracy of the measurements. It appears from the extinction coefficients given in the table that the light absorption at 275 and 300  $m\mu$  is almost proportional to the concentration of free chlorine ion for concentrations up to about 1 molar. Hence, it may be concluded that in the respective wave-length and concentration range mainly the monochloro complex is decisive for the light absorption.

#### c. SPACU and MURGULESCU'S Measurements in the Blue Mercury Line.

Using the visible Hg-lines and a König-Martens spectrophotometer, SPACU and MURGULESCU<sup>1</sup> performed some accurate measurements of the light absorption of cupric chloride solutions with varying potassium chloride contents at 20° C. The light absorption shows only a slight variation with the chlorine ion concentration in the Hg-lines 578 and 546  $m\mu$ , but, on the other hand, a very marked variation in the blue Hg-line 436  $m\mu$ . SPACU and MURGULESCU'S measurements at 436  $m\mu$  are repre-

<sup>1</sup> SPACU and MURGULESCU, *Z. physik. Chem. A* **170** (1934) 71.



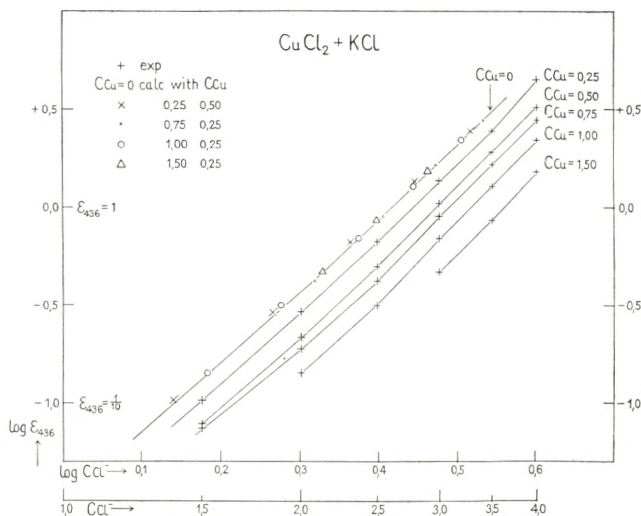


Fig. 2. SPACU and MURGULESCU's measurements of the light absorption in cupric chloride solutions with and without potassium chloride added. The figure gives the molar extinction coefficient in the Hg-line 436 m $\mu$  at various copper concentrations as a function of the total chlorine ion concentration.

sented graphically in Fig. 2. These authors measured at five different copper concentrations, and for each of these concentrations the logarithm of the molar extinction coefficient is plotted against the logarithm of the total chlorine ion concentration of the solution. For each copper concentration the slope of the curve  $\frac{\Delta \log \epsilon_{436}}{\Delta \log C_{Cl^-}}$  is very near 4 or, in other words, in the concentration range examined the molar extinction coefficient increases with almost the fourth power of the chlorine ion concentration.

SPACU and MURGULESCU observed this fact, and they realized that it is in favour of a highly absorbing tetrachloro complex present in the solution in a low concentration. On the other hand, SPACU and MURGULESCU give much reflexion to the question why BEER'S law is not valid at a constant total chlorine ion concentration. This is, of course, due to the fact that the total chlorine ion concentration and the concentration of free chlorine ions at finite copper concentrations are two different things owing to the complex-bound chlorine. A quantitative calculation of the prevailing conditions can easily be carried through by means of the above-mentioned principle, according to which solutions with

the same molar extinction coefficients have the same formation function and the same concentration of free chlorine ions. An example for the calculation of the respective magnitudes on the basis of SPACU and MURGULESCU's measurements is given in Table 3.

Table 3. Formation function, concentration of free chlorine ion, and the power with which the extinction coefficient depends on the chlorine concentration calculated from the measurements of SPACU and MURGULESCU.

$C_{Cl^-}$ ( $C_{Cu} = 0.75$ )	$\epsilon_{436}$	$\log \epsilon_{436}$	$\log C_{Cl^-}$ ( $C_{Cu} = 0.25$ )	$\bar{n}$	$[Cl^-]$	$\log [Cl^-]$	$\frac{A \log \epsilon_{436}}{A \log [Cl^-]}$
1.50	0.0741	-1.130	0.134	0.28	1.29	0.111	
2.00	0.1880	-0.726	0.250	0.44	1.67	0.223	3.60
2.50	0.4227	-0.374	0.346	0.56	2.08	0.318	3.70
3.00	0.8965	-0.047	0.432	0.60	2.55	0.407	3.67
3.50	1.637	+0.214	0.498	0.71	2.97	0.473	3.95
4.00	2.791	+0.446	0.557	0.79	3.41	0.533	3.87

In the first columns of Table 3 are given the total chlorine ion concentration and the experimentally determined extinction coefficients for all solutions with a copper concentration 0.75. The logarithm of the  $C_{Cl^-}$  concentration corresponding to the reported extinction coefficients and the copper concentration 0.25 are to be found in column 4 (determined graphically by means of Fig. 2). In the following columns are given the values for the formation function and the concentration of free chlorine ion calculated by means of (2) and (3). SPACU and MURGULESCU's measurements at other copper concentrations have been combined in an analogous manner with their measurements at the copper concentration 0.25. All corresponding values of  $\bar{n}$  and  $\log [Cl^-]$  calculated in this way are represented graphically in Fig. 5 (marked as  $\blacktriangle$  points) and together with the values calculated from DOEHLEMAN and FROMHERZ's measurements (marked as  $\blacktriangledown$  points) they determine the first part of the formation curve of the cupric chloride system. In Fig. 2  $\log \epsilon_{436}$  is plotted against the logarithm of the calculated values for the concentration of free chlorine ions. In the graph this is the curve

calculated for an infinitely small copper concentration, and it is seen that the calculated points fall very nearly on one and the same curve, independent of the copper concentration in the solutions used for the calculation. The slope of the curve

$$\frac{\Delta \log \varepsilon_{436}}{\Delta \log [\text{Cl}^-]}$$

calculated from point to point on the basis of the small circular points, representing the values of  $\log \varepsilon_{436}$  and  $\log [\text{Cl}^-]$  in Table 3, are given in the last column of the table. At chlorine ion concentrations in the range 1.5 to 2 N the slope of the curve is about 3.60, and the corresponding value for  $\bar{n}$  is about 0.40. Consequently,

$$\frac{\Delta \log \varepsilon_{436}}{\Delta \log [\text{Cl}^-]} \cong 4 - \bar{n}. \quad (4)$$

On the supposition that we may apply the concentration law of mass action, the relation between the concentration of the single complex ions and the concentration of free chlorine ions is given by the extended Bodländer formula.<sup>1</sup> According to this formula the change in the concentration of the tetrachloro complex is given by

$$\frac{d \log \frac{[\text{CuCl}_4^-]}{C_{\text{Cu}}}}{d \log [\text{Cl}^-]} = 4 - \bar{n}. \quad (5)$$

Comparing (4) and (5) it is obvious that there is an approximate proportionality between  $\varepsilon_{436}$  and the relative concentration of the tetrachloro complex. It appears from Table 3 that  $\frac{\Delta \log \varepsilon_{436}}{\Delta \log [\text{Cl}^-]}$  with increasing chlorine ion concentration exceeds the value  $4 - \bar{n}$ . This is hardly due to a formation of complexes with more than four chlorine ions, but is naturally explained by the fact that we have entered a concentration range where the activity coefficients of the ions begin to increase with increasing concentration. An increasing ligand concentration will always favour the formation of the complex richest in ligand and, hence, for sufficiently high concentrations of chlorine ion it seems justified

<sup>1</sup> See Metal Ammine Formation in Aqueous Solution, p. 28.

to calculate the concentration of the tetrachloro complex from the expression

$$[\text{CuCl}_4^{--}] = \frac{\varepsilon_{436}}{\varepsilon_{436}^0} C_{\text{Cu}}, \quad (6)$$

where  $\varepsilon_{436} \approx 500$  denotes the limiting extinction coefficient of the cupric chloride system at very high chlorine ion concentration.

#### d. An Application of P. JOB'S "Méthode des Variations Continues".

The validity of an expression like (6) is confirmed in a paper by T. MOELLER,<sup>1</sup> who, using P. JOB'S méthode des variations continues in the form modified by VOSBURGH and COOPER,<sup>2</sup> found that copper chloride solutions contain a tetrachloro complex. MOELLER mixed equimolecular solutions of cupric nitrate and various chlorides, and in that part of the spectrum where a change in absorption takes place (blue and green light) he found a maximum for the optical density at a proportion of the mixture corresponding to the tetrachloro complex, *i. e.* four volumes of chloride solution and one volume of cupric nitrate solution. According to the method this is a criterion for the existence of a tetrachloro complex.

Obviously MOELLER'S measurements do not preclude the existence of other chloro complexes, but they support the validity of (6), which will be used in what follows for the determination of the concentration of the tetrachloro complex in the cupric chloride solutions at high chlorine ion concentrations.

### 3. Theoretical Remarks on the Calculation of Complex Equilibria in Concentrated Chloride Solutions.

#### a. Variation of the Activity Coefficient with the Concentration.

In previous rough calculations the validity of the classical law of mass action was considered a supposition. This, of course,

<sup>1</sup> T. MOELLER, Journ. Physic. Chem. **48** (1944) 111.

<sup>2</sup> VOSBURGH and COOPER, Journ. Amer. Chem. Soc. **63** (1941) 437.

is not correct in the case of high and varying concentrations, and therefore we shall first discuss the question how for a number of chlorides the activity coefficient varies with the concentration. This interdependence is shown in Fig. 3. The mean activity coefficient is denoted by  $\gamma$  (and not by  $f$ ) in order to indicate

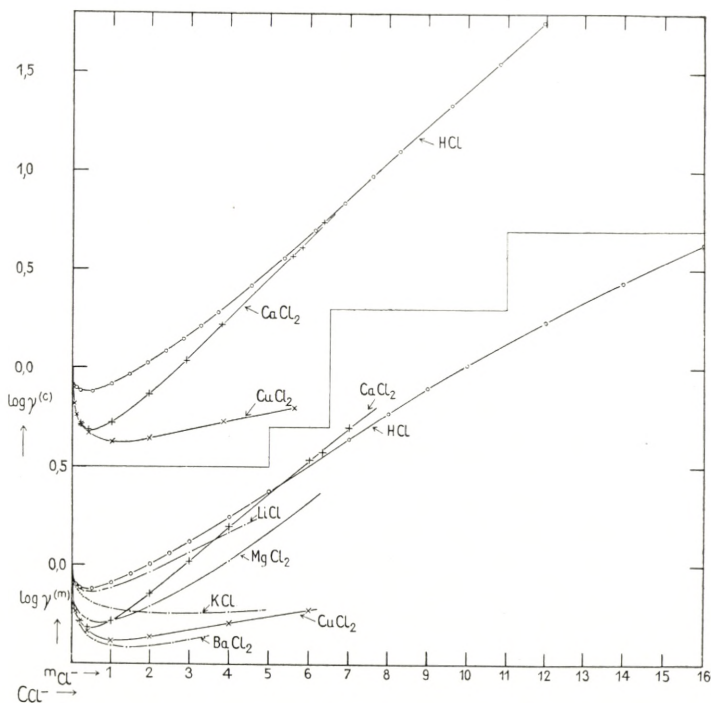


Fig. 3. The apparent mean ion activity coefficient of some chlorides as a function of the concentration. Above  $\gamma^{(c)}$  as a function of the molar chlorine ion concentration  $C_{Cl^-}$  in mols per litre solution, and below  $\gamma^{(m)}$  as a function of the chlorine ion molality  $m_{Cl^-}$  in mols per 1000 g.  $H_2O$ .

that a possible complex formation has not been taken into account. The indications  $\gamma^{(m)}$  and  $\gamma^{(c)}$  refer to the concentration scale used. In the lower part of the figure,  $\log \gamma^{(m)}$  is plotted against  $m_{Cl^-}$  or the chlorine ion normality per 1000 g. of water. These values are taken directly from LANDOLT-BÖRNSTEIN'S Tables<sup>1</sup> and are calculated thermodynamically either from cryoscopic measurements or from electrical chains without diffusion potential. In order to obtain a suitable basis of comparison for the

<sup>1</sup> II. Erg.-bd., p. 1111 and III. Erg.-bd., p. 2138.

chlorides examined in highly concentrated solutions, the upper part of the figure contains both the activity coefficients and the chlorine ion normality converted into the units used in the present investigation, *viz.* the concentration per litre solution.

It is seen that the activity coefficients decrease rapidly in the Debye-Hückel range (where mainly the type of the salt determines the course of the curve), passing through a minimum in the range of moderate concentrations where the classical law of mass action therefore holds approximately, and finally increasing at high chlorine ion concentrations. Thermodynamically we determine the activity of the non-hydrated salts; the increase in  $\gamma$  is due to the fact that the concentration of the non-hydrated ions increases with the decreasing water tension of the solution, the increase being more pronounced the more hydrated the salts.<sup>1</sup> Setting aside the cause of the increase in the activity coefficients, it is remarkable that  $\log \gamma^{(c)}$  for hydrochloric acid and calcium chloride (the only chlorides examined at very high concentrations) increases almost linearly with the ion normality for concentrations above 3 N up to the highest concentrations measured. The following formulae apply with approximation:

$$\begin{aligned}\log \gamma_{(\text{HCl})}^{(c)} &= -0.42 + 0.18 C_{\text{Cl}^-} \\ \log \gamma_{(\text{CaCl}_2)}^{(c)} &= -0.55 + 0.20 C_{\text{Cl}^-}.\end{aligned}$$

Our knowledge of the activity of the electrolytes in highly concentrated solution is indeed still very poor; however, it cannot be excluded that we have to do with a rather general rule.<sup>2</sup> The Debye-Hückel expression with a term of the first order added<sup>3</sup> formally leads to a rule of this kind; the square root expression  $\frac{1 + \sqrt{I}}{\sqrt{I}}$  being almost a constant for high values of the ionic strength  $I$ .<sup>4</sup>

<sup>1</sup> N. BJERRUM, Med. Vetenskapsakad. Nobelinst. **5**, No. 16 (1919).

<sup>2</sup> Cf. AKERLÖF, Journ. Amer. Chem. Soc. **56** (1934) 593, 1439.

<sup>3</sup> Cf. GUGGENHEIM, Phil. Mag. [7] **19** (1935) 588.

<sup>4</sup> In Fig. 3, the logarithm of the activity coefficients is deliberately plotted against the ion normality and not against the ion strength. A concept like ion strength, which is based on the supposition that the charge of the ions is of decisive importance for the activity coefficient, is of minor significance in the range of high concentration and is here naturally replaced by the total ion normality of the solution.

### b. The Basis of the Calculation of the Cupric Chloride System.

In all hitherto examined complex systems the cupric ion has the characteristic coordination number 4. This fact together with the optical finding of a monochloro and tetrachloro complex and, finally, the observation that the absorption spectra are independent of the copper concentration, which excludes polynuclear complexes, renders it probable that in cupric chloride solutions we have equilibria between the ions



The consecutive complexity constants  $k_1$ ,  $k_2$ ,  $k_3$ , and  $k_4$  corresponding to the formation of the four chloro complexes are defined by the expressions

$$\left. \begin{aligned} \frac{[\text{CuCl}^+]}{[\text{Cu}^{++}][\text{Cl}^-]} &= k_1 \frac{f_{\text{Cu}^{++}} \cdot f_{\text{Cl}^-}}{f_{\text{CuCl}^+}} \\ \frac{[\text{CuCl}_2]}{[\text{CuCl}^+][\text{Cl}^-]} &= k_2 \frac{f_{\text{CuCl}^+} \cdot f_{\text{Cl}^-}}{f_{\text{CuCl}_2}} \\ \frac{[\text{CuCl}_3^-]}{[\text{CuCl}_2][\text{Cl}^-]} &= k_3 \frac{f_{\text{CuCl}_2} \cdot f_{\text{Cl}^-}}{f_{\text{CuCl}_3^-}} \\ \frac{[\text{CuCl}_4^{--}]}{[\text{CuCl}_3^-][\text{Cl}^-]} &= k_4 \frac{f_{\text{CuCl}_3^-} \cdot f_{\text{Cl}^-}}{f_{\text{CuCl}_4^{--}}} \end{aligned} \right\} \quad (7)$$

For brevity, the water molecules have been omitted in the formulae and  $f_X$  denotes the activity coefficient of the molecule or ion X. In the mass action expressions (7) we find, besides the four unknown complexity constants, four activity coefficient expressions whose dependence on the concentration is unknown. It is therefore *a priori* obvious that a knowledge of the tetrachloro complex concentration  $[\text{CuCl}_4^{--}]$  (optically determined by means of (6)) and the chlorine ion concentration  $[\text{Cl}^-]$  is insufficient for an exact treatment of the cupric chloride system. Only an approximate treatment can be attempted with the aim to arrive at the essential features. Let us assume that the system

(7) may be described by a single mean activity coefficient  $F$  defined by the relations

$$F = \frac{f_{\text{Cu}^{++}} \cdot f_{\text{Cl}^-}}{f_{\text{CuCl}^+}} = \frac{f_{\text{CuCl}^+} \cdot f_{\text{Cl}^-}}{f_{\text{CuCl}_2}} = \frac{f_{\text{CuCl}_2} \cdot f_{\text{Cl}^-}}{f_{\text{CuCl}_3^-}} = \frac{f_{\text{CuCl}_3^-} \cdot f_{\text{Cl}^-}}{f_{\text{CuCl}_4^{--}}}. \quad (8)$$

This approximation corresponds to the assumption that  $\log f_{\text{CuCl}_n^{2-n}}$  changes evenly from  $f_{\text{Cu}^{++}}$  to  $f_{\text{CuCl}_4^{--}}$  and therefore is not quite unreasonable in the case of concentrated solutions, where chemical similarity between the ions rather than the charge of the ions determines the activity coefficients. As to the dependence of  $F$  on the concentration, we shall assume, in accordance with the above considerations, that in a concentrated solution

$$\log F = A + B \cdot C_{\text{ion}}, \quad (9)$$

where  $A$  and  $B$  are individual constants and  $C_{\text{ion}}$  is the total ion normality of the solution.

The validity of the classical law of mass action is a necessary condition for the application of the extended Bodländer formula

$$\frac{d \log \alpha_n}{d \log [\text{Cl}^-]} = n - \bar{n}, \quad (10)$$

where  $\alpha_n = \frac{[\text{CuCl}_n^{2-n}]}{C_{\text{Cu}}}$ . However, if only one mean activity coefficient is introduced, this formula may be written<sup>1</sup>

$$\frac{d \log \alpha_n}{d \log F + d \log [\text{Cl}^-]} = n - \bar{n}. \quad (11)$$

In expression (9) the total ion normality appears instead of the chlorine ion concentration; since, however, the experimental investigation was carried out at low copper concentrations and high chloride concentrations, and disregarding other complex formation, we may put

$$C_{\text{ion}} = [\text{Cl}^-]. \quad (12)$$

If (9) is differentiated, applying (12), with regard to the

<sup>1</sup> This is seen at once when, at the derivation of the formula, the expression for  $\alpha_n$  is differentiated with regard to  $F[\text{Cl}^-]$  instead of  $[\text{Cl}^-]$ .



chlorine ion concentration, and substituted in (11), this formula may be written

$$\frac{d \log \alpha_n}{d [\text{Cl}^-]} = \left( \frac{0.4343}{[\text{Cl}^-]} + B \right) (n - \bar{n}), \quad (13)$$

the constant A disappearing on differentiation. In this expression putting  $n = 4$  and, moreover, taking into account the proportionality between  $\alpha_4$  and  $\epsilon_{436}$ , according to (6), we obtain

$$\frac{d \log \epsilon_{436}}{d [\text{Cl}^-]} = \left( \frac{0.4343}{[\text{Cl}^-]} + B \right) (4 - \bar{n}). \quad (14)$$

In what follows, expression (14) has been used to determine the formation function  $\bar{n}$  and the constant B from  $\frac{d \log \epsilon_{436}}{d [\text{Cl}^-]}$  at various chlorine ion concentrations.

#### 4. Extinction Measurements of Mixtures of Cupric Chloride with other Chlorides.

##### a. Measurements and Experimental Details (in Collaboration with PALLE ANDERSEN).

Table 4 contains the measurements of the extinction coefficients of cupric chloride in concentrated solutions of hydrochloric acid, lithium-, magnesium-, and calcium chloride. The majority of the measurements in lithium- and magnesium chloride solutions has been carried out by Mr. PALLE ANDERSEN, the other measurements were performed by the author. The molar total concentrations of cupric chloride and of the chlorides added are recorded in columns 2 and 3 of the respective sections of the table; the last column but two gives the molar extinction coefficients found. The extinction coefficient of the wave-length  $\lambda$  was calculated according to the formula

$$\epsilon_\lambda = \frac{\log \frac{I_0}{I}}{C_{\text{Cu}} \cdot d}, \quad (15)$$

where  $I_0$  and  $I$  denote the intensity of the incident and the trans-

Table 4. Light absorption measurements of cupric chloride solutions containing an other chloride at 22–23° C.

## a. Cupric chloride + hydrochloric acid.

No.	C <sub>CuCl<sub>2</sub></sub>	C <sub>HCl</sub>	[Cl <sup>-</sup> ]	ε <sub>436</sub>	log ε <sub>436</sub>	$\frac{A \log \epsilon_{436}}{A t^\circ}$
1	0.001602	13.32	13.32	538	2.731	
2	0.001602	12.80	12.80	532	2.726	
3	0.002004	11.85	11.85	507	2.705	
4	0.002004	10.87	10.87	477	2.678	
5	0.001607	10.05	10.05	447	2.650	
6	0.002006	9.67	9.67	439	2.642	0.004
7	0.00401	8.59	8.59	369	2.567	
8	0.00397	8.52	8.52	359	2.555	
9	0.002004	8.21	8.21	332	2.521	
10	0.001990	7.82	7.82	297	2.473	
11	0.00401	7.51	7.51	272	2.434	
12	0.00399	7.02	7.02	217	2.337	
13	0.00998	6.44	6.44	167.0	2.223	0.008
14	0.01001	6.025	6.025	122.2	2.088	
15	0.00597	5.92	5.92	115.5	2.063	
16	0.00597	5.448	5.448	78.6	1.896	
17	0.003006	5.37	5.37	75.0	1.875	
18	0.01002	5.35	5.35	74.33	1.871	
19	0.01996	4.83	4.83	43.2	1.636	
20	0.0499	4.388	4.388	26.63	1.425	
21	0.01595	4.288	4.288	24.04	1.381	
22	0.02989	4.142	4.142	19.69	1.294	
23	0.02989	3.788	3.788	12.11	1.084	0.018
24	0.0499	3.625	3.625	9.63	0.984	
25	0.0499	3.625	3.625	9.95	0.998	
26	0.0995	3.313	3.313	6.64	0.822	
27	0.0299	3.222	3.222	5.50	0.740	
28	0.0499	3.203	3.203	4.77	0.679	∞ 0.02
29	0.0995	2.954	2.954	3.73	0.572	
30	0.0499	2.954	2.954	3.50	0.544	
				ε <sub>405</sub>	log ε <sub>405</sub>	$\frac{A \log \epsilon_{405}}{A^\circ t}$
31	0.000255	12.50	12.50	1290	3.11	0.004

Table 4 (continued).

## b. Cupric chloride + lithium chloride.

No.	C <sub>CuCl<sub>2</sub></sub>	C <sub>LiCl</sub>	$d_{40}^{-20}$	[Cl <sup>-</sup> ]	$\epsilon_{436}$	log $\epsilon_{436}$	$\frac{\Delta \log \epsilon_{436}}{\Delta t^{\circ}}$
1	0.003134	12.09 III	1.257	12.09	421	2.624	∞ 0.004
2	0.003129	11.01 III	1.237	11.02	407	2.610	
3	0.003339	10.31 III	1.220	10.32	383	2.583	
4	0.002786	9.75 II	1.207	9.76	358	2.554	
5	0.005012	9.22 II	1.198	9.24	331	2.520	
6	0.004218	8.64 III	1.185	8.65	291	2.463	
7	0.003921	7.88 I	1.169	7.90	234	2.370	
8	0.004338	7.81 III	1.168	7.81	216	2.334	
9	0.004941	7.76 II	1.167	7.77	218	2.338	
10	0.004572	7.18 III	1.155	7.19	172	2.235	
11	0.007135	6.86 III	1.148	6.86	140	2.147	
12	0.01723	6.79 III	1.148	6.80	150	2.175	
13	0.01065	6.26 II	1.137	6.29	93.2	1.970	
14	0.01005	6.24 III	1.135	6.24	94.2	1.974	
15	0.01824	5.75 III	1.128	5.76	64.8	1.812	
16	0.02837	5.22 III	1.115	5.22	40.3	1.605	
17	0.05291	4.77 III	1.109	4.78	26.2	1.419	
18	0.02358	4.76 II	1.105	4.76	23.8	1.377	
19	0.04217	4.50 III	1.104	4.50	17.0	1.231	
20	0.07404	4.26 III	1.104	4.27	14.8	1.170	
21	0.07111	3.92 II	1.095	3.93	9.30	0.967	
22	0.07710	3.77 III	1.094	3.77	7.72	0.888	
23	0.1014	3.22 II	1.084	3.23	3.73	0.572	
24	0.000246	13.34 I	1.284	13.34	$\epsilon_{405}$ 813	log $\epsilon_{405}$ 2.91	

Table 4 (continued).

## c. Cupric chloride + magnesium chloride.

No.	$C_{CuCl_2}$	$C_{MgCl_2}$	$d_{40}^{\sim 20^\circ}$	$[Cl^-]$	$\epsilon_{436}$	$\log \epsilon_{436}$	$\frac{\Delta \log \epsilon_{436}}{\Delta t^\circ}$
1	0.003427	5.080	1.340	10.16	308	2.489	
2	0.003431	4.976	1.331	9.95	307	2.487	
3	0.003313	4.897	1.327	9.79	280	2.447	0.007
4	0.003306	4.720	1.320	9.44	255	2.406	
5	0.005109	4.557	1.309	9.11	229	2.360	0.008
6	0.005743	4.331	1.292	8.66	204	2.310	
7	0.005757	4.185	1.285	8.37	182	2.260	0.010
8	0.006974	3.994	1.270	7.99	162	2.210	
9	0.008567	3.813	1.259	7.63	133	2.124	
10	0.01276	3.580	1.246	7.16	105	2.021	0.013
11	0.02905	3.330	1.232	6.66	80.1	1.904	
12	0.01592	3.205	1.222	6.41	65.7	1.818	
13	0.02399	3.056	1.213	6.11	52.6	1.721	
14	0.06732	2.695	1.195	5.39	30.1	1.479	
15	0.04829	2.480	1.180	4.96	19.1	1.281	0.017
16	0.07691	2.221	1.172	4.44	11.1	1.045	
17	0.08479	2.021	1.152	4.04	6.94	0.841	0.019
18	0.1021	1.815	1.140	3.63	4.07	0.610	
19	0.000255	4.908	1.327	9.82	740	2.87	

## d. Cupric chloride + calcium chloride.

No.	$C_{CuCl_2}$	$C_{CaCl_2}$	$d_{40}^{\sim 20^\circ}$	$[Cl^-]$	$\epsilon_{436}$	$\log \epsilon_{436}$	$\frac{\Delta \log \epsilon_{436}}{\Delta t^\circ}$
1	0.003333	7.025 II	1.522	14.05	297	2.473	
2	0.003333	6.76 II	1.506	13.52	302	2.480	$\infty$ 0.007
3	0.004004	6.365 II	1.482	12.73	296	2.472	
4	0.003333	5.71 II	1.440	11.42	275	2.440	
5	0.003212	5.25 II	1.407	10.50	249	2.396	
6	0.01002	4.725 I	1.372	9.51	208	2.318	
7	0.00600	4.378 II	1.350	8.76	169	2.227	
8	0.008034	4.160 II	1.333	8.32	145	2.160	
9	0.00804	3.875 I	1.305	7.62	103	2.013	
10	0.009998	3.435 II	1.279	6.87	70.5	1.848	
11	0.02006	3.14 I	1.260	6.34	49.4	1.694	
12	0.02415	2.895 I	1.242	5.84	35.0	1.544	
13	0.03309	2.674 II	1.227	5.35	22.8	1.358	
14	0.0400	2.49 I	1.210	5.03	16.6	1.220	
15	0.06662	2.244 II	1.194	4.49	9.73	0.988	
16	0.06662	2.043 II	1.177	4.09	6.15	0.789	
17	0.06662	1.883 II	1.164	3.77	4.26	0.630	

mitted light, respectively,  $C_{\text{Cu}}$  the total copper concentration, and  $d$  the thickness of the absorbing layer in cm. The extinction measurements were made by means of a König-Martens spectrophotometer, an Uviol mercury lamp being used as light source. The measurements were performed mainly with the mercury line  $436 \text{ m}\mu$  but, as appears from the table, a few were also made in the violet line  $405 \text{ m}\mu$ . However, the  $405$ -line is of very low visual intensity and, therefore, the latter measurements are encumbered with a considerably higher uncertainty than those at  $436 \text{ m}\mu$ . As absorption vessels were applied almost exclusively the standard cell of the "kleine Beleuchtungseinrichtung" of the König-Martens apparatus with its appurtenant "Schulzkörper" and glass cover. The effective thickness of layer of the cell is  $1 \text{ cm}$  (determined by the thickness of the Schulz body). Handling of the cell is most convenient, as it permits a rapid exchange of the solution by pipetting. It must furthermore be considered advantageous that the temperature of the solution can be checked relatively easily. The completely closed absorption tubes which are provided with screwed-on brass caps and are used in the "grosse Beleuchtungseinrichtung" of the König-Martens apparatus offer other advantages, thus the apparatus is well shielded against injurious vapours from the solutions. These tubes were therefore used for the measurement of the strongest hydrochloric acid solutions.

The absorption of blue light of cupric chloride solutions is rather dependent on temperature and, hence, the temperature had to be kept constant. The whole apparatus was therefore placed in an electrically regulated thermostat room. During the determination of the extinction coefficients recorded in Table 4 the temperature was kept at  $22$ – $22.5^\circ \text{C}$ . Generally, the solutions were a little warmer, but direct checking revealed that their temperature never exceeded  $23^\circ \text{C}$ . In some cases, the temperature dependence was determined by first measuring the extinction coefficient at the temperature of the unheated thermostat room ( $16$ – $20^\circ$ ) and, subsequently, at maximum heating of the room ( $27$ – $30^\circ$ ). The measurements at the two temperatures are comprised in the values for the temperature coefficient  $\frac{\Delta \log \epsilon_\lambda}{\Delta t^\circ}$  given in the last column of Table 4. The values marked by

*circa* are determined either at a considerably smaller temperature interval or they are less certain for other reasons.

For the preparation of the solutions, Merck's cupric chloride and magnesium chloride *pro analysi* were used; the hydrochloric acid was a completely colourless commercial product (37 per cent.). Two calcium chloride preparations were applied, *viz.* (I) an ordinary crystallized commercial product and (II) Merck's *pro analysi* preparation. Three lithium chloride preparations were used, *viz.* (I) an ordinary commercial product, (II) a recrystallized laboratory preparation, and (III) a Kahlbaum preparation. In Table 4, the Roman numerals after the lithium and calcium chloride concentrations refer to the respective salt preparation used. The solutions were made in measuring flasks from stock solutions of the different chlorides. The stock solutions were made dust-free by filtration through hard squeezed cotton. The concentration was determined by Volhard titration and, in the hydrochloric acid solutions, moreover acidimetrically. Generally, hydrochloric acid and cupric chloride were pipetted, while the concentrated viscous solutions of lithium-, magnesium-, and calcium chloride were always weighed into the measuring flasks. The specific gravity of the solutions was determined by weighing the contents of the measuring flasks, and are given in the fourth column of Table 4. Only the specific gravity of the hydrochloric acid solutions was not determined.

Solutions of the calcium chloride preparations I and the lithium chloride preparations I and II showed slight turbidity on addition of cupric chloride; however, the precipitate was dissolved after addition of a small quantity of hydrochloric acid. The hydrochloric acid thus added is included in the chlorine ion normality recorded in the fifth column of Table 4.

Three of the hydrochloric acid solutions measured are stronger than the usual commercial product and were prepared from a saturated solution of hydrogen chloride. Two of the magnesium chloride solutions and three of the calcium chloride solutions are supersaturated with regard to the respective salts.

## b. The Influence of the Salt Concentration on the Light Absorption.

The experimental material is given in Fig. 4.  $\log \epsilon_{436}$  is plotted as ordinates and the chlorine ion normality of the chloride used, *viz.* hydrochloric acid, lithium-, magnesium-, and calcium chloride as abscissae. The normality of the salts added is denoted

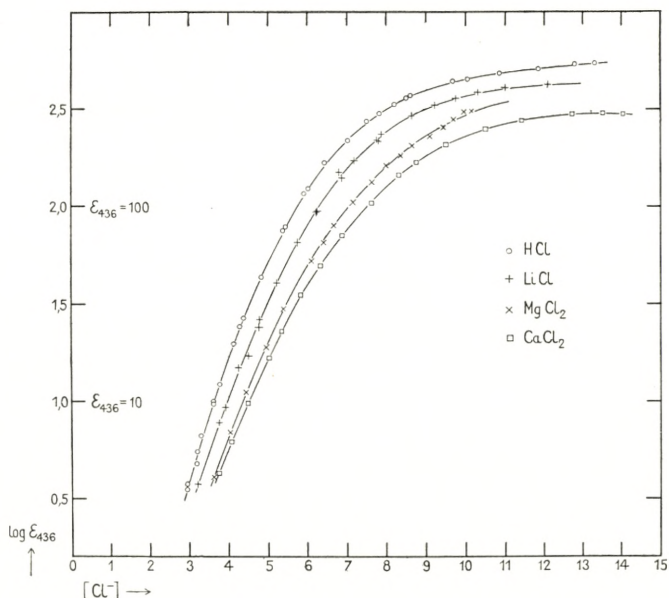


Fig. 4. Light absorption measurements of mixed cupric chloride solutions in the Hg-line 436  $m\mu$  at low copper concentration and high chloride concentrations.

as  $[Cl^-]$  because it approximates the concentration of free chloride (in the sense of chloride which is not complex-bound to copper); notably  $[Cl^-]$  does not deviate much from the total ion normality of the solution, since the copper concentration in all measured solutions is rather low. It is seen that the experimental points fall on smooth curves. The four curves are displaced rather much relative to each other. They become more flat with increasing chlorine ion concentration, and at very high chlorine ion concentrations above 10 N they are nearly horizontal. In this range it can be assumed that the tetrachloro complex is the only one existing, and therefore it is remarkable that the limiting absorption has not quite the same value in the different

chloride solutions. Of course this complicates the problem, but it is a natural consequence of the fact that the light absorption is determined in quite different salt media. HALBAN<sup>1</sup> has shown that this involves a considerable change (deformation) of the absorption spectrum as compared with the absorption in dilute solution. HALBAN and his coworkers investigated the absorption of the nitrate ion and found that generally the addition of salt causes an ultraviolet displacement of the absorption band, which depends in a specific way on the cation of the salt. HALBAN, and recently also KORTÜM,<sup>2</sup> brought the displacement of the absorption band in connection with the formation of an ion-associate between the cation and the nitrate ion in equilibrium with the original ions,<sup>3</sup> and it is natural to assume that the negatively charged tetrachloro complex forms similar ion-associates with the cations present. The extinction curves in Fig. 4 are determined at 436 m $\mu$ , only. This wave-length is found on the long-wave side of the absorption band of the chloro complex (cf. Fig. 1), and an ultraviolet displacement therefore means that the limiting absorption in the concentrated solutions is smaller than the absorption of the tetrachloro complex in dilute solution. This agrees well with the fact that the absorption in concentrated calcium chloride solutions after reaching a maximum in a *c.* 13 N solution by further increase in concentration shows a tendency to decrease. The extrapolated limiting absorption has the following values in the respective salt solutions (see p. 28):

	HCl	LiCl	MgCl <sub>2</sub>	CaCl <sub>2</sub>
log $\epsilon_{436}^0$ .....	2.742	2.65	2.66	2.50

To judge from this sequence, the deformation of the absorption curve is considerably greater in the calcium chloride- than in the alkali chloride and magnesium chloride solutions, and this is in qualitative agreement with the findings of HALBAN and KORTÜM as regards the influence of the same salts on the absorption of the nitrate ion.

According to KORTÜM,<sup>4</sup> the influence of the temperature on

<sup>1</sup> HALBAN, Z. Elektrochem. **34** (1928) 489.

<sup>2</sup> KORTÜM, Z. Elektrochem. **50** (1944) 144.

<sup>3</sup> Cf. N. BJERRUM, D. Kgl. Danske Vidensk. Selskab, Mat.-fys. Medd. **7**, No. 9 (1926).

<sup>4</sup> loc. cit., p. 149.



the absorption spectrum is also specific and inverse to the salt effect. With increasing temperature, most absorption bands are displaced towards red; the same holds here, however, it is worth noting that the temperature coefficient of the limiting absorption in calcium- and magnesium chloride solutions is higher than in lithium chloride and hydrochloric acid solutions (cf. Table 4). In all cases, the temperature coefficient increases markedly with decreasing chlorine ion concentration owing to the fact that the equilibrium between the complex ions is dependent on temperature (for further details, cf. p. 36).

In concentrated solutions of the alkali and the earth-alkali chlorides, not only the chloro complex ions, but also the chlorine ions probably form ion-associates with the metal ions, and in concentrated hydrochloric acid solutions we have a few per cent. of undissociated hydrogen chloride.<sup>1</sup>

Thus, the conditions are very complicated: if we shall altogether attempt a calculation of the concentration of the individual cupric chloride complexes as a function of the total chlorine ion concentration, this is due to the fact

(1) that the secondary salt effect on the light absorption as a whole is only small, and

(2) that by setting the concentration of the free chlorine ions equal to the total chlorine concentration of the chlorides added, an error appears which is, at least partly, neutralized by the application of the empirical activity function.

## 5. Calculation of the Experimental Material.

### a. The Activity Constant $B$ and the Formation Function $\bar{n}$ .

For the calculation of the formation function  $\bar{n}$  of the cupric chloride system we have the previously derived formula (14) (p. 17), where  $\frac{d \log \epsilon_{436}}{d [\text{Cl}^-]}$  is the slope of the extinction curves in Fig. 4, and  $B$  is the proportionality factor of the ion concentration in expression (9) for the mean activity coefficient  $F$ .  $B$  is

<sup>1</sup> Cf. ROBINSON, Trans. Faraday Soc. **32** (1936) 743.

*a priori* unknown, but fortunately it can be determined from the upper part of the extinction curves, since the limiting absorption can be roughly estimated by extrapolation of the curves of Fig. 4. According to (6), the following equation applies to the degree of formation of the tetrachloro complex

$$\alpha_4 = \frac{[\text{Cu Cl}_4^{--}]}{C_{\text{Cu}}} = \frac{\varepsilon_{436}}{\varepsilon_{436}^0}; \quad (16)$$

if  $\alpha_4 \gtrsim 0.5$ , it moreover holds that

$$1 - \alpha_4 \approx 4 - \bar{n}. \quad (17)$$

Consequently, an approximate value for B can be calculated by means of (14), and introducing this value into the same formula it becomes possible to calculate  $\bar{n}$  from the slope of the extinction curves over the whole range examined. By this method, a preliminary knowledge of the formation curve of the cupric chloride system was obtained, and it was estimated that the system had a positive ligand effect<sup>1</sup> of the order of magnitude of 0.2 to 0.3. This calculation was improved through successive approximations

(1) by finding a better value for the limiting absorption on the basis of our knowledge of B, and

(2) by substituting a better approximation for (17) on the basis of our knowledge of the ligand effect.

*ad* (1) For the fourth consecutive complexity constant the following equation applies in the range of high concentrations:

$$k_4 = \frac{\alpha_4}{(1 - \alpha_4)F \cdot [\text{Cl}^-]}. \quad (18)$$

By means of (9) and (16) this expression may be converted into

$$\varepsilon_{436}^0 - \varepsilon_{436} = \frac{1}{k_4 \cdot 10^A} \cdot \frac{\varepsilon_{436}}{[\text{Cl}^-] \cdot 10^{B[\text{Cl}^-]}}. \quad (19)$$

(19) is linear in  $\varepsilon_{436}$  and  $\frac{\varepsilon_{436}}{[\text{Cl}^-] \cdot 10^{B[\text{Cl}^-]}}$ , and the limiting absorption may therefore be determined by linear extrapolation

<sup>1</sup> See Metal Ammine Formation in Aqueous Solution, p. 39.

of a graph where  $\varepsilon_{436}$  is plotted against  $\frac{\varepsilon_{436}}{[\text{Cl}^-] \cdot 10^{B[\text{Cl}^-]}}$ . If we apply this method, the limiting absorption in the hydrochloric acid and lithium chloride solutions can be extrapolated with considerable certainty to an infinitely great chlorine ion concentration; however, it should be kept in mind that the values obtained are not corrected for the Halban salt effect. The extrapolation was more uncertain in the case of magnesium chloride solutions and was without any appreciable value in the case of calcium chloride solutions, where the salt effect is so great that the absorption passes a flat maximum already in the range studied experimentally. The values of the limiting absorption used for the final calculation are given on p. 24 and in Table 5.

*ad* (2) For a system with the characteristic coordination number 4 and a constant ligand effect  $L$  the interdependence between  $\bar{n}$  and  $\alpha_4$  is given by the formulae<sup>1</sup>

$$\alpha_4 = \frac{p^4}{1 + 4x^3p + 6x^2p^2 + 4x^3p^3 + p^4} \quad (20)$$

$$\bar{n} = \frac{4x^3p + 12x^2p^2 + 12x^3p^3 + 4p^4}{1 + 4x^3p + 6x^2p^2 + 4x^3p^3 + p^4}, \quad (21)$$

where  $x = 10^{L/2}$  is the spreading factor of the system, and  $p$  a parameter which, for  $\bar{n} = 2$ , has the value 1. The application of (20) and (21) presupposes our knowledge of the ligand effect. However, on the basis of only an approximate knowledge of this quantity the formulae offer a much better approximation than (17) which holds the worse the smaller the ligand effect. Formulae (20) and (21) are most easily applied graphically by substituting rounded-off values for  $p$  and by plotting against each other the calculated values for  $\alpha_4$  and  $\bar{n}$ . This method was used for the final calculation of the constant  $B$ ,  $L$  being tentatively put at 0.2 ( $x = 1.26$ ); and, in order to arrive at an estimation of the significance of a variation in  $L$ , the latter was also put at 0.3 ( $x = 1.41$ ).

The results of the final calculation in the four different salt media, hydrochloric acid, lithium-, magnesium-, and calcium chloride are recorded in Table 5.

<sup>1</sup> See Metal Ammine Formation in Aqueous Solution, pp. 29 ff.

Table 5. Calculation of the constant B in the expression for the mean activity coefficient of the cupric chloride system.

## a. Hydrochloric acid solutions.

$$\log \varepsilon_{436}^0 = 2.742$$

[Cl <sup>-</sup> ]	$\alpha_4 = \frac{\varepsilon_{436}}{\varepsilon_{436}^0}$	$4 - \bar{n}$		$\frac{d \log \varepsilon_{436}}{d [Cl^-]}$	$\frac{0.4343}{[Cl^-]}$	B	
		x = 1.26	x = 1.41			x = 1.26	x = 1.41
10.87	0.865	0.135	0.135	0.030	0.0400	0.182	0.182
10.05	0.810	0.202	0.20	0.042	0.0432	0.165	0.167
9.67	0.796	0.215	0.213	0.050	0.0449	0.187	0.190
8.59	0.670	0.36	0.355	0.095	0.0506	0.213	0.217
8.21	0.602	0.45	0.44	0.116	0.0529	0.205	0.211
7.82	0.538	0.535	0.52	0.138	0.0556	0.202	0.210
7.51	0.493	0.60	0.58	0.160	0.0578	0.209	0.218
						0.195	0.199

B = 0.20

## b. Lithium chloride solutions.

$$\log \varepsilon_{436}^0 = 2.65$$

9.5	0.777	0.237	0.234	0.069	0.0457	0.245	0.249
9.0	0.711	0.317	0.309	0.088	0.0482	0.229	0.237
8.5	0.631	0.411	0.401	0.112	0.0511	0.222	0.229
8.0	0.543	0.529	0.511	0.149	0.0543	0.228	0.237
7.5	0.447	0.671	0.647	0.190	0.0579	0.225	0.236
						0.230	0.238

B = 0.23

## c. Magnesium chloride solutions.

$$\log \varepsilon_{436}^0 = 2.66$$

9.5	0.575	0.487	0.473	0.110	0.0457	0.180	0.187
9.0	0.504	0.581	0.565	0.131	0.0482	0.177	0.184
8.5	0.427	0.704	0.680	0.160	0.0511	0.177	0.184
8.0	0.349	0.836	0.806	0.188	0.0543	0.171	0.179
7.5	0.275	0.98	0.945	0.222	0.0579	0.169	0.177
						0.175	0.182

B = 0.18

## d. Calcium chloride solutions.

$$\log \varepsilon_{436}^0 = 2.50$$

10.50	0.788	0.225	0.222	0.059	0.0413	0.221	0.225
9.51	0.657	0.378	0.370	0.100	0.0457	0.219	0.224
8.76	0.533	0.543	0.528	0.142	0.0496	0.212	0.219
8.32	0.458	0.652	0.631	0.168	0.0522	0.206	0.214
7.62	0.326	0.88	0.85	0.210	0.0570	0.182	0.190
						0.208	0.214

B = 0.21

It appears from the table that the computed values for B only to a slight degree depend on the value for x, which has been made the basis of the calculation, and that for one and the same salt they are almost independent of the salt concentration. The B-values found are of the same order of magnitude as in the expressions for  $\gamma_{\text{HCl}}^{(c)}$  and  $\gamma_{\text{CaCl}_2}^{(c)}$  (p. 14). B is highest (0.23) in the lithium chloride solutions and lowest (0.18) in the magnesium chloride solutions. A high B-value involves a faster convergency towards the limiting absorption, and this is seen to be in qualitative agreement with the course of the extinction curves of Fig. 4. The calculations in hydrochloric acid- and calcium chloride solutions were carried out by using the directly determined values for  $\epsilon_{436}$  and  $[\text{Cl}^-]$  given in Table 4. In the cases of lithium- and magnesium chloride solutions, however, for which the points in Fig. 4 are not quite so nicely placed, the calculations were performed with interpolated values for the extinction coefficients corresponding to rounded-off chlorine ion concentrations.  $\frac{d \log \epsilon_{436}}{d[\text{Cl}^-]}$  is always determined graphically from the slope of the levelled curves in Fig. 4.

With the values found for B substituted in (14), the formation function is estimated for rounded-off chlorine ion concentrations in the rest of the experimental range. Moreover, the degree of formation of the tetrachloro complex is computed, and in Table 6 a selection of the calculated values is given.

When applying (14) it was not taken into consideration that the absorption of the tetrachloro complex is not quite independent of the concentration. This necessarily involves an error in the calculated data. In order to correct for this omission or at least to obtain an idea of the order of magnitude of this error, B and  $\bar{n}$  in the calcium chloride medium, where the salt effect is highest (cf. p. 24), were calculated on the following basis. It is assumed that we may completely disregard the salt effect in the hydrochloric acid solutions, and that  $\epsilon_{436}$  in the calcium chloride solutions varies linearly with the concentration. This leads to the following formula:

$$\epsilon_{436}^0 = 550 - 18 [\text{Cl}^-], \quad (22)$$

Table 6. Calculation of the formation function and the degree of formation of the tetrachloro complex in the range from about 4 to 7 N.

a. Hydrochloric acid solutions.

$$B = 0.20, \quad \log \varepsilon_{436}^0 = 2.742.$$

$[\text{Cl}^-]$	$\frac{d \log \varepsilon_{436}}{d [\text{Cl}^-]}$	$\frac{0.4343}{[\text{Cl}^-]}$	$\bar{n}$	$\log \varepsilon_{436}$	$\alpha_4$	$\log [\text{Cl}^-] + B[\text{Cl}^-]$
7.0	0.202	0.0620	3.23	2.340	0.396	2.25
6.0	0.308	0.0724	2.87	2.089	0.222	1.98
5.0	0.440	0.0869	2.47	1.711	0.0931	1.70
4.25	0.540	0.1021	2.21			1.48
3.50	0.660	0.124	1.96			1.24

a. Lithium chloride solutions.

$$B = 0.23, \quad \log \varepsilon_{436}^0 = 2.65.$$

7.0	0.231	0.0620	3.21	2.192	0.348	2.46
6.0	0.322	0.0724	2.93	1.899	0.177	2.16
5.0	0.413	0.0869	2.70	1.501	0.071	1.85
4.0	0.540	0.1086	2.41	1.010	0.0229	1.52

c. Magnesium chloride solutions.

$$B = 0.18, \quad \log \varepsilon_{436}^0 = 2.66.$$

7.0	0.266	0.0620	2.90	1.985	0.211	2.11
6.0	0.350	0.0724	2.61	1.690	0.107	1.86
5.0	0.455	0.0869	2.29	1.300	0.0437	1.60
4.0	0.560	0.1086	2.06	0.806	0.0140	1.32

d. Calcium chloride solutions.

$$B = 0.21, \quad \log \varepsilon_{436}^0 = 2.50.$$

7.0	0.242	0.0620	3.11	1.878	0.239	2.32
6.0	0.324	0.0724	2.85	1.595	0.125	2.04
5.0	0.436	0.0869	2.53	1.210	0.0513	1.75
4.29	0.497	0.1012	2.40	0.890	0.0245	1.53

where 550 is the limiting absorption in hydrochloric acid solutions, and the factor 18 is chosen so that putting  $[\text{Cl}^-] = 13.5$  we arrive at the found maximum absorption in the calcium chloride solutions. Substituting (22) in (16) and differentiating with regard to the chlorine ion concentration, we get

$$\frac{d \log \alpha_4}{d [\text{Cl}^-]} = \frac{d \log \varepsilon_{436}}{d [\text{Cl}^-]} + \frac{0.4343 \cdot 18}{550 - 18 [\text{Cl}^-]}. \quad (23)$$

A combination of (23) with (13) and (14) leads to the expression

$$\frac{d \log \epsilon_{436}}{d [\text{Cl}^-]} = \left( \frac{0.4343}{[\text{Cl}^-]} + B \right) (4 - \bar{n}) - \frac{0.4343 \cdot 18}{550 - 18 [\text{Cl}^-]}. \quad (24)$$

By means of (22) and (24)  $B$ ,  $\bar{n}$ , and  $\alpha_4$  are calculated from the measurements in the calcium chloride solutions as in the previous calculations. The corrected values are recorded in Table 7. It is seen that the correction results in somewhat lower values for both  $B$  and  $\bar{n}$ .

Table 7. Recalculations in the calcium chloride medium paying due regard to the change in the limiting absorption according to the expression:

$$\epsilon_{436}^0 = 550 - 18 [\text{Cl}^-]$$

a. Calculation of  $B$  ( $x = 1.26$ )

$[\text{Cl}^-]$	$\alpha_4 = \frac{\epsilon_{436}}{\epsilon_{436}^0}$	$4 - \bar{n}$	$\frac{d \log \epsilon_{436}}{d [\text{Cl}^-]}$	$\frac{-0.4343 \cdot 18}{550 - 18 [\text{Cl}^-]}$	$\frac{0.4343}{[\text{Cl}^-]}$	$B$
9.51	0.548	0.522	0.100	0.0206	0.0457	0.185
8.76	0.430	0.697	0.142	0.0199	0.0496	0.182
8.32	0.361	0.813	0.168	0.0195	0.0522	0.179
						0.182

b. Calculation of  $\bar{n}$  and  $\alpha_4$  ( $B = 0.18$ )

$[\text{Cl}^-]$	$\frac{d \log \epsilon_{436}}{d [\text{Cl}^-]}$	$\frac{-0.4343 \cdot 18}{550 - 18 [\text{Cl}^-]}$	$\frac{0.4343}{[\text{Cl}^-]}$	$\bar{n}$	$\log \epsilon_{436}$	$\alpha_4$	$\log [\text{Cl}^-] + B [\text{Cl}^-]$
7.0	0.242	0.0185	0.0621	2.93	1.878	0.178	2.11
6.0	0.324	0.0177	0.0724	2.64	1.595	0.089	1.86
5.0	0.436	0.0170	0.0869	2.30	1.210	0.0353	1.60
4.29	0.497	0.0165	0.1012	2.17	0.890	0.0164	1.40

b. Distribution of the Copper on the Different Chloro Complexes.

Fig. 5 represents a survey of the result of the investigations performed. In the lower section the formation curve for the cupric chloride system is drawn. In the more dilute range around 1 N, where the formation function is estimated on the basis of the theory for corresponding solutions from the measurements of DOEHLEMAN and FROMHERZ and SPACU and MURGULESCU (cf. p. 10), the abscissa represents the logarithm of the free

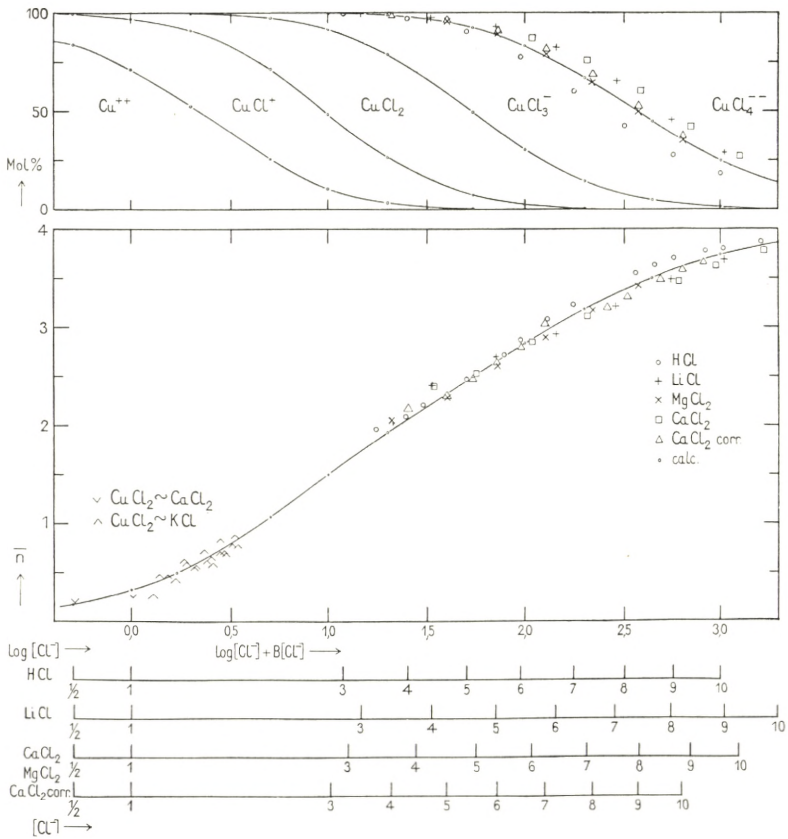


Fig. 5. Survey of the results obtained in the investigations of the cupric chloride system. The main graph shows the formation function  $\bar{n}$  as a function of  $\log [\text{Cl}^-]$  up to moderate salt concentrations, and as a function of  $\log [\text{Cl}^-] + B [\text{Cl}^-]$  at high salt concentrations. The upper part of the figure referring to the same abscissa shows the distribution of the copper on respective complexes. Finally, a number of concentration scales corresponding to each of the chlorides used are plotted below.

chlorine ion concentration. The points of this section of the curve are marked with  $\vee$  and  $\wedge$ . In the more concentrated solutions, where the  $\bar{n}$ -values are calculated according to (14) or (24),  $\log [\text{Cl}^-] + B [\text{Cl}^-]$  is plotted as abscissa, the unknown constant  $A$  in the expression for  $\log F$ , which only gives a parallel displacement of the activity scale, being put equal to 0. Putting  $A = 0$  is justified by the fact that the parts of the curve which are determined experimentally fall properly in continuation of each other. From another point of view it is most reasonable to



assume that A, corresponding to the square root term of the Debye-Hückel formula, is of the order of magnitude  $-0.5$  (cf. Fig. 3), and perhaps the whole course of the curve should be displaced correspondingly.

Below the activity scale are plotted a number of concentration scales for the chlorides used, which independent of the value chosen for A correspond directly to the values for the formation function calculated by means of (14) or (24). The  $\bar{n}$ -values of the various chloride solutions are denoted by the following signatures, *viz.* HCl  $\circ$ , LiCl  $+$ ,  $\text{MgCl}_2$   $\times$ , and  $\text{CaCl}_2$   $\square$  or  $\triangle$ , if the values are corrected for the change of absorption of the tetrachloro complex with the concentration. In the present graph it has been possible to depict the whole experimental material in one and the same curve. The points determined for hydrochloric acid fall above, and those for the other salt solutions below the curve, but the spreading is so small that it seems justified to render all the measurements by a single set of mean values for the complexity constants. On the basis of the present formation curve a set of constants has been calculated by successive approximation from a set of preliminary constants. As preliminary values for the consecutive constants the reciprocal values of  $[\text{Cl}^-]$  or  $[\text{Cl}^-] \cdot 10^{B[\text{Cl}^-]}$  at all half  $\bar{n}$ -values (see Table 8) are used. The activity correction does not give rise to any complication, since  $[\text{Cl}^-] \cdot 10^{B[\text{Cl}^-]}$  under the given assumption (8) directly replaces the ligand concentration in the previously derived formulae.<sup>1</sup>

Table 8. Calculation of a set of consecutive complexity constants corresponding to the assumption of  $A = 0$ .

$\bar{n}$	$\log [\text{Cl}^-]$ ( $F \sim 1$ )	$\frac{1}{[\text{Cl}^-]}$	$k_n = \frac{[\text{CuCl}_n^{2-n}]}{[\text{CuCl}_{n-1}^{3-n}][\text{Cl}^-]} \cdot \frac{1}{F}$
0.50	0.23	0.59	$k_1 = 0.366$
	$\log [\text{Cl}^-] + B[\text{Cl}^-]$	$\frac{1}{[\text{Cl}^-] \cdot 10^{B[\text{Cl}^-}]}$	
1.50	1.00	0.10	$k_2 = 0.114$
2.50	1.73	0.0186	$k_3 = 0.0189$
3.50	2.64	0.00229	$k_4 = 0.00315$

<sup>1</sup> Kupferammoniakverb. I, p. 18; Metal Ammine Formation in Aqueous Solution, pp. 35 ff.

From the consecutive constants the following values for the ligand effect are determined:

$$L_{1,2} = 0.08, \quad L_{2,3} = 0.43 \quad \text{and} \quad L_{1,4} = 0.35.$$

It is seen that the mean value  $L = 0.29$  is just of the order of magnitude assumed in the calculation of the constant  $B$ . By means of the estimated constants, the percentage distribution of the respective complexes is calculated with rounded-off values for  $[\text{Cl}^-] \cdot 10^{\text{B}[\text{Cl}^-]}$  (or in the more dilute range  $[\text{Cl}^-]$ ) and is represented graphically in the upper section of Fig. 5. The graph permits a direct reading of the percentages of the various complexes present in any solution. Thus, in a 4 N hydrochloric acid solution with  $\bar{n} = 2.05$  there are 2 per cent.  $\text{Cu}^{++}$ , 18 per cent.  $\text{CuCl}^+$ , 52 per cent.  $\text{CuCl}_2$ , 25 per cent.  $\text{CuCl}_3^-$ , and 2 per cent.  $\text{CuCl}_4^{--}$ .

The points drawn around the curve defining the range of existence of the tetrachloro complex are calculated directly from the optical measurements by means of (16). The same signature is used as in the lower part of the figure, and it appears that the points fall nicely around the calculated mean curve. The agreement at low chlorine ion concentrations does not appear from the figure, but Table 9 shows that it is still fairly good in 3 N chloride solutions.

Table 9.

	3 N HCl		3 N LiCl		3 N KCl
$\log \epsilon_{436}$	0.566		0.42		0.24
$\log [\text{Cl}^-] + B[\text{Cl}^-]$	1.08		1.17		
	found	calc.	found	calc.	found
Mol % $\text{CuCl}_4^{--}$ = 100 $\alpha_4$	0.67	0.40	0.59	0.65	0.32

In Table 9 are given the values for  $\alpha_4$  in 3 N hydrochloric acid and 3 N lithium chloride, both those found directly and those calculated by means of the complexity constants. For the sake of comparison, a value for  $\alpha_4$  in 3 N potassium chloride is also recorded. This value is determined on the basis of SPACU and MURGULESCU'S measurements of the extinction coefficient in solutions with  $[\text{Cl}^-] = 3$  (see Table 3), the limiting extinction

coefficient being put at 550. The corresponding value for  $\alpha_4$  in potassium chloride solutions with  $[\text{Cl}^-] = 1$  is as low as  $5.6 \cdot 10^{-5}$  (extrapolated from SPACU and MURGULESCU's measurements by means of Fig. 2), but nevertheless this value is much higher than the value  $\alpha_4 = 0.18 \cdot 10^{-5}$  calculated from the estimated formation constants, disregarding any activity correction. The discrepancy might be due to the assumption that the tetrachloro complex is not the only complex absorbing in the blue Hg-line at an  $\alpha_4$  considerably below 0.01. Ordinary cupric chloride with two molecules of crystal water is undoubtedly a dichloro compound<sup>1</sup>, and the fact that this salt is of a faint blue-green colour<sup>2</sup> indicates that the dichloro complex, and probably also the trichloro complex, have a not quite negligible absorption in blue light. The discrepancy may, however, also be due to the fact that the calculated value for  $\alpha_4$  is too low, because the activity constant A was set equal to 0. If  $A = -0.5$  (cf. p. 32) we arrive at about three times higher values for the consecutive constants  $k_3$  and  $k_4$ . It is more difficult to predict the influence on  $k_1$  and  $k_2$ , since the first part of the formation curve (Fig. 5) plotted against the chlorine ion concentration is not quite correct, either. After a displacement of the activity scale, the two sections of the curve no longer are in continuation of each other; in this connection it should, however, be taken into consideration that the  $\bar{n}$ -values which are determined from corresponding solutions containing potassium chloride and calcium chloride, are probably too low. At least, the use of hydrochloric acid or lithium chloride obviously results in higher  $\bar{n}$ -values (cf. p. 39). If all the consecutive constants of Table 8 are multiplied by  $10^{0.5}$ , the same distribution of complexes is obtained at high chlorine ion concentrations, since the displacement of the activity scale just corresponds to the change of the constants. However, this does not apply beyond the concentration range where  $\log F$  varies linearly with the chlorine ion concentration. If we put  $\log F$  in a 1 N chloride solution equal to  $-0.2$  (cf. Fig. 3), and using the constants corresponding to  $A = -0.5$ , we find  $\alpha_4$  to assume the value  $2.1 \cdot 10^{-5}$

<sup>1</sup> According to an X-ray examination by HARKER (Z. Krist. A **93** (1936) 136) the cupric chloride dihydrate is a trans-diaquo dichloro compound with four ligands in a plane square configuration round the cupric ion.

<sup>2</sup> Cf. J. BJERRUM, Kemisk Maanedstidning **26** (1945) 29.

in moderate agreement with the directly determined and probably too high value  $5.6 \cdot 10^{-5}$ .

The conclusion to be drawn from the above discussion is that the consecutive activity constants for the cupric chloride system presumably lie somewhere between the constants which correspond to the two assumptions  $A = 0$  and  $A = -0.5$ , *i. e.*

$$k_1 \lesssim 1, \quad k_2 \approx 0.1 - 0.4, \quad k_3 \approx 0.02 - 0.06, \quad k_4 \approx 0.003 - 0.01.$$

### c. The Order of Magnitude of the Temperature Effect.

On heating, blue cupric chloride solutions turn green, and the minimum solubility of cupric chloride in hydrochloric acid at  $0^\circ \text{C}$ . is found at a much higher hydrochloric acid concentration (about  $8 \text{ N}^1$ ) than corresponds to the formation curve valid at room temperature. Qualitatively, this shows that the complex formation increases with increasing temperature. More quantitative information may be obtained in connection with the temperature coefficients  $\frac{\Delta \log \varepsilon_{436}}{\Delta t^\circ}$  recorded in Table 4.

In blue light the tetrachloro complex solely determines the absorption, and the temperature coefficients corrected for the temperature dependence of the limiting absorption must, therefore, mainly be due to changes in the concentration of this complex. Consequently, we may put

$$\frac{\Delta \log \varepsilon_{436} - \Delta \log \varepsilon_{436}^\circ}{\Delta t^\circ} \approx \frac{d \log \alpha_4}{dT}. \quad (25)$$

In the range  $\bar{n} \approx 2$ , the change in concentration of the tetrachloro complex is of the same order of magnitude as that in the corresponding complexity constant

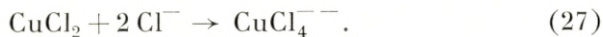
$$k_3 k_4 = \frac{[\text{CuCl}_4^{--}]}{[\text{CuCl}_2][\text{Cl}^-]^2}.$$

Thus we have

$$\left( \frac{d \log \alpha_4}{dT} \right)_{\bar{n}=2} \approx \frac{d \log k_3 k_4}{dT} = 0.4343 \frac{\Delta H}{RT^2}, \quad (26)$$

<sup>1</sup> According to ENGEL, *Ann. chim. phys.* [6] **17** (1889) 350.

where  $\Delta H$  denotes the increase in heat content for the reaction



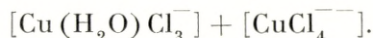
In the range in question ( $\bar{n} \cong 2$ ,  $[\text{Cl}^-] \cong 4$ )  $\frac{\Delta \log \varepsilon_{436}}{\Delta t^\circ}$  was determined in both hydrochloric acid and magnesium chloride solutions (cf. Table 4) and in both cases the corrected temperature coefficient may be put at 0.012. Applying this value,  $\Delta H$  turns out to be 4.8 kcal.

STACKELBERG and FREYHOLD<sup>1</sup> carried out some thermochemical measurements of the heat of reaction on mixing 0.2 molar cupric sulphate with 1 to 3 molar sodium chloride solutions; to judge from these measurements the increase in heat content during the reaction  $\text{Cu}^{++} + \text{Cl}^- \rightarrow \text{CuCl}^-$  is about 1.2 kcal. or considerably less than the average value per chlorine ion in reaction (27).

## 6. On the Auto Complex Formation in Concentrated Cupric Chloride Solutions.

### a. Transference Number of the Cupric Ion.

In concentrated cupric chloride solutions, the cupric ion migrates towards the anode and, according to quantitative experiments by KOHLSCHÜTTER<sup>2</sup> and DENHAM,<sup>3</sup> the cupric ion in such solutions shows even a considerably negative transference number. This is *a priori* surprising, because the formation function in pure cupric chloride solutions is necessarily below 2, from which it follows that the sum of the concentrations of the copper cations  $[\text{Cu}(\text{H}_2\text{O})_4^{++}] + [\text{Cu}(\text{H}_2\text{O})_3\text{Cl}^+]$  is higher than the corresponding sum of the copper anions:



That the transference number nevertheless is negative may

<sup>1</sup> Stackelberg and Freyhold, Z. Elektrochem. **46** (1940) 128.

<sup>2</sup> KOHLSCHÜTTER, Ber. deutsch. chem. Ges. **37** (1904) 1160.

<sup>3</sup> DENHAM, Z. physik. Chem. **65** (1909) 641; WATKINS and DENHAM, J. Chem. Soc. **115** (1919) 1269.

most naturally be explained by assuming that the cations transport more water than do the anions. The aquo cupric ion and the monochloro cupric ion contain more water of constitution than the complex anions; moreover, cations are more hydrated than anions. In the author's opinion, this may explain the negative transference number in concentrated cupric chloride solutions, where the quantity of water bound to the complexes is considerable, relative to the total amount of water.<sup>1</sup>

#### b. Estimation of the Formation Function and the Distribution of Complexes.

In order to estimate the tetrachloro complex content and the magnitude of the formation function, the light absorption of the blue Hg-line was measured for a number of cupric chloride solutions of different concentrations. The measurements were performed by means of the König-Martens spectrophotometer and are given in Table 10. The extinction of the most concentrated solutions was measured in the 2 cm tubes with inserted 1.9 cm glass cylinders, a combination which by gauging with a spherometer showed a layer thickness of 0.0950 cm.

Table 10. Molar extinction coefficients of some cupric chloride solutions.

$$\lambda = 436 \text{ m}\mu, t = 20-22^\circ.$$

$C_{\text{CuCl}_2}$ .....	1.20	1.60	1.92	2.42	2.88	3.60
$\epsilon_{436}$ .....	0.249	0.564	1.15	2.04	3.41	6.23
$\log \epsilon_{436}$ .....	-0.604	-0.249	0.061	0.310	0.533	0.795

The measurements recorded in Table 10 are represented graphically in Fig. 6 and here they are compared with SPACU and MURGULESCU'S measurements of some more dilute cupric chloride solutions. It is seen that  $\log \epsilon_{436}$  increases continuously with the cupric chloride concentration, more slowly, however, with increasing concentration.

Applying (6) or (16), the degree of formation of the tetrachloro complex may be calculated on the basis of the material

<sup>1</sup> Cf. SILLÉN and ANDERSSON, *Svensk kemisk Tidskrift* **55** (1943) 13.

given in Table 10, and by means of this quantity we may also calculate the formation function, as the relation between  $\bar{n}$  and  $a_4$  is exclusively determined by the ligand effect or, in other words, by the relative magnitude of the consecutive constants. Consequently, it is all the same whether the calculation is carried through with the set of constants corresponding to  $A = 0$  or to  $A = -0.5$ . Table 11 shows the result of such a calculation for three cupric chloride solutions.

In the calculation the limiting extinction coefficient is put at 550. For purposes of comparison, the table moreover contains the values for the formation function determined by comparing the pure cupric chloride solutions with corresponding mixed

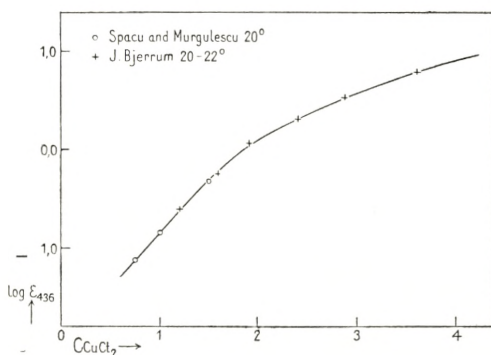


Fig. 6. Some light absorption measurements of pure cupric chloride solutions in the blue Hg-line.

Table 11. Values for the formation function in some cupric chloride solutions estimated in different ways.

$C_{\text{CuCl}_2}$	$\log \epsilon_{436}$	$a_4$	$\bar{n}$ (calc.	$\bar{n}$ (HCl)		$\bar{n}$ (LiCl)		$\bar{n}$ (CaCl <sub>2</sub> )	
			from $a_4$ )	sp.	col.	sp.	col.	sp.	col.
1.62	-0.21	0.00112	1.29	—	0.67	—	0.58	—	0.44
2.98	0.566	0.0067	1.75	0.99	—	0.92	—	0.78	—
4.06	0.92	0.0151	1.98	1.13	1.21	1.05	1.04	0.93	0.92

solutions containing hydrochloric acid, lithium- or calcium chloride. The  $\bar{n}$ -values recorded are calculated either by means of the extinction curves of Fig. 4 (the columns sp.) or on the basis of a colorimetric titration (the columns col.). The latter values originate from the author's previous paper<sup>1</sup>). The spectroscopic-

<sup>1</sup> D. Kgl. Danske Vidensk. Selskab, Mat.-fys. Medd. **21**, No. 4 (1944) 10.

ally and the colorimetrically determined values are in pretty good agreement, but otherwise the  $\bar{n}$ -values are greatly dependent on the method and the chloride used for their determination. In this connection, the values of the formation function rendered in Tables 2 and 3 should be kept in mind; these values are presumably somewhat less dependent on the chloride used, because of the lower copper concentration and because (Table 3) both corresponding solutions are mixtures.

The  $\bar{n}$ -values calculated from the light absorption by means of (16) and from our knowledge of the ligand effect undoubtedly are too high (cf. the value in the 4.06 molar cupric chloride solution according to which all the chlorine is complex-bound). This must directly or indirectly be due to the high copper concentration, as the light absorption, at least in the two strongest cupric chloride solutions, is so great that we may reckon with the validity of (16) (see Table 9). It appears from the absorption spectra that the formation of polynuclear complexes plays a minor part and, hence, it is most probable that the main discrepancy between the  $\bar{n}$ -values calculated in different ways must be ascribed to the fact that in concentrated cupric chloride solutions we have a distribution of complexes which corresponds to a smaller ligand effect (greater dismutation of the intermediary complexes) than in corresponding mixtures with a low copper concentration. This explanation involves not only that the values for the formation function calculated by means of (16) and the estimated sets of constants are too high, but moreover that the values determined by means of corresponding solutions are too low.

Table 11 shows the distribution of complexes calculated for the three cupric chloride solutions; tentatively, not only  $L_{1,2}$ , but the whole ligand effect is put at 0.08 (cf. p. 33). This value, which is considerably lower than the mean value found for the mixed solutions ( $L = 0.29$ ), seems to account satisfactorily for the distribution of the complexes in the concentrated cupric chloride solutions. The calculated values for  $\alpha_4$  agree fairly well with those found experimentally and, moreover, the  $\bar{n}$ -values and the concentrations of free chlorine ion calculated from the total chlorine ion concentrations are of a reasonable order of magnitude.  $\alpha_4$  increases with a very high power of the chlorine



ion concentration (higher than  $4 - \bar{n}$ ), but this, too, is characteristic of the mixtures in the range where F begins to increase with the concentration (see p. 11 and Fig. 4).

### c. Estimation of the True Mean Activity Coefficient of the Cupric Chloride.

The curves of Fig. 3 representing the apparent activity coefficient of cupric chloride are calculated thermodynamically without taking the complex formation into consideration. For the calculation of the true mean activity coefficient of the cupric chloride  $f_{\text{CuCl}_2}^{(e)}$  we have the relation

$$\left(f_{\text{CuCl}_2}^{(e)}\right)^3 \cdot \alpha_0 \cdot C_{\text{CuCl}_2} \cdot [\text{Cl}^-]^2 = \left(\gamma_{\text{CuCl}_2}^{(e)}\right)^3 \cdot 4 C_{\text{CuCl}_2}^3, \quad (28)$$

in which  $\alpha_0 \cdot C_{\text{CuCl}_2}$  denotes the concentration of the aquo cupric ion. The values of  $\log \gamma_{\text{CuCl}_2}^{(e)}$  which may be read from Fig. 3 and the values of  $f_{\text{CuCl}_2}^{(e)}$  computed on this basis by means of (28) for the 1.62 and 2.98 molar cupric chloride solution are recorded in Table 12.

Table 12. The distribution of the complexes and the apparent and true mean activity coefficients of cupric chloride in some concentrated cupric chloride solutions.

$C_{\text{CuCl}_2}$	$\bar{n}$	$[\text{Cl}^-]$	$\alpha_0$	$\alpha_1$	$\alpha_2$	$\alpha_3$	$\alpha_4$	$\log \gamma_{\text{CuCl}_2}^{(e)}$	$\log f_{\text{CuCl}_2}^{(e)}$
1.62	0.83	1.90	0.39	0.44	0.16	0.01	$0.97 \cdot 10^{-4}$	-0.304	-0.02
2.98	1.20	2.38	0.20	0.45	0.32	0.04	$7.2 \cdot 10^{-4}$	-0.186	+0.31
4.06	1.35	2.64	0.13	0.41	0.40	0.06	$1.74 \cdot 10^{-3}$	-	-

The estimated values for  $\log f_{\text{CuCl}_2}^{(e)}$ , when compared with Fig. 3, show that the true activity coefficient is little lower than the apparent activity coefficient of the calcium chloride at the same total concentration. This is a reasonable result and agrees with our presumption that cupric chloride is a greatly hydrated salt.

## 7. Summary.

In the present paper the complex formation in solutions of cupric chloride in the absence and in the presence of other chlorides has been investigated on the basis of light absorption measurements. The main results of the work may be summarized as follows.

A. In cupric chloride solutions there are mainly mononuclear complexes, only, and the system has a formation curve of normal appearance in accordance with the characteristic coordination number four.

B. The complexity is only slight, but nevertheless it is possible, especially in more concentrated solutions, semiquantitatively to express the contents of the different complexes as a function of the chloride concentration. Exact values for the complexity constants cannot be given, but no doubt the following set of consecutive constants corresponds fairly well to the prevailing conditions  $k_1 \lesssim 1$ ,  $k_2 \approx 0.1 - 0.4$ ,  $k_3 \approx 0.02 - 0.06$ ,  $k_4 \approx 0.003 - 0.01$ .

The more special results of the investigations may be summarized as follows.

1. In blue light, the tetrachloro complex is the only cupric complex showing any measurable light absorption and, if the concentration of free chlorine ion  $[\text{Cl}^-]$  is sufficiently high ( $> 1 \text{ N}$ ), the concentration of the tetra complex can be calculated by means of the expression

$$[\text{CuCl}_4^{--}] = C_{\text{Cu}} \frac{\varepsilon_{436}}{\varepsilon_{436}^{\circ}},$$

where  $C_{\text{Cu}}$  denotes the total copper concentration,  $\varepsilon_{436}$  the extinction coefficient in the blue mercury line, and  $\varepsilon_{436}^{\circ}$  the limiting extinction coefficient at high chlorine ion concentrations.

2. The limiting absorption, *i. e.* the light absorption of the tetrachloro complex, depends to some degree on the salt concentration and on the chloride used, and  $\varepsilon_{436}^{\circ}$  assumes the following values in the respective chloride solutions:

	HCl	LiCl	MgCl <sub>2</sub>	CaCl <sub>2</sub>
$\log \varepsilon_{436}^{\circ}$	2.742	2.65	2.66	2.50

3. The formation curve of the system was calculated (1) by means of the author's optical principle, which is based upon the

supposition that solutions with the same extinction coefficient have also the same distribution of complexes, irrespective of the total concentration of metal ion and of ligand in the solutions and, (2) on the basis of the extended Bodländer formula, applying our knowledge of the change in the concentration of the tetrachloro complex.

4. For the calculation of the formation function  $\bar{n}$  in mixtures poor in copper, but with very high chloride concentrations, the following formula was used:

$$\frac{d \log \varepsilon_{436}}{d [\text{Cl}^-]} = \left( \frac{0.4343}{[\text{Cl}^-]} + B \right) (4 - \bar{n}).$$

This formula has been derived under the tacit assumption that the system in the range of concentrations  $3.5 < C_{\text{ion}} < 10-12 \text{ N}$  is ruled by only one mean activity coefficient  $F$ , which varies with the total ion normality in accordance with the expression

$$\log F = A + B \cdot C_{\text{ion}},$$

where  $A$  and  $B$  are individual constants for the different salt media.

5. In the cupric chloride system, the constant  $B$  in the expression for  $F$  was found to assume on an average the following values in the respective chloride media:

	HCl	LiCl	MgCl <sub>2</sub>	CaCl <sub>2</sub>
B	0.20	0.23	0.18	0.21 corr. 0.18

6. In pure concentrated cupric chloride solutions the dismutation of the dichloro cupric complex to the neighbouring complexes and, further, to the aquo cupric- and the tetrachloro complex to some degree depends on the copper concentration, the dismutation of the intermediary complexes being considerably higher than in mixed solutions poor in copper.

The author is greatly obliged to the Carlsberg Foundation for a grant which enabled Mr. PALLE ANDERSEN to carry out some of the light absorption measurements recorded in this paper.

