Investigation of Possible Interactions between Thallium(I) and Thallium(III) in Solution and in the Crystalline Thallium Sesqui-halides

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I. INVESTIGATION OF POSSIBLE INTERACTIONS BETWEEN THALLIUM (I) AND THALLIUM (III) IN SOLUTION AND IN THE CRYSTALLINE THALLIUM SESQUI-HALIDES.

II. SPECTROPHOTOMETRIC INVESTIGATION OF THE COPPER (II) CHLORO-COMPLEXES IN AQUEOUS SOLUTIONS OF UNIT IONIC STRENGTH.

III. OPTICAL INTERACTION BETWEEN THE CHLORO-COMPLEXES OF COPPER (I) AND COPPER (II) IN SOLUTIONS OF UNIT IONIC STRENGTH. INTERPRETATIONS OF THE SPECTRAL ABSORPTION OF A COPPER(I)-COPPER (II) CHLORO-COMPLEX.

IV. SPECTROPHOTOMETRIC INVESTIGATION OF THE INTERACTION BETWEEN IRON (II) AND IRON (III) IN HYDROCHLORIC ACID SOLUTIONS.

Thesis by

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Contact with men such as Professors Linus Pauling, John Kirkwood and Don Yost in courses and seminars cannot be said to be without beneficial effect on any research carried out at the California Institute of Technology.

Abstract

A radiochemical and spectrophotometric investigation of the interactions between thallium (I) and thallium (III) is used to show that the majority of the thallium (I) and thallium (III) atoms in the crystalline thallium sesquihalides do not occupy equivalent positions in the crystalline lattice and that there is no strong optical interaction between thallium (I) and thallium (III) in aqueous solutions containing perchlorate or chloride ion.

The absorption spectra of mixed solutions of copper (II) perchlorate, perchloric acid and hydrochloric acid at a constant ionic strength of 1.00 in the wavelength range 250-300 mμ are interpreted in terms of the equilibria, $Cu^{++} + Cl^- = CuCl^+$, $CuCl^+ + Cl^- = CuCl_2$. The equilibrium constants for these reactions are determined and the enthalpy of formation of $CuCl^+$ is estimated.

The non-additive light absorption in the 400-600 mμ wavelength range of solutions maintained at unit ionic strength with perchloric acid and containing copper (I) and copper (II), and low concentrations of chloride ion, has been interpreted in terms of an "interaction complex", Cu_2Cl_3. At higher chloride ion concentrations in solutions of the same ionic strength, interaction complexes of higher chloride coordination (but still containing only one copper (I) and one copper (II) in each complex) are important.

Abstract (cont.)

Two interpretations of the 400-600 mμ spectral absorption of Cu_2Cl_3 are advanced and discussed. At present no conclusions can be drawn as to which interpretation is to be preferred.

The light absorption in the 450-900 mμ wavelength range by mixed solutions of iron (II) and iron (III) in hydrochloric acid is interpreted as evidence for the formation of unstable but strongly absorbing interaction complexes, each interaction complex containing one atom of iron (II) and one atom of iron (III) and a number of coordinating chloride ligands. The light absorption by interaction complexes decreases with decreasing hydrochloric acid concentration and there is no interaction absorption by solutions containing $Fe(H_2O)_6^{++}$,$Fe(H_2O)_6^{+++}$ and no chloride ion.

Absorption spectra of iron (II) in solutions of varying hydrochloric acid concentration observed in the 700-900 mμ wavelength range are used to show the presence of iron (II) chloro-complexes.

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PART II

PART I

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Investigation of Possible Interactions between Thallium(I) and Thallium(III) in Solution and in the Crystalline Thallium Sesqui-halides

By Harden McConnell and Norman Davidson

The discovery[1] that the rate of radioactive exchange between Tl(I) and Tl(III) in aqueous solutions is slow has prompted us to: (1) examine, by a radiochemical method, whether or not the substances Tl_2Cl_3 and Tl_2Br_3 contain non-equivalent Tl(I) and Tl(III) ions; (2) look for non-additive light absorption[2] in some aqueous solutions containing Tl(I) and Tl(III). Problems (1) and (2) are related because the Tl_2X_3 compounds are more colored than the corresponding TlX or TlX_3 compounds.[3]

(1) For the exchange experiment with Tl_2Cl_3, 4 ml. of dilute HCl solution containing 5.2 mg. of dissolved Tl_2Cl_3 and 1.46 mg. of active $TlCl_3$ (containing Tl^{204}) were evaporated nearly but not quite to dryness by evacuation at room temperature for forty-five minutes. It follows from the data of Benrath that under these conditions essentially all of the Tl(I) was initially precipitated as Tl_2Cl_3, and there might be small amounts of $TlCl_2$ or hydrated $TlCl_3$ formed subsequently, depending on the completeness of evaporation.[3] (Furthermore by visual inspection of the precipitate one saw only the characteristic hexagonal yellow flakes of Tl_2Cl_3.)[4] This entire residue, the yellow solid Tl_2Cl_3 and the adhering excess of $TlCl_2$ or $TlCl_3$ (solid or solution), was redissolved in water and divided into two 2-ml. samples. Thallous chromate was precipitated from one portion, using the conditions developed by Harbottle and Dodson,[1] washed, and slurried onto a counting plate. The second sample was reduced with sulfur dioxide so that all the thallium could be precipitated as the chromate and the total activity counted. There was no appreciable self absorption in the samples.

A blank experiment was performed which was identical to the above except that the evaporation to give solid Tl_2Cl_3 was omitted, and the sample was allowed to stand for twenty minutes.

For the Tl_2Br_3 experiment, 30 ml. of a solution containing 1.2 g. of $TlBr_3$ was saturated with inactive TlBr at room temperature to insure the absence of bromine. The solution was then saturated with active TlBr at 50°. Two 10-ml. aliquots of this solution were allowed to cool to room temperature, and the red Tl_2Br_3 precipitated out.[5] The thallous activity was determined with one sample and the total activity with the other. For control measurements, the thallous and total activities of 1-ml. aliquots of the solution at 50° were determined.

(1) Harbottle and Dodson, This Journal, 70, 880 (1948); Prestwood and Wahl, *ibid.*, 71, 3137 (1949); see also pp. 226, 205 of "Isotopic Exchange Reactions and Chemical Kinetics," Brookhaven National Laboratory, Patchogue, New York, Dec., 1948.

(2) Whitney and Davidson, This Journal, 69, 2076 (1947).

(3) Benrath, *Z. anorg. Chem.*, 93, 161 (1915); 136, 358 (1924)

(4) Another sample of Tl_2Cl_3 was further identified by a thallium analysis; for a description of the crystalline form, *cf.* Meyer, *Z. anorg. Chem.*, 24, 354 (1900).

(5) The identification of this substance as Tl_2Br_3 is based on its color and crystalline form corresponding to the descriptions given by Benrath[3] and Meyer[4] and on the solubility data determined by Benrath

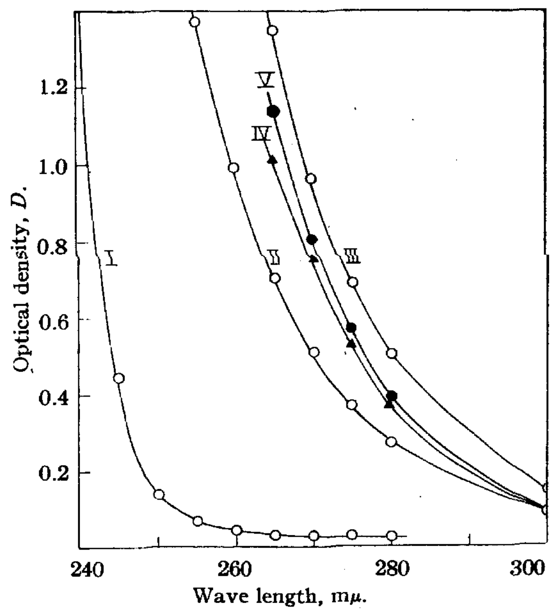

Fig. 1.—The absorption spectra of some thallium(I) and (III) solutions in perchloric acid: I, Tl(I) 0.068 *F;* II, Tl(I) 0.034 *F*, Tl(III) 0.079 *F;* III, Tl(III) 0.157 *F*, I, II, III in 3.2 *F* $HClO_4$; IV, Tl(III) 0.079 *F;* V, Tl(I) 0.113 *F*, Tl(III) 0.079 *F;* IV, V in 1.6 *F* $HClO_4$.

Table I

Exchange Experiments with Thallium Sesqui-halides

Experiment	Composition of exchange mixture, mg. Tl(I)	Tl(III)	Specific activities,[a] c./min. mg. Tl(I)	Tl(III)	Ratio of specific activities of Tl(III) and Tl(I)
Solid Tl_2Cl_3	3.12	2.00[b]	31.5	321	10 (±1)
Tl_2Cl_3 control	3.12	2.00[b]	18.6	241	13 (±1)
Solid Tl_2Br_3	32.4[c]	10.8[c]	102	27.8	0.27 ± (0.05)
Tl_2Br_3 control	8.1	18.4	87.7	20.2	0.23 ± (.05)

[a] For the Tl_2Cl_3 experiment, the specific activities were calculated on the basis of the amounts of Tl(I) and Tl(III) added; for the Tl_2Br_3 experiment, see footnote (c). [b] Including 0.96 mg. of active Tl(III). [c] These numbers, estimated from the solubility data of Benrath, are included to indicate the probable size of the Tl_2Br_3 precipitate; only the ratio of activities is important for the interpretation of the experiment.

The experimental results (Table I) are that within the uncertainties of the experiments there is no exchange in the solid state. These uncertainties are due to experimental errors and due to the possibilities of differences between the control experiments and the experiments in which solid Tl_2X_3 compounds were separated as to: (a) degree of homogeneous exchange in solution, (b) degree of induced exchange on precipitation of thallous chromate. For the Tl_2Cl_3 experiment, the calculated ratio of specific activities of Tl(III) and Tl(I) for complete equivalence in the solid is 2.1 accepting the validity of the control experiment (and assuming no exchange between the solid Tl_2Cl_3 and the excess adhering Tl(III)). For the Tl_2Br_3 experiment this ratio is 1.0. Because of the evidence that Tl_2Cl_3 has 64 thallium atoms per unit cell,[6] it is worthwhile to emphasize that our data are not sufficiently accurate to exclude the possibility that a small fraction of the Tl(I) and Tl(III) atoms occupy equivalent positions in the Tl_2X_3 lattice.

(2) Figure 1 exhibits the absorption spectra of some thallium (I) perchlorate, thallium (III) perchlorate, and mixed solutions in 3.2 and 1.6 *F* perchloric acid. Thallium (III) is more colored than Tl(I) and there is no appreciable non-additive absorption in the mixed solutions. The extinction coefficients of Tl(III) calculated from these data (Table II) show that Tl(III) is more colored at lower acidities, suggesting an increased hydrolysis of Tl^{+++} to $Tl(OH)^{+}$ or $Tl(OH)_2^{++}$. Harbottle and Dodson[1] and Prestwood and Wahl[1] have previously suggested such a hydrolysis to explain the variation of the rate of exchange between Tl(I) and Tl(III) with acidity.

TABLE II

EXTINCTION COEFFICIENTS OF Tl(III) AS A FUNCTION OF ACIDITY

λ (mμ)	290	280	270	265
ϵ (Tl(III))(1.6 *F* $HClO_4$)	2.25	4.6	9.5	13.3
ϵ (Tl(III))(3.2 *F* $HClO_4$)	1.8	3.25	6.1	8.5

(6) Jerslev and Hägg, *Experientia*, **2**, 495 (1946).

Most of the known cases of interaction absorption in solution are in media containing excess chloride ions. The insolubility of thallous chloride in water and dilute solutions of thallic chloride, and the presence of free chlorine in concentrated thallic chloride solutions (3.5 *F*) in which thallous chloride has an appreciable solubility[3] prevented an exact spectrophotometric study of solutions having significant concentrations of thallous and thallic chlorides. We can report however that as successive portions of solid thallous chloride were added to a 3.4 *F* thallic chloride solution containing some (*ca.* 0.03 *F*) free chlorine, the optical density of the resulting solutions decreased (as the chlorine was removed) and became constant at the values: λ = 380 mμ, D = 0.065; μ = 360 mμ, D = 0.66, for a solution that contained 0.04 *F* excess Tl(I). Since the optical densities of the solutions never increased as the TlCl was added, there was probably no significant interaction absorption in the solution.

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PART II

Spectrophotometric Investigation of the Copper (II) Chloro-complexes in Aqueous Solutions of Unit Ionic Strength

Introduction

The marked influence of chloride ion on the formal extinction coefficient, $\overline{\epsilon}$, of copper (II) in aqueous solutions, as illustrated in Fig. 1 for the 230-400 mμ wavelength range, is generally attributed to strongly absorbing chloro-complexes of copper (II). One may therefore consider the equilibria represented in equations (1).

$$\left.\begin{aligned} CuCl_{n-1}^{3-n} + Cl^- &= CuCl_n^{2-n} \\ [CuCl_n^{2-n}]/[CuCl_{n-1}^{3-n}][Cl^-] &= K_n \end{aligned}\right\} n = 1,2,3,4 \qquad (1)$$

The quantities in brackets in the equations are taken to be concentrations in units of moles/liter, so that the mass action constants, K_n, are functions of the activity coefficients of the various ions. Of the previous investigations of these equilibria[1,2,3,4,5], the most satisfactory is that by J. Bjerrum[5]. By using spectrophotometric measurements and rough activity approximations, Bjerrum found that only the copper (II) chloro-complexes for $1 \leqslant n \leqslant 4$ in (1) are of importance in aqueous solutions of cupric chloride and that the approximate values of the stability constants, K_n^o, at infinite dilution and at 22.5°C

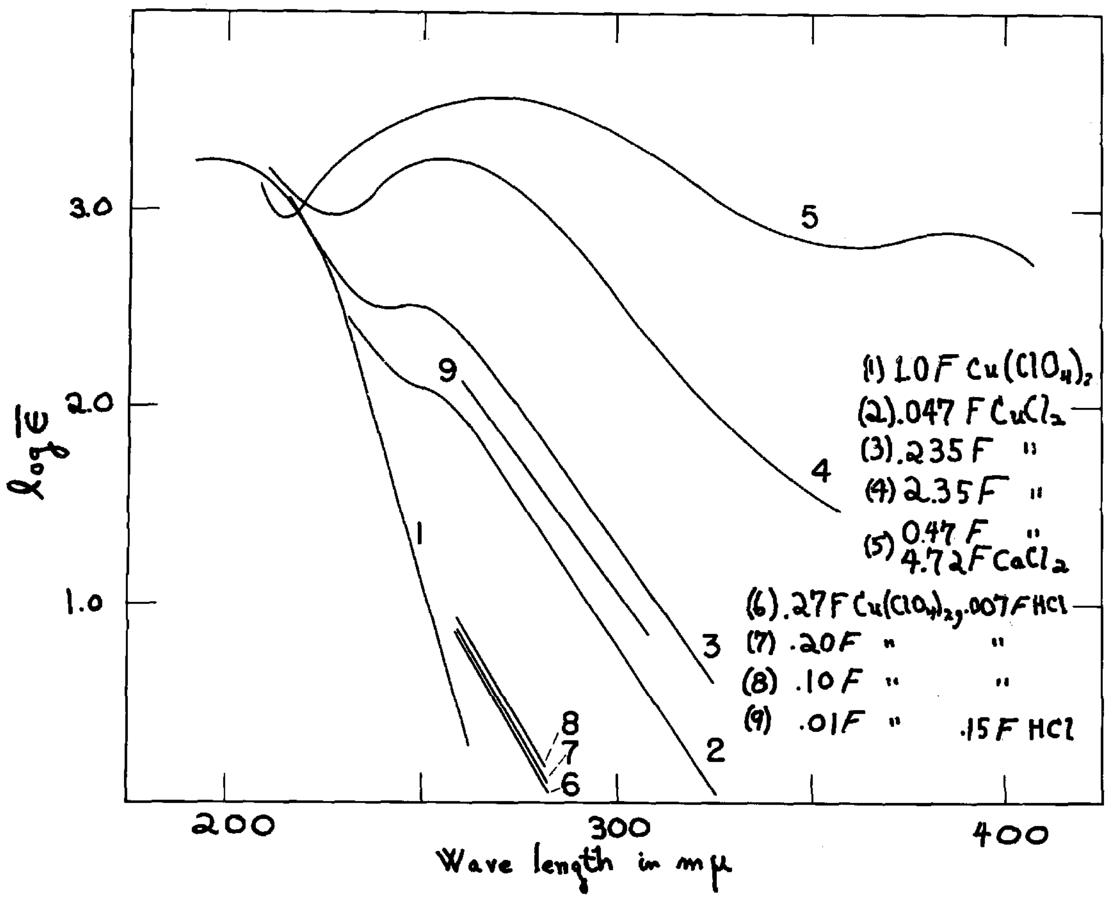

Fig. 1. Effect of chloride ion on the formal extinction coefficient, $\overline{\epsilon}$, of copper (II).

(Curves 1 - 5, Fromherz, ref. 2: curves 6 - 9, this research, μ = 1.00) are $K_1^o \leqslant 1$, $K_2^o = 0.1\text{-}0.4$, $K_3^o = 0.02\text{-}0.06$, $K_4^o = 0.003\text{-}0.01$ liter/mole.

More accurate information about the equilibria of equation (1) was desired for studies of the non-additive light absorption in solutions containing the chloro-complexes of copper (I) and copper (II). This dissertation describes a spectrophotometric study of the equilibria of equations (1) in solutions containing copper (II) perchlorate, hydrochloric acid, and perchloric acid and at an ionic strength of unity. The ionic strength was fixed at this value in order to minimize the variation of the activity coefficients of the particular ions as the composition of the solution was varied. The interpretation of the results is based on the assumption that these variations are indeed negligible, so that one can deduce mass action equilibrium constants valid at the ionic strength of the measurements. (Actually the assumption is that the variations of the activity coefficient functions which relate the mass action equilibrium constants to the thermodynamic constants are negligibly small.) It may be said at this point that this assumption has been found to be in accord with the results of the present investigation. Such a simplifying assumption is not applicable for most of the previous investigations of the equilibria (1) which have been carried out at high and varying ionic strengths. On the other hand, because of the ready dissociation of the copper (II) chloro-complexes, they cannot readily be studied in much more dilute solutions. Indeed, in the solutions studied in this investigation, only $CuCl^+$ and $CuCl_2$ have been present in detectable concentrations.

Preparation and Analysis of Materials

A stock solution of cupric perchlorate was prepared by adding an excess of basic cupric carbonate, $CuCO_3 \cdot Cu(OH)_2$, to a solution of perchloric acid, removing the excess solid by centrifugation and then adding a slight excess, 0.005 F, of perchloric acid. That there is no detectable hydrolysis of Cu^{++} to $Cu(OH)^+$ in the solutions used is shown by the fact that the extinction coefficients of Cu^{++} ion in perchloric acid observed in the present research agree with the literature values for neutral cupric perchlorate solutions[1].

The copper (II) concentration in the stock solution was determined using three independent analytical procedures: (a) iodometry with a standard thiosulfate solution, (b) the silver reductor method of Birnbaum and Edmonds[6], and (c) spectrophotometric determination using the extinction coefficients of copper (II) in cupric perchlorate given in the literature and assuming Beer's law to hold for these solutions. The agreement between the results of (a), (b) and (c) was excellent.

Hydrochloric and perchloric acid concentrations were determined acidimetrically.

Apparatus

Measurements of optical density were made with a Model DU Beckmann Spectrophotometer, using a hydrogen lamp and rectangular right prism quartz cells of 1.00 cm. path length. The cells were maintained at constant temperature, $25.2 \pm 0.05^\circ$ C or $46.9 \pm 0.1^\circ$ C, by means of a specially constructed cell compartment having a jacket through which thermostatted water was circulated. The cell compartment was provided with quartz windows. The design and construction of this cell compartment is largely due to Messrs. W. Schuelke and S. Hart of the machine shop.

As solutions placed in the cell compartment required more than one hour to come to thermal equilibrium at the higher temperature, glass stoppered quartz cells were used to minimize evaporation.

General Equation

The general equation which gives the total optical density, D ($=\log_{10} I_0/I$), of a solution containing the copper (II) chloro-complexes of equations (1) (page 3) will be derived here. The "working equations" used in the next two sections are most easily obtained by neglecting the proper terms in the general expression for D derived below. The optical absorption by chloride ion will not be included as this is completely negligible at the wavelengths employed in this investigation.

We let

K_n = equilibrium constants defined in equations (1),

ϵ_n = extinction coefficient of the n^{th} chloro-complex,

a = formal concentration of copper (II) perchlorate,

b = formal concentration of hydrochloric acid,

C_n = concentration of the n^{th} chloro-complex in moles/liter,

$[Cl^-]$ = concentration of free chloride ion in moles/liter.

The quantities C_o, K_o and ϵ_o refer to Cu^{++} and K_o is taken to be unity. The total optical density of a solution containing copper (II) and chloride ion is then

$$D = \sum_{n=0}^{4} \epsilon_n C_n \qquad (2)$$

From equations (1) C_n may be written

$$C_n = C_o \prod_{i=0}^{n} K_i [Cl^-]^n \qquad (3)$$

The equation representing the conservation of copper (II) is

$$a = C_o\sum_{n=0}^{4}[Cl^-]^n\prod_{i=0}^{n}K_i \quad . \tag{4}$$

By combining equations (2), (3) and (4) one obtains the desired equation,

$$D = a\,\frac{\sum_{n=0}^{4}[Cl^-]^n\epsilon_n\prod_{i=0}^{n}K_i}{\sum_{n=0}^{4}[Cl^-]^n\prod_{i=0}^{n}K_i} \, . \tag{5}$$

This equation is useful for the determination of the ϵ_n and K_n when it is possible to estimate the free chloride ion concentration in aqueous solutions containing copper (II). In the absence of a convenient direct experimental method for the determination of the free chloride ion concentration it is necessary to consider, in addition to equation (5), the equation representing the conservation of chloride ion,

$$[Cl^-] = b - a\,\frac{\sum_{n=0}^{4}n[Cl^-]^n\prod_{i=0}^{n}K_i}{\sum_{n=0}^{4}[Cl^-]^n\prod_{i=0}^{n}K_i} \, . \tag{6}$$

Fortunately in both this and Bjerrum's investigation it has been possible to employ solutions containing concentrations of copper (II) and chloride ion such that the second term on the right hand side in equation (6) may be neglected in a first approximation.

If the K_n were independent of the composition of solutions containing cupric perchlorate, hydrochloric and perchloric acids, then equations (5) and (6) would permit an interpretation of the observed dependence of the optical density, D, on the formal concentrations of copper (II) and chloride and wavelength in terms of the ϵ_n and K_n. Actually solutions containing appreciable concentrations of $CuCl_3^-$ and $CuCl_4^=$ require large concentrations of free chloride ion (4-10 F) and for such solutions the K_n are expected to depend upon the composition of the solutions. Bjerrum's determination of the K_n requires unverified assumptions concerning the variation of the K_n over large concentration ranges and in this respect his results may not be completely satisfactory.

It may be mentioned that if the concentration of free chloride ion approaches infinity, equation (5) simplifies to

$$D = a\epsilon_4 .$$

Bjerrum has attempted to realize this condition by extrapolating the optical densities of concentrated hydrochloric acid solutions containing small concentrations of copper (II) to infinite chloride ion concentration. If the absence of higher chloro-complexes is assumed, then this extrapolation gives the extinction coefficients of $CuCl_4^=$ regardless of considerations of activity coefficients. The extinction coefficients, ϵ_4, obtained in this extrapolation are close to those given in Fig. 4. Since in general the extinction coefficients of a particular ionic species do not depend strongly on the ionic strength of a solution, it is possible to compare the ϵ_4 obtained by Bjerrum with the ϵ_1 and ϵ_2 obtained in this investigation.

Determination of the Absorption Spectrum, Equilibrium Constant, and Enthalpy of Formation of $CuCl^+$ in Aqueous Solutions of Unit Ionic Strength

In order to isolate the light absorption of the first chloro-complex, $CuCl^+$, the optical densities of solutions containing very small chloride ion concentrations and much larger copper (II) concentrations were determined. Representative values of the extinction coefficients of copper (II) in such solutions are displayed in Fig. 1 (curves 6, 7 and 8); these show that $CuCl^+$ is much more colored than Cu^{++} in the 260-280 mμ wavelength range. (This is not the case at longer wavelengths, 550-1,000 mμ, where the formal extinction coefficients of copper (II) are far less sensitive to the concentration of chloride ion.)

The simple equation,

$$\frac{a\ b}{D-D'} = \frac{a}{\epsilon_1-\epsilon_0} + \frac{1}{K_1(\epsilon_1-\epsilon_0)}, \qquad (7)$$

where $D' = a\epsilon_0$, was used to interpret the experimental data so as to obtain K_1 and ϵ_1 for $CuCl^+$. This equation may be derived from equation (5) and may be used to determine K_1 and ϵ_1 subject to the following conditions.

(a) The concentrations C_n for $n \geq 2$ are negligible compared to C_o and C_1.

(b) The optical densities $\epsilon_n C_n$ are small compared to $\epsilon_1 C_1$.

(c) The concentration C_1 is small compared to C_o.

(d) The value of K_1 is independent of the composition of solutions containing Copper (II) perchlorate, hydrochloric acid and perchloric acid when these solutions are maintained at a constant ionic strength of unity.

(e) Both terms on the right hand side of equation (7) are comparable in magnitude.

(f) The optical densities of the solutions are measurable with the apparatus available.

(g) Complexes of copper (II) other than those given in equations (1) do not exist in detectable concentration in the solutions described in (d).

The experimental data is used to show that all of these conditions do hold for the concentration range, a = 0.007, b = 0.1-0.3, and for the wavelength range 260-280 mμ, to within the experimental error.

The experimental values of ab/(D-D') are plotted against a in Fig. 2 for three wavelengths and two temperatures. The plots are straight lines within the experimental errors, as predicted by equation (7). According to this equation the ratio of the "y" intercept to the slope gives K_1 and the reciprocal of the slope gives $\epsilon_1 - \epsilon_0$. (For the wavelengths used, 260 - 280 mμ, ϵ_0 is negligibly small in comparison to ϵ_1.) The results of a least squares treatment of these data, giving the most probable values of K_1 together with the probable errors, are given in Table I.

The linear character of the plots in Fig. 2 and the concordant values of K_1 obtained at different wavelengths establish the validity of the assumptions made in deriving equation (7).

Back calculations using the values of K_1 and ϵ_1 and the values of K_2 and ϵ_2 determined subsequently, show that the numerical approximations used in formulating equation (7) introduce no appreciable error in the evaluation of K_1 and ϵ_1.

The approximate value 600 $\pm$ 350 cal. for the enthalpy of formation of $CuCl^+$ from Cu^{++} and Cl^-, ΔH at unit ionic strength, is obtained from the data of Table I giving K_1 at two temperatures by neglecting any variation of ΔH with temperature. The corresponding entropy change is ΔS = 2.5 $\pm$ 1.2 cal./deg. The value of ΔH is in agreement with Bjerrum's "order of magnitude" estimate of this quantity, 1.2 k.cal./mole.

The positive value of ΔH is not unreasonable in view of the probable loss of hydration energy corresponding to the formation of $CuCl^+$ from cupric and chloride ions. The increase in entropy may also be accounted for in large part by the different hydration entropies of these three ions. From the relative magnitudes of ΔH and $T\Delta S$ (750 cal.) it is clear that the entropy term $T\Delta S$ contributes strongly towards the stability of $CuCl^+$ in aqueous solutions.

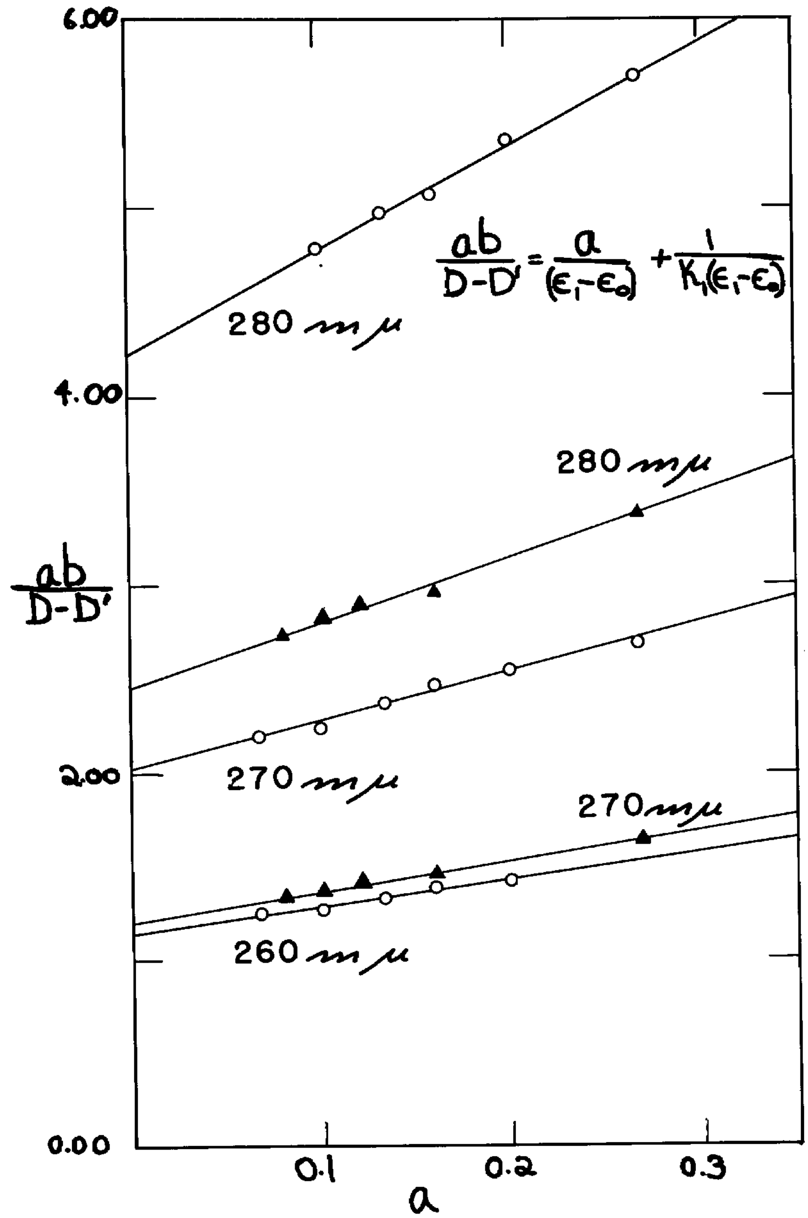

Fig. 2. Determination of K_1 at two temperatures, O, 25.2° C; ▲, 46.9° C.

Table I

Determination of the Equilibrium Constants K_1 and K_2

Temperature °C	Wavelength mμ		Most Probable K_1 liter/mole
25.2	260		1.29 ± 0.10
"	270		1.30 ± 0.06
"	280		1.30 ± 0.04
		K_1 =	1.30 ± 0.03
46.9	270		1.39 ± 0.05
"	280		1.39_5 ± 0.11
		K_1 =	1.39 ± 0.05
			Best value K_2 liter/mole
25.2	280		0.11 ± 0.02
"	290		0.29 ± 0.04
"	300		0.18 ± 0.11
		K_2 =	0.23 ± 0.15

Determination of the Absorption Spectrum and Equilibrium Constant of $CuCl_2$ in Aqueous Solutions of Unit Ionic Strength

The extinction coefficients, ϵ_2, and equilibrium constant, K_2, of $CuCl_2$ were determined by measuring the optical densities of solutions in which the ratio of the chloride to copper formal concentrations (b/a) was increased over that used in the above experiments until solutions were obtained in which the copper (II) was largely present as Cu^{++} and $CuCl^{+}$ along with smaller concentrations of $CuCl_2$. The equation used to determine K_2 and ϵ_2 from the optical densities of such solutions is

$$\frac{a}{D_c} = \frac{F}{\epsilon_2 K_1 K_2} + \frac{1}{\epsilon_2}, \tag{8}$$

where $$F = \frac{\epsilon_1 K_1}{[Cl^-]^2}\left[\frac{1}{\epsilon_1 K_1} + \frac{[Cl^-]}{\epsilon_1} - \frac{a[Cl^-]}{D_c}\right]$$

and $$D_c = \epsilon_1 C_1 + \epsilon_2 C_2 .$$

This equation may be derived from equation (5) and may be used to determine K_2 and ϵ_2 subject to the following conditions.

(a) The concentrations C_n for $n \geq 3$ are negligible compared to C_o, C_1 and C_2. (This condition is expected to hold when C_2 is small compared to C_o and C_1.)

(b) The optical densities $\epsilon_n C_n$ are negligible for $n \geq 3$.

(c) The values of K_1 and K_2 are independent of the composition of solutions containing copper (II) perchlorate, hydrochloric and perchloric acids when these solutions are maintained at a constant ionic strength of unity.

(d) Both terms on the right hand side of equation (8) are comparable in magnitude.

(e), (f) Conditions (f) and (g) of the preceding section must of course hold here also.

Again the experimental results will be used to establish the validity of the assumptions made in deriving the working equation for the wavelength and concentration ranges employed. In this case, a = 0.002-0.10, b = 0.1-0.8, λ = 250 - 300 mμ.

Satisfactory first approximations to $[Cl^-]$ and D_c in equation (8) are $[Cl^-] = b$ and $D_c = D - D'$*. A numerical

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*The definition of D' given in the preceeding section would be adequate here if the solutions employed were free of minute concentrations of impurities and cupric perchlorate solutions obeyed Beer's law over wide concentration ranges. In this section we shall let $D' = \epsilon_0 [Cu^{++}]$ + (optical density of "impurities"). The second term in this equation can be important only when ϵ_0 is small and is completely negligible in the experiments described in the preceding section. The uncertainties in D' described later in this section may be attributed to impurities, deviations of cupric perchlorate solutions from Beer's law, or both. In any case these uncertainties are so small that they cannot account for the spread in the experimental values obtained for K_2, showing that impurities or deviations from Beer's law cannot be the principal source of error. The problem discussed here is commonly encountered in spectrophotometric work when one attempts to distinguish between the very weak absorption of an ionic species (here Cu^{++}) and that of possible impurities contained in the solvent.

and graphical analysis of the data using equation (8) and these first approximations yielded values of ϵ_2K_2 and ϵ_2 at six wavelengths in the 250-300 mμ range and values of ϵ_1K_1 at wavelengths 250,290 and 300 mμ. (Calculations at 260, 270 and 280 mμ were considerably simplified by using values of $\epsilon_1 K_1$ found in the determination of K_1.) The fact that practically all of the data fitted the form of equation (8) indicates that, within the experimental errors, the assumptions used in formulating equation (8) are justified. In particular, the linear character of the plots of a/D_c vs. F as shown in Fig. (3), shows that there is no detectable contribution of $CuCl_3^-$ to the color of these solutions.

For a second approximation to the solution of equation (8) the deviation between b and $[Cl^-]$ has been calculated using the first approximation to K_2. The chloride correction is small, ~1%, and only slightly different values of K_2 are obtained in the second approximation.

The evaluation of K_2 appears to suffer from two serious sources of error. At the shorter wavelengths of the 250-300 mμ range, the scatter of the experimental points in the plot of a/D_c vs. F results in considerable uncertainty in the value of the small intercept, $1/\epsilon_2$, and thus in the value of K_2 given by $(1/K_1)$ times the ratio of the intercept to the slope. Values of K_2 ranging from 0.15 to 0.54 liter/mole were obtained at the wavelengths 250, 260 and 270 mμ. At the longer wavelengths, 280, 290 and 300 mμ, the principal known source of error is the uncertainty as to the exact dependence of D' on the concentration of Cu^{++}. As the uncertainties due to experimental scatter are smaller at these longer wavelengths and as the extreme limits of K_2 due to the uncertainty as to D' may be accurately determined (D' may be taken proportional to the Cu^{++} concentration, or it may be taken as constant, this uncertainty usually amounting to $\pm$ .005 in D_c), it is thought that the experimental values of K_2 determined at these three wavelengths are most reliable. In Table I, the margin of error given for K_2 at each wavelength was calculated solely from the uncertainty in D'. It is evident from Table I that there are systematic sources of error in K_2 which are greater than those due to the uncertainty in D' alone. The sources of these errors are unknown. By weighting the determinations at the longer wavelengths most heavily, one obtains for K_2 the value 0.23 liter per mole with a safe margin of error, $\pm$ 0.15.

It may be noted that the slopes of the lines of Fig. 3 give values of $1/(K_1K_2\epsilon_2)$ which are much more accurate than the separate values of K_2 and ϵ_2. The absorption spectrum of $CuCl_2$, given in Fig. 4 together with those of $CuCl^+$ and Cu^{++}, has been calculated from the values of ϵ_2K_2 assuming the value of K_2 to be 0.23 liter/mole. The apparent extinction coefficients of Cu (II) in 4.7 F $CaCl_2$

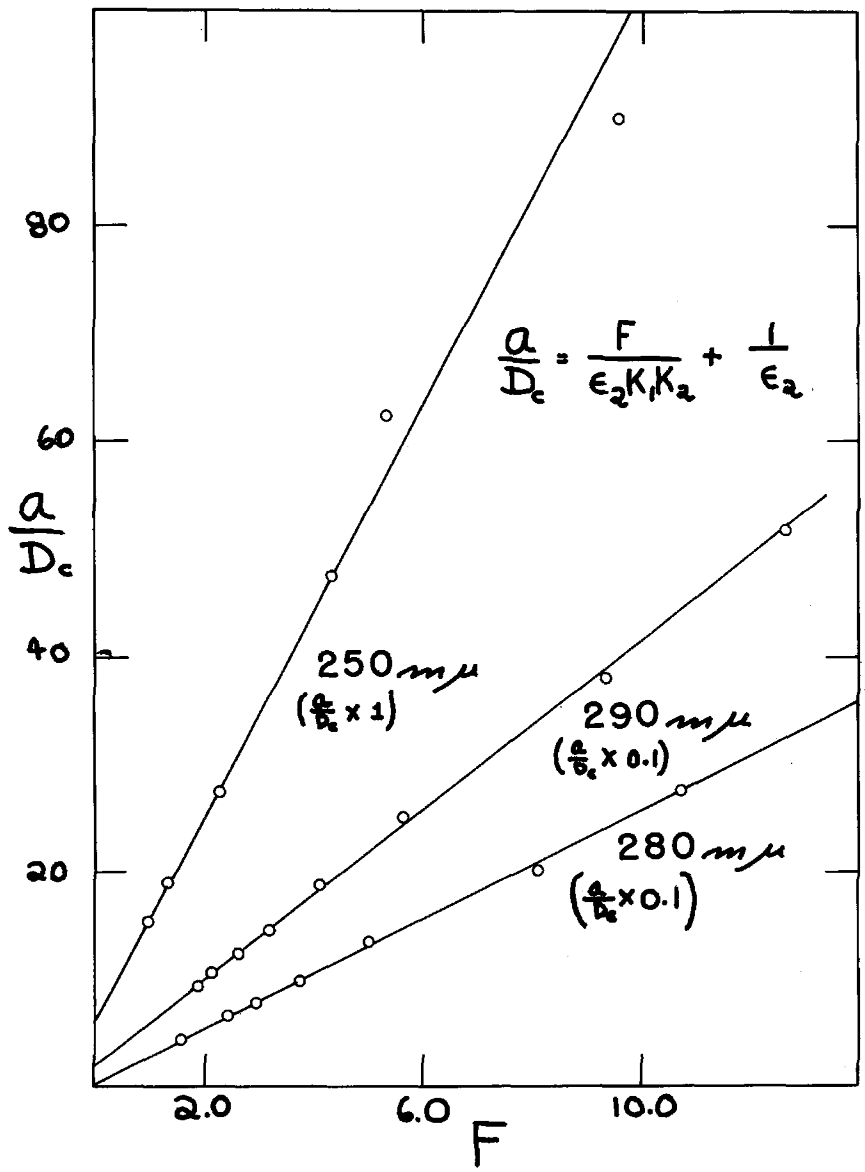

Fig. 3. Determination of K_2

are also included for comparison[1]. This curve is usually assumed to be due principally to $CuCl_4^{=}$. The apparent shift of the "electron transfer" spectrum of Cu(II) to longer wavelengths with increasing chloride coordination is similar to that which has been observed for several other systems of cation-anion complexes[7].

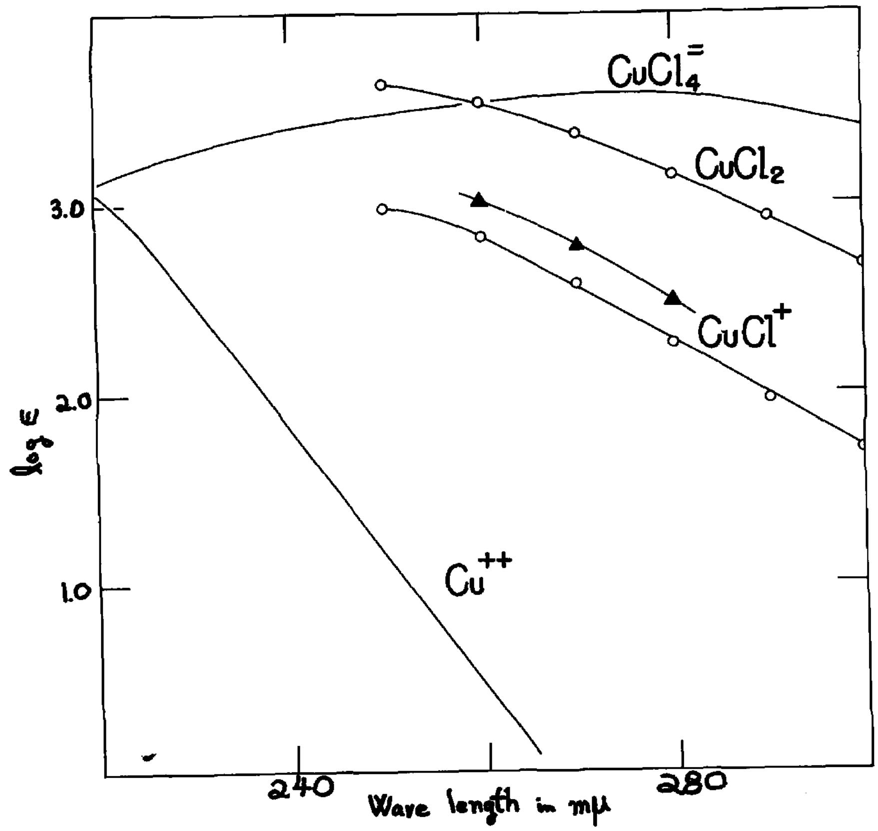

Fig. 4. Absorption spectra of Cu^{++}, $CuCl^+$, $CuCl_2$ and the supposed absorption spectrum of $CuCl_4^=$. O, 25.2°; ▲, 46.9°. ($CuCl_4^=$ curve, curve 5 of Fig. 1.)

REFERENCES

Part II

(1) E. Doehlemann and H. Fromherz, Z. physik. Chem., A 171, 353 (1934)

(2) G. Spacu and J. Murgulescu, ibid., A 170, 71 (1934)

(3) T. Moeller, J. Phys. Chem. 48, 111 (1944)

(4) V. Kohlschutter, Ber., 37, 1160 (1904)

(5) J. Bjerrum, D. Kgl. Danske. Vidensk. Selskab., Mat. -fys. Medd., 22, No. 18 (1946)

(6) N. Birnbaum and S. Edmonds, Ind. Eng. Chem., Anal. Ed., 12, 155 (1940)

(7) E. Rabinowitch, Rev. Mod. Phy., 14, 112 (1942)

PART III - A

Part III - A

Optical Interaction between the Chloro-complexes of Copper (I) and Copper (II) in Aqueous Solutions of Unit Ionic Strength

Introduction

Several investigators have remarked upon the fact that hydrochloric acid solutions containing copper in two states of oxidation, copper (I) and (II), exhibit an optical absorption in the 400-600 mμ wavelength range which is markedly greater than that which might be predicted from Beer's Law and the absorptions of the individual components[(1),(2)(3)]. Similar phenomena have been observed in 6-12 F hydrochloric acid solutions containing the mixed oxidation states of other elements[(3),(4)]: tin (II) and (IV), antimony (III) and (V) and iron (II) and (III). For each of these three systems, it has been found that the optical interaction absorption, defined as the difference between the optical density ($D = \log_{10} I_0/I$) of the solution containing the mixed oxidation states of the element and the optical density predicted from Beer's Law and the absorption of the components, is proportional to the product of the formal concentrations of the two oxidation states of the element. Apparently chloride coordination, or perhaps in general halogen coordination, of either or both of the oxidation states of the element is essential, as no interaction is observed in aqueous solutions free of halogen ion and the interaction absorption has always been observed to increase with increasing chloride ion concentration.

If one takes the point of view that the optical interaction in these solutions is due to one or more "interaction complexes" (either ions or uncharged species), then the above mentioned facts indicate that such interaction complexes will contain two atoms of the interacting element, one in each oxidation state, together with a number of coordinating chloride ions.

The chemical formulae of the interaction complexes of a particular element might be established by a determination of the dependence of the optical interaction on the activities of the several complex species of the two oxidation states of this element. At present, the lack of completely quantitative information on the constitutions, concentrations and activity coefficients of each of the chloro-complexes of the two oxidation states of tin, antimony, iron and copper in 6-12 F hydrochloric acid solutions, where the interaction is usually observed, prevents a quantitative study of the interaction complexes in any of these solutions.

However, the optical interaction absorption of the copper (I,II)-hydrochloric acid system is sufficiently intense that, by employing a 10.0 cm. light path, it is possible to measure the interaction absorption in relatively

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*Experiments by Mr. J. Ibers of this Institute show that there is no optical interaction between the amine complexes of copper (I) and copper (II), or between $Fe(CN)_6^{-4}$ and $Fe(CN)_6^{-3}$.

dilute solutions (μ = 1.0) in which the formulae and concentrations of the predominate chloro-complexes of copper (I) and (II) are known and where it is reasonable to assume a negligible variation of the activity coefficients of particular ions as the composition of the solution is varied at a constant ionic strength.

The purpose of this dissertation is to: (a) give the quantitative data used in the determination of the concentrations of the predominant chloro-complexes of copper (I) and copper (II), (b) give the results of a determination of the dependence of the optical interaction absorption on the concentrations of the complex ions of (a), (c) present the conclusions that have been drawn from (b). It is to be emphasized that all of the solutions used for the studies (a) and (b) were maintained at a fixed total ionic strength of 1.0 with perchloric acid and that the conclusions of (c) are based on the assumption that the activity coefficients of individual ions are constant in such solutions.

Copper (I) Chloro-complexes

The studies of Noyes and Chow[5] and Chang and Cha[6], as well as others[7],[8] indicate that only two copper (I) chloro-complexes, $CuCl_2^-$ and $CuCl_3^{=}$ are present in 0.2-0.8 F hydrochloric acid solutions saturated with cuprous chloride.

If k_1 and k_2 are the mass action equilibrium constants for the reactions,

$$\begin{aligned} CuCl(s) + Cl^- &= CuCl_2^- , \\ CuCl(s) + 2Cl^- &= CuCl_3^=, \end{aligned} \qquad (1)$$

then the formal solubility, S, of copper (I) chloride in solutions containing a free chloride concentration, $[Cl^-]$, is given by the equation,

$$S = k_1 [Cl^-] + k_2 [Cl^-]^2. \qquad (2)$$

The determinations of the solubility of cuprous chloride in solutions containing varying amounts of chloride ion, copper (II) and copper (I) chloro-complexes, hydrogen ion, and perchlorate ion and adjusted to an ionic strength of 1.0, are represented by the above equation with $k_1 = 0.075$ and $k_2 = 0.034$ liter/mole. This is illustrated in Fig. 5 where $0.075[Cl^-] + 0.034[Cl^-]^2$ is plotted, together with the observed values of S, against the calculated concentration of free chloride ion. Consequently, for solutions saturated with cuprous chloride, we take $0.075\,[Cl^-]$ as the concentration of $CuCl_2^-$ and $0.034\,[Cl^-]^2$ as the concentration of $CuCl_3^=$. The values of k_1 and k_2 determined at 25.1° are in fair agreement with Noyes' value of $k_1 = 0.066$ and Chang's value of $k_2 = 0.034$, determined at 25.0° from the solubility of cuprous chloride in pure hydrochloric acid. The applicability of the last two constants to our solutions of ionic strength 1.0 is not certain however.

It is to be emphasized that for the solutions employed in this investigation the solubility of CuCl depends only on the concentration of free chloride ion and not on the formal cupric ion concentration, to within the experimental error. This fact indicates that the total concentration of complexes copper (I) and copper (II) is small compared to the concentration of complexes containing copper (I) alone. On the basis of the data presented in Fig. 5 the upper limit to the total concentration of complexes containing copper (I) and copper (II) is estimated to be 5×10^{-3}F.

Copper (II) Chloro-complexes

The concentrations of the predominate copper (II) chloro-complexes and the concentration of free chloride ion present in solutions of 0.080 - 0.300 F copper (II) and 0.80 - 0.20 M free chloride ion and maintained at unit ionic strength were calculated from the mass action stability constants for the equilibria,*

$$Cu^{++} + Cl^{-} = CuCl^{+},$$
$$\frac{[CuCl^{+}]}{[Cu^{++}][Cl^{-}]} = K_1 = 1.30 \pm .03 \text{ liter/mole.} \tag{3}$$
$$CuCl^{+} + Cl^{-} = CuCl_2,$$
$$\frac{[CuCl_2]}{[CuCl^{+}][Cl^{-}]} = K_2 = 0.23 \pm .15 \text{ liter/mole.} \tag{4}$$

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* See Part II of this Thesis.

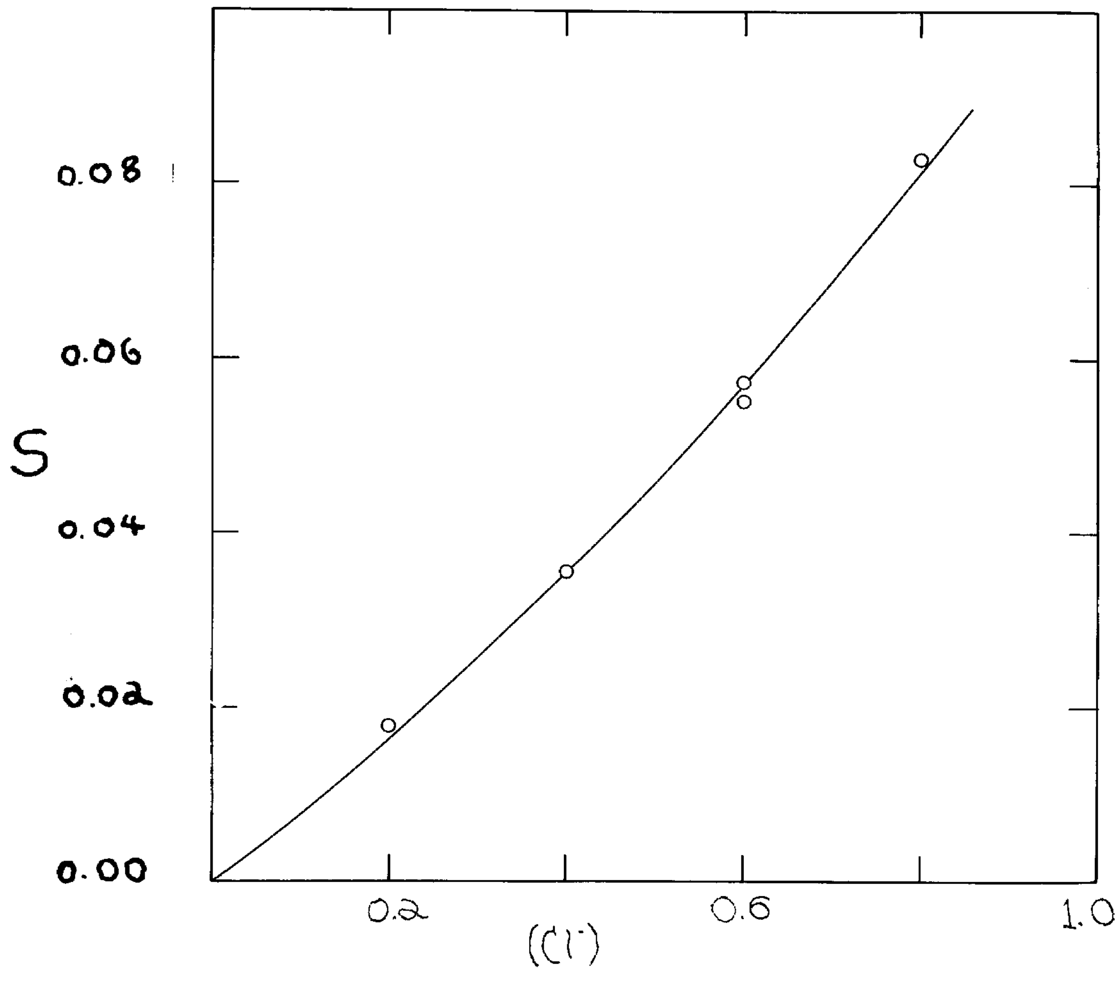

Fig. 5. o, Experimentally measured solubilities of CuCl in chloride containing solutions of unit ionic strength. Curve is drawn from equation (1), $S = .075 [Cl^-] + .034[Cl^-]^2$. Units are moles/liter.

Fig. 6 shows the calculated distribution of copper (II) among the species Cu^{++}, $CuCl^{+}$ and $CuCl_2$ as a function of the free chloride ion concentration, using the above values of K_1 and K_2.

Determination of the Optical Interaction Between Copper (I) and Copper (II) Chloro-complexes

The plots of Fig. 7 are typical examples of the data obtained for the determination of the dependence of the optical interaction on the concentration of the chloro-complexes of copper (I) and copper (II). The optical densities* of the solutions containing copper (II) and chloride ion but no copper (I), given in the "b" plots of Fig. 7, are due to the absorption by Cu^{++}, $CuCl^{+}$ and $CuCl_2$. The "a" plots of Fig. 7 give the optical densities of solutions which contain the same calculated concentrations of Cu^{++}, $CuCl^{+}$ and $CuCl_2$, as do the corresponding "b" plots, but which in addition are saturated with copper (I) chloride. The corresponding "a" and "b" plots which contain the same formal concentration of copper (II) and the same calculated concentration of free chloride ion, have been designated with the same Roman Numeral in Fig. 7. Since the two predominant copper (I) chloro-complexes in these solutions, $CuCl^{-}_2$ and $CuCl_3^{=}$, are colorless in this wavelength range, the optical interaction absorption ΔD, is obtained directly by subtraction of the ordinates of the corresponding "a" and "b" curves.

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* All optical densities have been reduced to a light path of 1.00 cm.

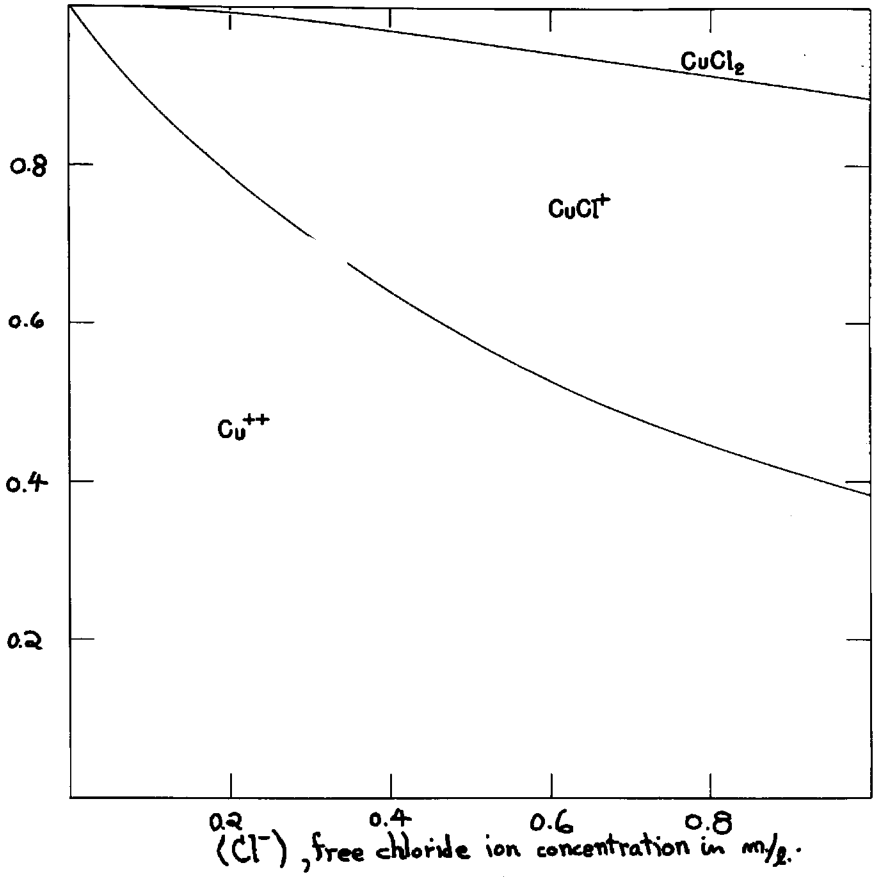

Fig. 6. Fractional distribution of Cu(II) among Cu^{++}, $CuCl^+$, and $CuCl_2$ in chloride containing solutions at unit ionic strength.

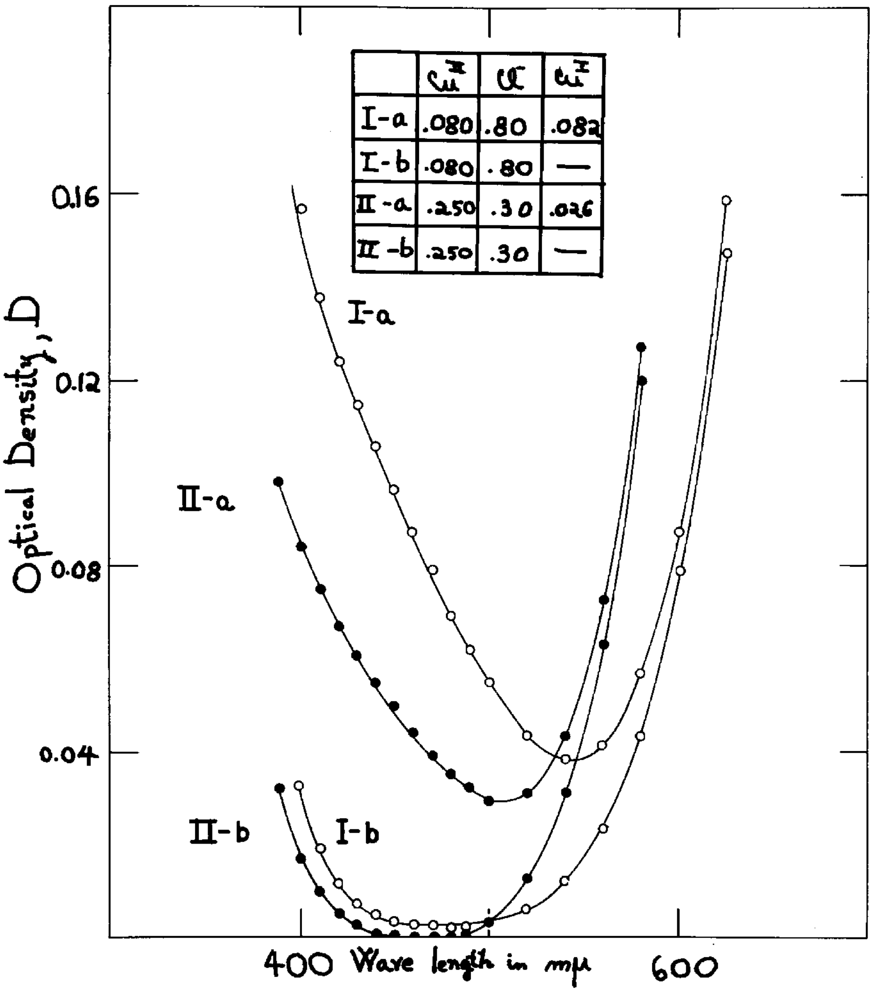

Fig. 7. Typical data used for the determination of optical interaction absorption. I-a [Cu(II)] = 0.080 F, [Cl^-] = 0.80 M, [Cu(I)] = 0.082 F; I-b, [Cu(II)] = 0.080 F, [Cl^-] = 0.80 M; II-a, [Cu(II)] = 0.250 F, [Cl^-] = 0.30 M, [Cu(I)] = 0.026 F; II-b, [Cu(II)] = 0.250 F, [Cl^-] = 0.30 M.

Several dilution experiments at 0.60 M free chloride ion concentration have shown that the optical interaction absorption, ΔD, is within the experimental error, proportional to the product of the formal concentrations of copper (I) and copper (II). As stated previously, this shows that the interaction absorption is due to one or more chloro-complexes, each containing one atom of copper (I) and one atom of copper (II). For solutions which are saturated with copper (I) chloride, the interaction complexes can be considered as being formed according to the equations,

$$CuCl(s) + Cu^{++} + nCl^{-} = Cu_2Cl_{1+n}^{2-n}, \qquad (3)$$

with mass action equilibrium constants, L_n.

$$L_n = \frac{[Cu_2Cl_{1+n}^{2-n}]}{[Cu^{++}][Cl^{-}]^n}. \qquad (4)$$

One may assume here that the L_n's are sufficiently small so that the total formal concentration of the interaction complexes is small compared to the formal concentration of copper (I) and copper (II). (This assumption is in accordance with the results of investigations of interaction absorption in systems containing other elements[3],[4]). Then the concentration of free cupric ion, $[Cu^{++}]$, appearing in (4) is related to the total formal concentration of copper (II), $[Cu(II)]$, by the equation,

$$[Cu(II)] = [Cu^{++}]\left(1 + K_1[Cl^-] + K_1K_2[Cl^-]^2\right).$$

The free chloride ion concentration, $[Cl^-]$, can be calculated from the total formal concentration of chloride and amount of chloride bound in copper (I) and copper (II) complexes. Then if E_n is the extinction coefficient of $Cu_2Cl_{1+n}^{2-n}$, $\Delta D = \sum_n E_n \left[Cu_2Cl_{1+n}^{2-n}\right]$. A suitable function for graphical analysis is Q, given by the equation,

$$Q = \frac{\Delta D\left(1 + K_1[Cl^-] + K_1K_2[Cl^-]^2\right)}{[Cu(II)]} \qquad (5)$$
$$= \sum_{n=0} L_n E_n [Cl^-]^n$$

The results of the present investigation are that for solutions containing 0.2, 0.3 and 0.4 M calculated free chloride ion concentration and 0.30, 0.25 and 0.20 F copper (II) the function Q is proportional, within the experimental error of 4-6%, to the square of the chloride ion concentration; that is the third term in the summation of equation (5) is most important in these solutions. This dependence on the chloride ion concentration is found to hold for all wave lengths in the range 425-600 mμ. Representative data at two wavelengths are given in Fig. 8. For these solutions, the uncertainties in Q and in the calculated free chloride ion concentrations due to the uncertainty in K_2, are less than the 4-6% experimental error.

This quadratic dependence on the chloride ion concentration implies the existence of a strongly colored uncharged interaction complex, Cu_2Cl_3, and practically no contribution to the interaction absorption by the complexes Cu_2Cl^{++} and $Cu_2Cl_2^{+}$.

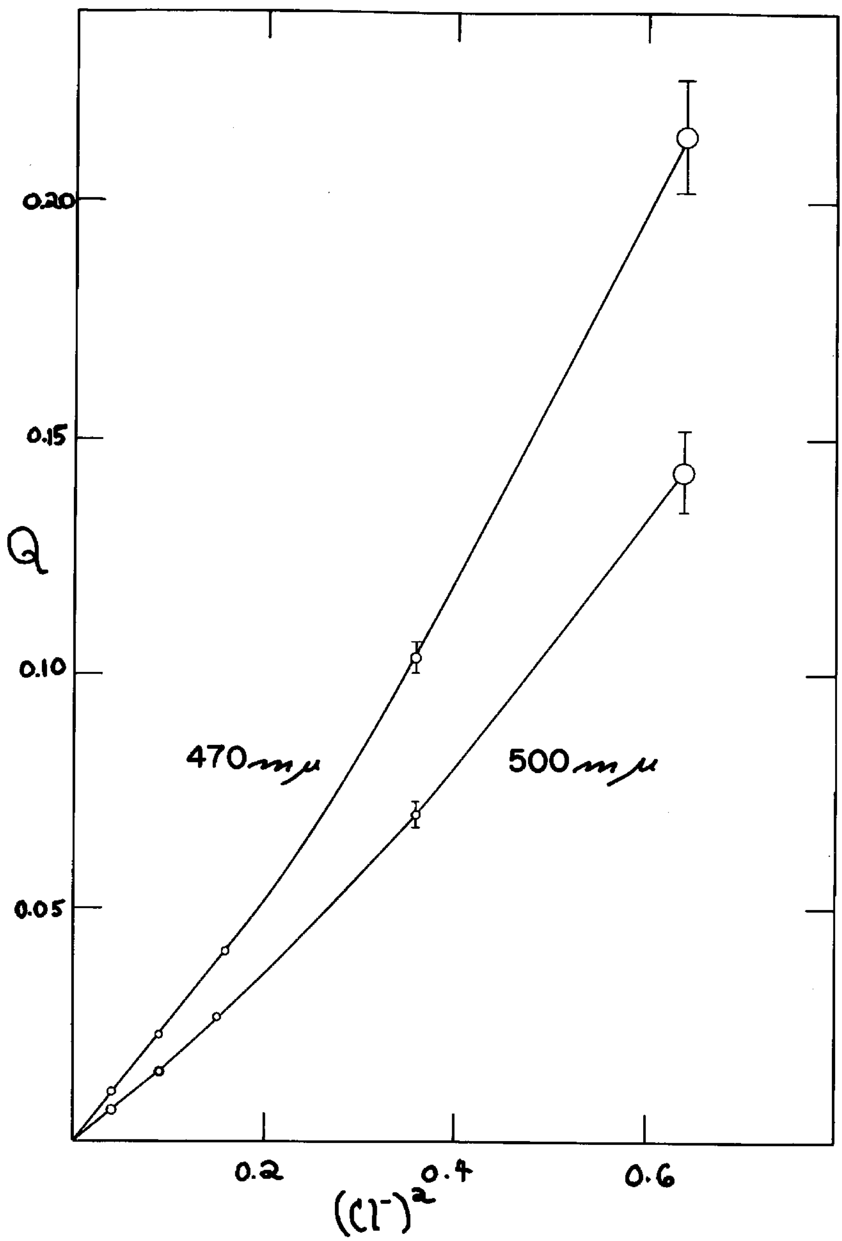

Fig. 8. Typical plots used for the determination of the relative magnitudes of the first terms in the power series of equation (3) for solutions of low free chloride ion concentrations.

Plots of $Q/[Cl^-]^2$ vs. wavelength are given in Fig. 9 for the calculated chloride concentrations 0.2, 0.3, and 0.4 M. Since Cu_2Cl_3 is the complex primarily responsible for the interaction absorption in these solutions, the vertical coordinates of Fig. 9 are proportional to the extinction coefficients, E_2, of this complex, the proportionality factor being L_2.

It may be seen from Fig. 8 that at higher concentrations of free chloride ion, 0.6 and 0.8 F, Q increases somewhat more rapidly than the square of the free chloride concentration. However, the uncertainties in Q in this concentration range, 7-11%, due to the uncertainty in K_2 ($K_2=0.23\pm.15$) and due to experimental errors, do not allow a determination of the relative magnitudes of the higher terms in equation (5), especially the relative values of the coefficients of the $[Cl^-]^3$ and $[Cl^-]^4$ terms. The evidence for contribution of higher (than quadratic) terms to the interaction absorption is in accord with earlier observations of much greater interaction in more concentrated hydrochloric acid solutions. For example, Fig. 10 shows an absorption curve similar to that of Fig. 7, giving the interaction absorption between copper (I) and (II) in 6 F hydrochloric acid[3].

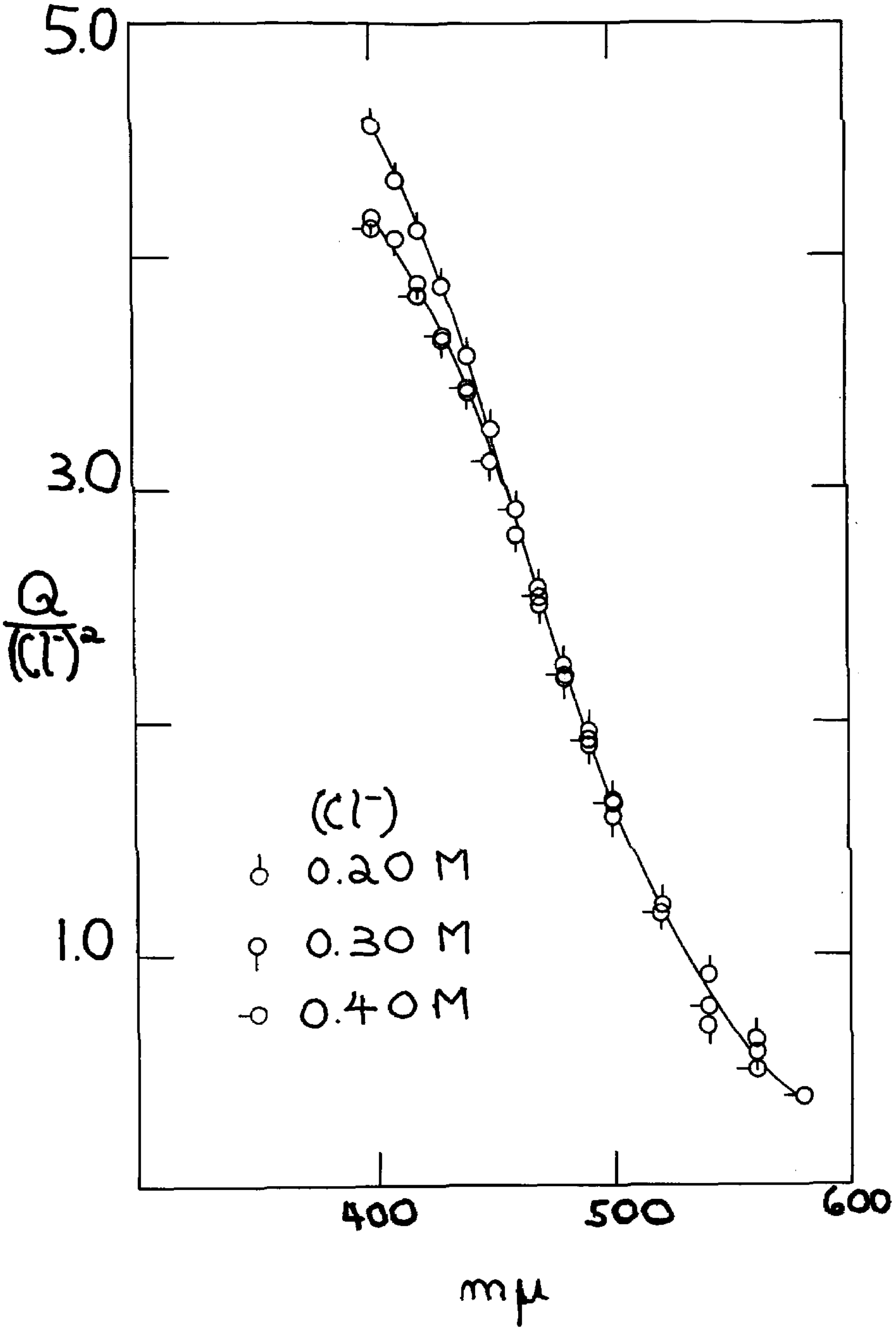

Fig. 9. Relative absorption spectrum of the postulated interaction complex, Cu_2Cl_3. The vertical coordinate is proportional to the extinction coefficient of this complex, E_2. Calculated free chloride ion concentration, $[Cl^-]$; ♁, 0.20 M; ♀, 0.30 M; -o, 0.40 M.

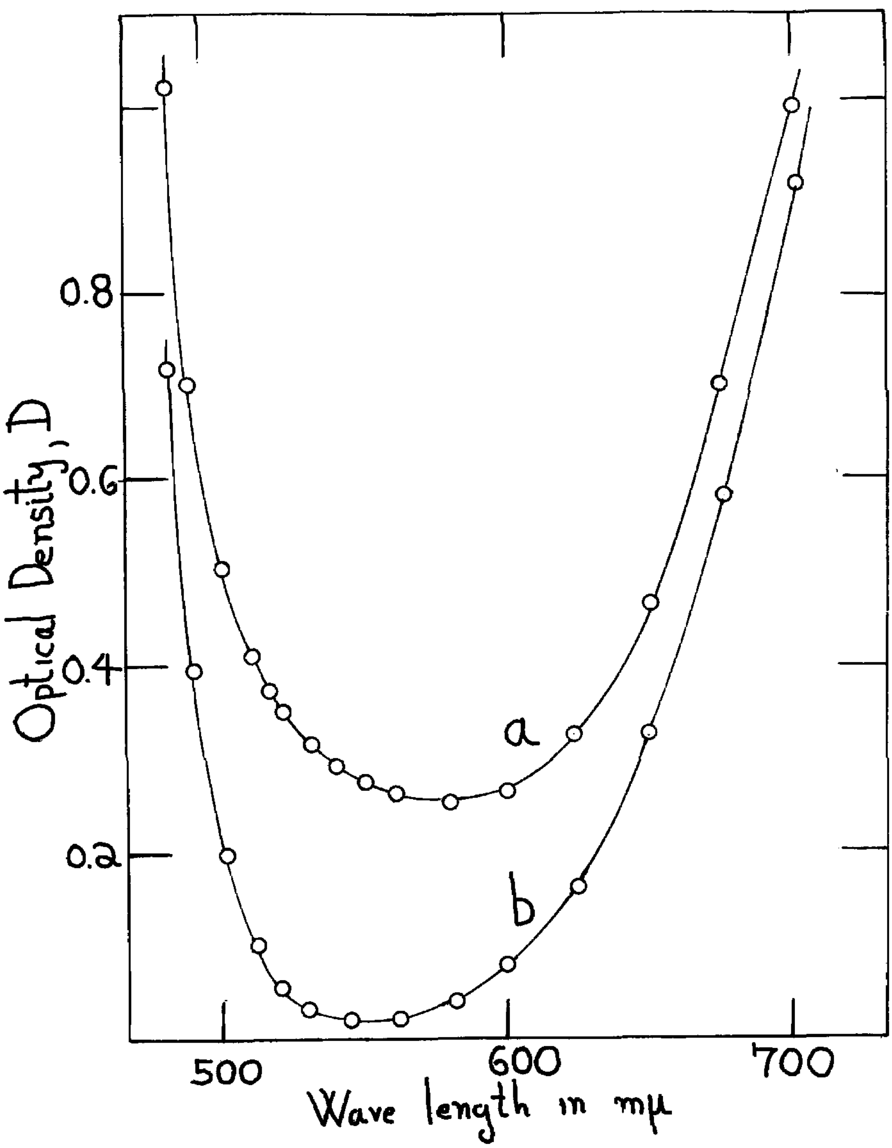

Fig. 10. Optical interaction in 6 F hydrochloric acid solutions. a, [Cu(II)] = 0.025 F, [Cl$^-$] = 6.0 F, [Cu(I)] = 0.05 F; b, [Cu(II)] = 0.025 F, [Cl$^-$] = 6.0 F. (Data of C.I. Browne and Rollie J. Myers.)

Materials and Procedures

A stock solution of cupric perchlorate was prepared as described in Part II. Solutions of cupric perchlorate and cupric chloride were analyzed for copper (II) by the silver reductor method of Birnbaum and Edmonds[9], using pure copper metal as a primary standard. This involves the analysis of a copper (I) solution by treatment with excess iron (III) and titration with cerium (IV) to an o-phenanthroline end point, the same procedure was used for the determination of copper (I) in the interaction mixtures. This method of analysis for copper (II) was checked with the usual iodometric analysis, employing a standard thiosulfate solution. Perchloric and hydrochloric acid solutions were standardized acidimetrically.

In general, a copper (I,II) (or "interaction") solution was prepared by shaking an excess of reagent grade copper (I) chloride with a copper (II) solution contained in a centrifuge bottle placed in a thermostat at 25.1°. The solid copper (I) chloride was washed several times with portions of the copper (II) solution before the final saturation in order to remove any copper (II) present with the solid due to air oxidation. The washing was carried out under a carbon dioxide atmosphere. The composition of the copper (II) solution, which was prepared from standard solutions of cupric perchlorate, cupric chloride, hydrochloric and perchloric acids, was calculated to be such that the resulting copper (I,II) solution had the desired free chloride ion concentration and an ionic strength of 1.0. The change in volume on solution of copper (I) chloride was assumed negligible. The uncertainty in the calculated free chloride ion concentration in these solutions, due to the uncertainty in K_2, was never greater than 2.5%.

It was found necessary to carefully centrifuge (2500g.) each copper (I,II) solution in order to remove suspended particles of solid copper (I) chloride which were otherwise responsible for considerable scattered light. After centrifugation, the solution was replaced in the thermostat for 1/2-1 hour and then transferred under a carbon dioxide atmosphere to a glass stoppered quartz spectrophotometer cell of 10.0 cm. light path. The absorption spectrum was then measured as rapidly as possible (15-20 min.) using the Model DU Beckmann Spectrophotometer. As the room temperature was always within 3° of 25° (usually $25 \pm 1^{\circ}$) and as the volume of the solution contained in the cell was about 30 ml., it is probable that little change in the temperature of the solutions occurred during the time required for the spectrophotometric measurements.

The cell solution was then immediately analyzed for copper (I) and for total copper by the method outlined above[9]. In this fashion the solubilities of copper (I) chloride were measured and a constant check was maintained to insure the absence of any air oxidation of copper (I). No such oxidation was observed within the accuracy of the analyses for total copper, ca. ± 0.0015 F.

An example of the method of making up the solutions and an indication of (a) the reliability of the equilibrium constants K_1, K_2, k_1 and k_2, (b) the reproducibility of the solubility determinations and (c) the accuracy of the assumption of constant activity coefficients, is given by the following experiments: A solution containing 0.150 F $CuCl_2$, 0.445 F HCl and 0.251 F $HClO_4$ was saturated with CuCl. The calculated concentrations (in moles/liter) of the various components of this solution are: $[Cu^{++}] = 0.0794$, $[CuCl^+] = 0.062$, $[CuCl_2] = 0.0086$, $[CuCl_2^-] = 0.045$, $[CuCl_3^=] = 0.012$, $[H^+] = 0.696$, $[ClO_4^-] = 0.251$ and $[Cl^-] = 0.597$. The calculated ionic strength of this solution is 1.01. The experimentally observed solubility of CuCl in this solution was 0.057 F.

A second solution was prepared containing 0.075 F $CuCl_2$, 0.561 F HCl and 0.280 F $HClO_4$ and was saturated with CuCl. The calculated composition of this solution is: $[Cu^{++}] = 0.0397$, $[CuCl^+] = 0.031$, $[CuCl_2] = 0.0043$, $[CuCl_2^-] = 0.045$, $[CuCl_3^=] = 0.012$, $[H^+] = 0.841$, $[ClO_4^-] = 0.282$ and $[Cl^-] = 0.602$. The ionic strength is 1.00. The experimentally observed solubility was 0.058 F.

In general, the uncertainties of the calculated total ionic strengths of these solutions, due to the probable errors in the stability constants of the chloro-complexes of copper (I) and copper (II) are estimated to be 5% or less.

PART III - B

Part III - B

Interpretations of the Spectral Absorption of a Copper (I) - copper (II) Chloro-complex

Introduction

Although the semiquantitative interpretation of the visible absorption spectra of certain organic dyes containing nitrogen in two oxidation states appears to be well established(10), no satisfactory qualitative interpretation of the marked coloration of systems containing a metallic element in two oxidation states has been given. The complex, Cu_2Cl_3, present in small concentrations in dilute hydrochloric acid solutions containing copper (I) and copper (II), may be considered a typical example of a strongly colored compound containing a metallic element in two oxidation states. In this Part two interpretations of the 400-600 mμ absorption spectrum of Cu_2Cl_3 are advanced and discussed. Interest in the visible spectral absorption of small*concentrations of Cu_2Cl_3 stems from the fact that much larger concentrations of $Cu(I)Cl_2^-$ or $Cu(II)Cl_2$ are transparent in this wavelength range**.

The average conformation of Cu_2Cl_3 in aqueous solutions

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* The concentration of Cu_2Cl_3 in the solutions described in Part III - A is estimated to be between 10^{-5} and 0.01 M. A careful experimental investigation of the effect of Cu(II) on the solubility of CuCl(s) might serve to reduce the larger limit.

** The absorption spectrum of $CuCl_2$ in aqueous solution is given in Fig. 4, and the relative absorption spectrum of Cu_2Cl_3 is given in Fig. 9. The absorption spectrum of $CuCl_2^-$ is not known exactly but it is practically certain that it lies to the short wavelength side of the absorption spectrum of $CuCl_2$. In general, only absorption spectra in the 200-700 mμ wavelength are considered in Part III-B.

is not known. Interpretations of the absorption spectrum of this complex require specific assumptions concerning its structure (including water molecules). In the following discussions it will be assumed that the average molecule of this complex which is responsible for the greater part of the observed optical absorption is topologically linear with copper and chlorine atoms occupying alternate positions in the molecular chain. This structure appears to be as reasonable as any other and bears considerable formal resemblance to the structures of the organic dyes referred to above. The average conformation of Cu_2Cl_3 will be schematically represented by Cl-Cu-Cl-Cu-Cl. Coordinating water molecules are understood to be present.

Although a thorough treatment of the electronic energy levels of a molecule of this type is highly impractical at present, it is felt that some progress in understanding the optical properties of this complex may be possible through analogy with simpler systems which are more amenable to quantitative treatment. The two "interpretations" of the spectral absorption of Cu_2Cl_3 given below represent limiting cases in the sense that the alternative idealized descriptions of the ground and excited electronic states of Cu_2Cl_3 correspond to simpler systems whose quantum mechanical descriptions are essentially different. It is of course possible that the best description of the ground and first excited states of Cu_2Cl_3 in the 400-600 mμ range is intermediate to these limiting cases.

Interpretation I

The Cyanine Dye Model

Possible electronic structures of Cu_2Cl_3 in aqueous solution are*

$$\mathrm{Cl-\overset{*}{Cu}(II)-Cl-Cu(I)-Cl} \qquad (1)$$

$$\mathrm{Cl-Cu(I)-Cl-\overset{*}{Cu}(II)-Cl} \qquad (2)$$

$$\left.\begin{array}{l} \mathrm{\overset{*}{Cl}-Cu(I)-Cl-Cu(I)-Cl} \\ \mathrm{Cl-Cu(I)-\overset{*}{Cl}-Cu(I)-Cl} \\ \mathrm{Cl-Cu(I)-Cl-Cu(I)-\overset{*}{Cl}} \end{array}\right\} \qquad (3)$$

The asterisk indicates the position of an unpaired electron in an atomic orbital. The three structures (3) represent electronic configurations of Cu_2Cl_3 which are of higher energy than those given in (1) and (2). This description of excited electronic configurations of Cu_2Cl_3 is similar to the "electron transfer" description of the excited states** of cation-anion complexes which has been employed by Rabinowitch(11). With respect to probable charge distribution along a molecular chain, the above structures for Cu_2Cl_3 bear considerable resemblance to the valence bond structures used by Pauling, Herzfeld and Sklar(10) for the interpretation of the visible absorption spectra of the symmetrical cyanine dyes. The valence bond structures

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* The positions of the nuclei of copper, chlorine, oxygen and hydrogen are the same in all of these structures. In these structures dashes indicate contributions of both covalent and ionic bonds. Except for these five structures dashes will in general indicate completely convalent bonds.

** Generally 3-6 e.v. above the ground state.

employed by these authors are

$$\begin{matrix}R_1\\R_2\end{matrix}\!\!>\overset{+}{N}=CH-(CH=CH)_n-N\!<\!\!\begin{matrix}R_1\\R_2\end{matrix} \qquad (1')$$

$$\begin{matrix}R_1\\R_2\end{matrix}\!\!>N-(CH=CH)_n-CH=\overset{+}{N}\!<\!\!\begin{matrix}R_1\\R_2\end{matrix} \qquad (2')$$

$$\left.\begin{matrix}\begin{matrix}R_1\\R_2\end{matrix}\!\!>N-(CH=CH)_p-\overset{+}{C}H-(CH=CH)_{n-p}-N\!<\!\!\begin{matrix}R_1\\R_2\end{matrix}\\ \begin{matrix}R_1\\R_2\end{matrix}\!\!>N-(CH=CH)_{p-1}-CH-\overset{+}{C}H-CH-(CH=CH)_{n-p}-N\!<\!\!\begin{matrix}R_1\\R_2\end{matrix}\end{matrix}\right\} \qquad (3')$$

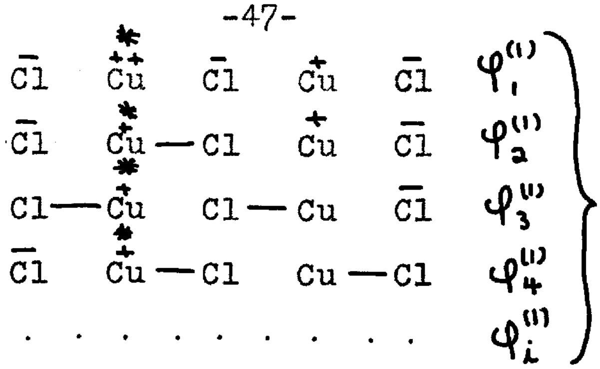
The quantum mechanical interaction of structures (1') and (2') with the excited electronic structures (3') gives rise to two low-lying electronic energy levels, the ground state and a first excited electronic state. The intense visible absorption of such dyes is attributed to an electronic transition between these two energy levels. The present interpretation attributes the visible absorption of Cu_2Cl_3 to electronic states resulting from the interaction of structures (1), (2) and (3). Uncertainties as to the geometrical structure, electronic configuration, and hydration energy of Cu_2Cl_3 in aqueous solution clearly prevent even a satisfactory semiquantitative quantum mechanical treatment of the interaction between these electronic structures. Nevertheless, a qualitative treatment will be shown to indicate the plausibility of this interpretation.

This treatment will be presented in some detail since (a) the required quantum mechanical simplifications are not commonly encountered in treatments of the electronic states of dye molecules, and (b) it is desirable to clearly formulate all important assumptions and approximations employed in these calculations.

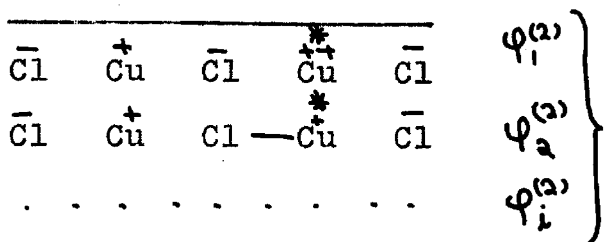
In the quantum mechanical treatment of the interaction of structures (1), (2) and (3), it will be best to consider first the case in which the two copper atoms in the molecule are assumed to be completely equivalent. That is, the energies of structures (1) and (2) are taken to be identical.

<u>Valence Bond Structures for Cu_2Cl_3</u>

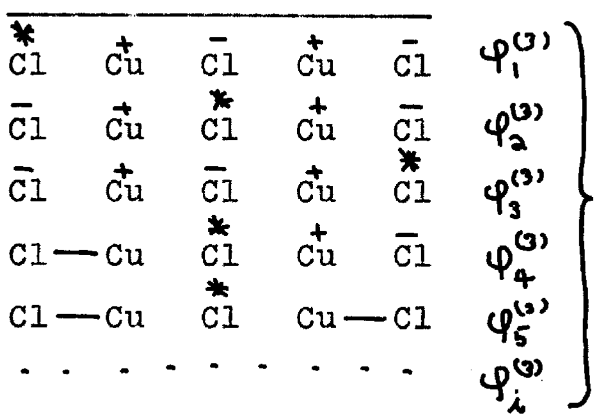
The real normalized wave function $\varphi_i^{(j)}$ represents an atomic orbital approximation to a particular valence bond structure of Cu_2Cl_3. The superscript j refers to the position of the unpaired electron: j = 1, 2, 3 indicates the unpaired electron is localized to an atomic orbital of the left hand copper atom, the right hand copper atom, or a chlorine atom, respectively. The subscript i refers to a particular arrangement of covalent and ionic bonds and, in case j = 3, also indicates the chlorine atom on which the unpaired electron is localized. Only doublet spin states are considered. Some of the $\varphi_i^{(j)}$ are defined in the following structures, where dashes indicate completely covalent bonds and the asterisk indicates the position of the unpaired electron.



(1'')



(2'')



(3'')

<u>Resonance between the Valence Bond Structures</u>

This interpretation considers only those electronic states which are adequately represented by wave functions of the type

$$\Psi = \sum_{i}\sum_{j=1}^{3} a_i^{(j)} \varphi_i^{(j)} . \tag{4}$$

Only the functions $\varphi_i^{(j)}$ which are linearly independent are included in equation (4). Since the position of the unpaired electron in structures (1'') and (2'') differs by about two interatomic distances, the approximations,

$$\int \varphi_i^{(1)} \varphi_{i'}^{(2)} d\tau = 0 \ , \int \varphi_i^{(1)} H \varphi_{i'}^{(2)} d\tau = 0 \tag{5}$$

are satisfactory, irrespective of the particular valence bond structures to which i and i' refer. Here the Hamiltonian operator includes terms representing solvent interactions. It will be convenient to imagine a linear transformation of equation (4) which gives

$$\Psi = \sum_k \sum_{j=1}^{3} b_k^{(j)} \psi_k^{(j)}, \tag{6}$$

where $\psi_k^{(j)}$ is some linear combination of the $\varphi_i^{(j)}$ and where

$$\int \psi_k^{(j)} \psi_{k'}^{(j)} d\tau = 0, \int \psi_k^{(j)} \psi_k^{(j)} d\tau = 1. \tag{7}$$

The equations,

$$\int \psi_k^{(1)} \psi_{k'}^{(2)} d\tau = 0, \int \psi_k^{(1)} H \psi_{k'}^{(2)} d\tau = 0 \tag{8}$$

follow immediately from equations (5), irrespective of the values of k and k'. By definition,

$$H_{kk'}^{jj'} = \int \psi_k^{(j)} H \psi_{k'}^{(j')} d\tau, \tag{9}$$

$$H_{kk}^{jj} < H_{k+1,k+1}^{jj}. \tag{10}$$

This interpretation assumes the inequalities (for equivalent copper atoms),

$$H_{11}^{11} = H_{11}^{22} \ll H_{22}^{11} = H_{22}^{22}, \quad * \tag{11}$$

---

* The energy H_{11}^{11} is obtained by minimizing the integral (9) (with k = k' = j = j' = 1) with respect to the parameters of equation (4). H_{kk}^{jj} is taken positive.

$$\left|H^{13}_{kk'}\right|, \left|H^{23}_{kk'}\right| \ll \left(H^{11}_{22} - H^{11}_{11}\right), \tag{12}$$

$$H^{11}_{11} \ll H^{33}_{kk}. \tag{13}$$

It is further assumed that only two wave functions, $\psi^{(1)}_{1}$ and $\psi^{(2)}_{1}$, correspond to the energy $H^{11}_{11}\left(= H^{22}_{11}\right)$. Assumptions (11) and (12) were made to simplify the calculations. Assumption (11) may indeed be incorrect, but $\left(H^{11}_{22} - H^{11}_{11}\right)$ cannot be calculated at present and a modification of inequality (11) would not seriously affect the conclusions eventually drawn from these calculations.

Some justification can be given assumption (13). The quantity H^{33}_{kk} represents the energy of some linear combination of valence bond structures in which an unpaired electron is always on one or another chlorine atom. Since both the covalent and ionic bonding power of this atom (s) is small, H^{33}_{kk} does represent an excited state relative to H^{11}_{11} in that a bond has been broken in going from one set of structures to the other. The fact that copper (II) is not observed to oxidize chloride in aqueous solutions suggests that the electron affinity of copper (II) and the strength of a copper (I) chlorine bond are not sufficient to overbalance the above mentioned excitation energy.

Lowest Electronic States of Cu_2Cl_3 with Equivalent Copper Atoms

On considering inequalities (11), (12) and (13) it is seen that the wave functions for the two lowest electronic states of Cu_2Cl_3 will have the form

$$\Psi = c_1\psi_1^{(1)} + c_2\psi_1^{(2)} + c_3\psi^{(3)},$$

where $$\psi^{(3)} = \sum_k b_k^{(3)}\psi_k^{(3)}$$

and $$\sum_k (b_k^{(3)})^2 = 1.$$

Since the copper atoms are equivalent, $|c_1| = |c_2|$. In general, equation (14) will lead to a large secular determinant and the determination of the $b_k^{(3)}$ will be complicated. According to the assumptions, $|c_3|$ is small in the two lowest electronic states. The following procedure is therefore used to obtain the two lowest energy levels. Pick out an arbitrary set of the $b_k^{(3)}$ *. Holding the $b_k^{(3)}$ fixed, minimize the energy with respect to the c_i. This procedure leads to the secular determinant,

$$\begin{vmatrix} H_{11}^{11}-E & 0 & \alpha_{13} \\ 0 & H_{11}^{22}-E & \alpha_{23} \\ \alpha_{13} & \alpha_{23} & H^{33}-E \end{vmatrix} = 0,$$

and the two lowest energies,

$$E_1 = H_{11}^{11} - \frac{2\alpha^2}{(H^{33}-H_{11}^{11})}, \quad E_2 = H_{11}^{11},$$

---

* This calculation, which groups a number of excited state wave functions into a single variational function, $\psi^{(3)}$, is valid only if (a) $\psi^{(3)}$ has the symmetry properties of $(\psi_1^{(1)}-\psi_1^{(2)})$ or $(\psi_1^{(1)}+\psi_1^{(2)})$, and (b) the contribution (to Ψ_1 or Ψ_2) of excited state wave functions having symmetry properties different from those of $\psi^{(3)}$ may be neglected. As implied in the footnote to page 51 and in equations (29) and (30), the calculations presented here assume that $\psi^{(3)}$ in equation (14) has the same symmetry properties as does $(\psi_1^{(1)}+\psi_1^{(2)})$ and that condition (b) above is fulfilled. If this simplifying assumption is not made it is found that the wave functions $\psi_k^{(3)}$ contribute to both Ψ_1 and Ψ_2. (See equations (29) and (30)). The more general treatment does not alter the qualitative conclusions but does give rise to equations of unwarranted complexity.

where*

$$\alpha_{13} = \sum_k b_k^{(3)} H_{1k}^{13}, \tag{17}$$

and $$2\alpha^2 = \alpha_{13}^2 + \alpha_{23}^2$$

and $$H^{33} = \sum_k (b_k^{(3)})^2 H_{kk}^{33} + 2\sum_{k>k'} b_k^{(3)} b_{k'}^{(3)} H_{kk'}^{33}.$$

In obtaining these results it has been assumed that $2\alpha^2/(H^{33} - H_{11}^{11})$ is small (see (11),(12) and (13)) and that $\int \psi_1^{(1)}\psi_1^{(3)} d\tau = 0$. The following discussion will indicate the latter assumption to be reasonable. Now it is clear that that set of the b_k is to be chosen which maximizes $2\alpha^2/(H^{33} - H_{11}^{11})$.

To recapitulate: Thus far an attempt has been made to show under what conditions the interaction of a multitude of valence bond structures might give rise to two qualitatively well defined electronic states, the ground state and a first excited electronic state.

Nature of the Exchange Integrals

The next step is to show that when reasonable electronic configurations are assumed for the structures (1''), (2'') and (3''), the exchange integrals found contributing to the separation of E_1 and E_2 may be appreciable. To show that exchange integrals of the type

$$\int \varphi_i^{(1)} H \varphi_{i'}^{(3)} d\tau, \int \varphi_i^{(2)} H \varphi_{i'}^{(3)} d\tau \tag{18}$$

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* Each $\psi_k^{(3)}$ in the expansion of $\psi^{(3)}$ represents equivalent copper atoms. In general, $\alpha_{13} = \alpha_{23}$, or $\alpha_{13} = -\alpha_{23}$. The sign of this equality determineswhether $c_1 = c_2$ or $c_1 = -c_2$ in the ground electronic state. Without affecting any of the conclusions, $c_1 = c_2$ is assumed for the ground electronic state.

are non-zero is entirely equivalent to showing that α^2 in equation (16) is non-zero. This is true since α_{13} and α_{23} are in general, linear combination of the integrals (18) and this linear combination is always taken so as to make α^2 non-zero.

A typical integral appearing in the expansion of the H_{1k}^{13} in equation (17) is

$$\int \varphi_1^{(1)} H \varphi_2^{(3)} d\tau . \tag{19}$$

In formulating this integral, one may to a good approximation consider only the electronic configurations of

$$\overset{*}{\overset{++}{Cu}} \quad \overset{-}{Cl} \tag{20}$$

and

$$\overset{+}{Cu} \quad \overset{*}{Cl} . \tag{21}$$

For simplicity dsp^2 hybridization of the atomic orbitals of copper will be assumed here. This assumption is not necessary insofar as the following arguments are purely qualitative and different types of hybridization can lead to the same qualitative conclusions. We let t_x represent that member of the four tetragonal plane dsp^2 orbitals which is directed toward the chlorine atom in (20)*. A pure $4p_z$ orbital of copper, designated by p_{1z}, is perpendicular to this plane of the dsp^2 orbitals. Two pure p orbitals of the chlorine atom will be considered, a $3p$ orbital (p_{2z}) which is taken parallel to the p_{1z} orbital

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*Two dsp^2 orbitals may be considered to be engaged in bond formation with water molecules.

of the copper atom, and a 3p orbital (Px) which overlaps strongly with t_x. If the unpaired electron in structure (21) is in the p_{2z} orbital, then (19) reduces to

$$\int \{p_{1z}(1)\, p_{2z}(2)\, p_{2z}(3)\} H \{p_{1z}(1)\, p_{1z}(2)\, p_{2z}(3)\} d\tau. \qquad (22)$$

This is a typical three electron resonance integral and is not expected to be zero although its magnitude will depend strongly on the copper-chlorine interatomic distance. Not all of the exchange integrals appearing in the expansions of the H_{1k}^{13} in equation (17) are expected to be nearly as large as (19). In particular exchange integrals such as

$$\int \varphi_1^{(1)} H \varphi_3^{(2)} d\tau \qquad (23)$$

are essentially zero and multiple exchange integrals such as

$$\int \varphi_1^{(1)} H \varphi_4^{(3)} d\tau \qquad (24)$$

are expected to be small.

A second type of exchange integral which might appear in the equations for the interaction of structures (1'') and (3'') should be considered. In the above equations for the exchange integral between (20) and (21) it was assumed that the unpaired electron in (21) was in the p_{2z} orbital of chlorine. This unpaired electron might also be taken to be in a p_x (bonding) orbital of the chlorine atom. In this case it is expected that (19) would be small since p_{1z} and p_x may be assumed to overlap only slightly in a first order approximation. On the other hand, it might not be immediately obvious that exchange integrals of the type

$$\int \varphi_2^{(1)} H \varphi_2^{(3)} d\tau \tag{25}$$

are small when the unpaired electron in $\varphi_2^{(3)}$ is in the p_x bonding orbital of the chlorine atom. In calculating (25) one may use as a first order approximation the integral,

$$\frac{1}{\sqrt{2\,3!}}\int\left\{\sum_P(-1)^P P\, p_{1z}\alpha(1)\, t_x(2)\, p_x(3)\left[\alpha(2)\beta(3)-\alpha(3)\beta(2)\right]\right\} \cdot H\left\{\sum_P(-1)^P P\, p_{1z}\alpha(1)\, p_{1z}\beta(2)\, p_x\alpha(3)\right\} d\tau. \tag{26}$$

By neglecting terms containing factors of the type

$$\int\left\{p_{1z}(1)\, t_x(2)\, p_x(3)\right\} H \left\{p_{1z}(3)\, p_{1z}(2)\, p_x(1)\right\} d\tau$$

the integral of (26) becomes

$$\frac{1}{\sqrt{2}}\int\left\{p_{1z}(1)\, t_x(2)\, p_x(3)\right\} H \left\{p_{1z}(1)\, p_{1z}(2)\, p_x(3)\right\} d\tau. \tag{27}$$

Of course the complexity of H makes the assessment of the magnitude of (27) difficult, but there is no apparent reason why (27) should be large. It might be thought that

$$\int p_{1z}(1)\, t_x(2)\left(\frac{e^2}{r_{12}}\right) p_{1z}(1)\, p_{1z}(2)\, d\tau \tag{28}$$

would make a large contribution to (27). It can be shown, however, that when p_{1z} and t_x are taken to be Slater-like wave functions(assuming a constant radial factor in the hybridization of the 3d, 4s, and 4p orbitals of copper) this integral (28) vanishes. It is probable then that structures (3'') contribute more strongly to the separation of the two electronic states, E_1 and E_2, when the unpaired electron is taken to be in the p_{2z} orbital of the chlorine atoms.

The Transition Probability

The formation of two distinct low-lying electronic states of Cu_2Cl_3 with equivalent copper atoms having been established as at least a plausible possibility, the probability of an optical transition between these two electronic states may be considered.

The wave functions for these two electronic states are

$$\Psi_1 = \frac{1}{\left[2+\frac{2\alpha^2}{(H^{33}-H^{11}_{11})^2}\right]^{\frac{1}{2}}}\left\{\psi_1^{(1)}+\psi_1^{(2)}-\left(\frac{2\alpha_{13}}{H^{33}-H^{11}_{11}}\right)\psi^{(3)}\right\} \tag{29}$$

and $$\Psi_2 = \frac{1}{\sqrt{2}}\left\{\psi_1^{(1)}-\psi_1^{(2)}\right\}. \tag{30}$$

Since in the preceding calculations $c_3\psi^{(3)}$ represented only a small contribution to the ground state electronic wave function, Ψ_1, one may approximate Ψ_1, by

$$\Psi_1 = \frac{1}{\sqrt{2}}\left(\psi_1^{(1)}+\psi_1^{(2)}\right).$$

Letting

$$\vec{\mu}_{12} = \int \Psi_2\vec{\mu}\,\Psi_1 d\tau = \int \Psi_2\left(\sum_i e_i\vec{r}_i\right)\Psi_1 d\tau, \tag{31}$$

one obtains

$$\vec{\mu}_{12} = \frac{1}{2}\left\{\int \psi_1^{(1)}\vec{\mu}\,\psi_1^{(1)}d\tau - \int \psi_1^{(2)}\vec{\mu}\,\psi_1^{(2)}d\tau - 2\int \psi_1^{(1)}\vec{\mu}\,\psi_1^{(2)}d\tau\right\}.$$

By neglecting the last term this becomes

$$\vec{\mu}_{12} = \frac{1}{2}\left(\vec{\mu}_1-\vec{\mu}_2\right) = \vec{\mu}_1\,, \tag{32}$$

where $\vec{\mu}_1$ and $\vec{\mu}_2$ are the dipole moments of the structures represented by $\psi_1^{(1)}$ and $\psi_1^{(2)}$.

The order of magnitude of $|\vec{\mu}_{12}|$ is estimated by assuming (a) a completely linear molecule, (b) copper-chlorine interatomic distances equal to 2.3 Å and (c) that $\psi_1^{(1)}$ corresponds to a structure in which the average charge distribution on each successive atom in the chain in structure (1) is (left to right): $-\frac{1}{2}$, +1, 0, 0, $-\frac{1}{2}$. This charge distribution is obtained by equally weighting all possible covalent and ionic structures intermediate to and including $\overset{-}{Cl}\ \overset{++}{Cu}\ \overset{-}{Cl}\ \overset{+}{Cu}\ \overset{-}{Cl}$ and $Cl\text{-}Cu\text{-}\overset{+}{Cl}\text{-}\overset{-}{Cu}\text{-}Cl$. This calculation amounts to assuming about 50% ionic character in the copper-chlorine bonds in structure (1). Using these assumptions one obtains

$$|\vec{\mu}_{12}| = e(2.3\,\text{Å}) = 11 \times 10^{-18}\ \text{e.s.u.} \qquad (33)$$

This dipole moment is of the order of magnitude of those calculated for the most strongly colored organic dyes. This general interpretation then appears consistent with the fact that the spectral absorption of Cu_2Cl_3 is easily observed even when the concentration of Cu_2Cl_3 is too small to be measured by chemical methods.

The Effect of Solvation on the Absorption Spectrum of Cu_2Cl_3 in Aqueous Solution; the Effect of Solvation in Reducing the Equivalence of the Copper Atoms*

Up to this point the preceding theory is inadequate to account for the 400-600 mμ spectral absorption of Cu_2Cl_3. That is, the assumptions** made in deriving the

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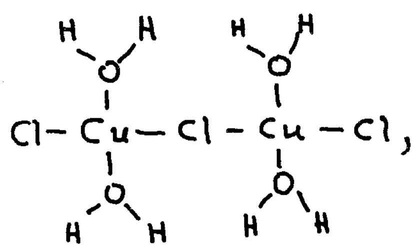
* Professor Verner Schomaker has pointed out that effects other than those considered here may serve to reduce the equivalence of the copper atoms in Cu_2Cl_3.

** These assumptions are essentially those represented in inequalities (11) - (13).

expressions for the separation of the two lowest electronic energy states are probably not adequate when this separation is 2-3 e.v. Nevertheless, a consideration of solvation effects indicates that many of the essential features of the preceding calculations may be retained and yet account for an energy separation of 2-3 e.v.

The effect of solvent on the separation of the ground and first excited electronic states may be first considered in an extremely idealized and approximate fashion. The Hamiltonian operator in all the preceding calculations is now taken to include only the interactions of the two copper atoms, three chlorine atoms and four water molecules. That is, all the preceding calculations are now understood to be carried out for $Cu_2Cl_3 \cdot 4H_2O$ in vacuum. This molecule is assumed to have the structure,



(34)

(symmetry D_{2h}) with copper-chlorine interatomic separations of 2.3 Å. The lowest electronic states of (34) are then given by equations (16), where $E_2 - E_1 = 2\alpha^2/(H^{33} - H''_{11})$

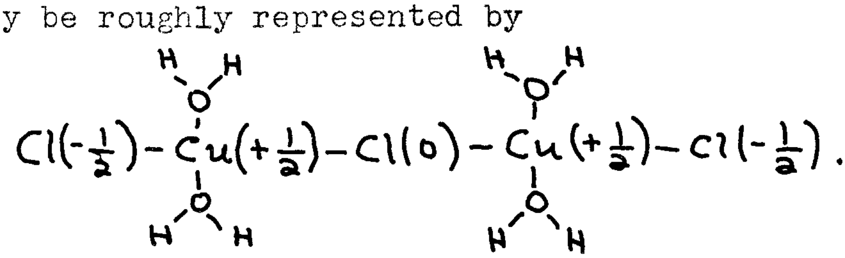
The effect of solvation (not including the four water molecules directly bonded to the copper atoms in (34)) is treated as a perturbation which serves to change the separation of the ground and first excited electronic states of $Cu_2Cl_3 \cdot 4H_2O$ from $(E_2 - E_1)$ (vacuum) to $(E_2' - E_1')$ (solution).

The solvation energy, S, of $Cu_2Cl_3 \cdot 4H_2O$ is approximated by the energy of interaction between a permanent dipole moment of $Cu_2Cl_3 \cdot 4H_2O$ and a surrounding homogenous dielectric of constant K. For simplicity, the order of magnitude of this interaction energy is estimated by assuming $Cu_2Cl_3 \cdot 4H_2O$ to be contained in a spherical cavity of radius R which is immersed in the homogenous dielectric. For this order of magnitude calculation the equation,

$$S = -\frac{\mu^2}{R^3}\frac{K-1}{2K+1}, \tag{35}$$

may be used. In (35) μ is the permanent dipole moment of $Cu_2Cl_3 \cdot 4H_2O$ in one particular electronic state. The dielectric constant K is taken to be 80. The following considerations indicate that the interaction of a permanent dipole moment of $Cu_2Cl_3 \cdot 4H_2O$ with the surrounding dielectric may give rise to non-equivalent copper atoms and to the inequality, $(E_2' - E_1') > (E_2 - E_1)$.

It is noted that if the copper atoms are assumed to be completely equivalent when $Cu_2Cl_3 \cdot 4H_2O$ is immersed in the dielectric, the average charge distribution (see page 55) may be roughly represented by

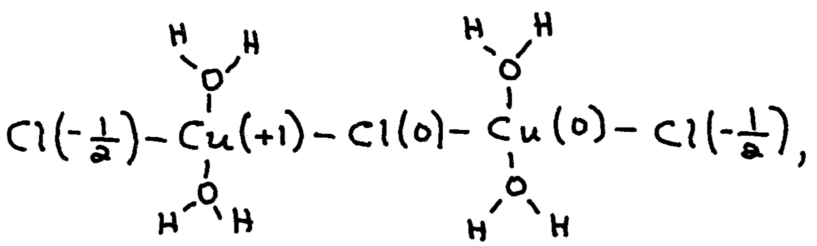


(36)

In this case the solvation energy, S, is zero if only equation (35) is considered. (Actually (36) has a large quadrupole moment and the solvation energy is certainly not zero. Nevertheless the solvation energy of (36) will be taken to be zero since the magnitude of this solvation energy due to the quadrupole moment is certainly smaller than that due to the large dipole moment considered below*) Since the copper atoms in (36) are equivalent, the electronic resonance stabilization of the ground state (equation (16)) is $2\alpha^2/(H^{33}-H^{11}_{11})$ and $E_2-E_1=E_2'-E_1'=2\alpha^2/(H^{33}-H^{11}_{11})$.

Furthermore, according to equation (33) the probability of an electronic transition between E_1 and E_2 is very large.

On the other hand, if the copper atoms in $Cu_2Cl_3 \cdot 4H_2O$ are completely non-equivalent** (but still retaining a D_{2h} symmetry for the nuclei of $Cu_2Cl_3 \cdot 4H_2O$), corresponding to the charge distribution,


(37)

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* Professor Verner Schomaker suggested the necessity of considering the quadrupole interaction.

** Non-equivalent is meant to imply that the ground electronic state is represented by contributions of $\psi_1^{(1)}$ and $\psi^{(3)}$ alone. Strictly speaking, in this case $\psi^{(3)}$ (see equation (14)) need not form a basis for a representation of D_{2h}, but rather C_{2v}.

then by equation (35) the solvation energy is no longer zero, since (37) has a large dipole moment. In this case the electronic stabilization* of E_1' is <u>less</u> than the resonance stabilization of $Cu_2Cl_3 \cdot 4H_2O$ when the copper atoms are completely equivalent. (The ground state wave function for completely equivalent copper atoms is given in equation (29); the wave function for completely non-equivalent copper atoms is largely $\psi_1^{(1)}$ or $\psi_1^{(2)}$, with a small contribution of $\psi^{(3)}$.) If E_1' is principally represented by $\psi_1^{(1)}$, and E_2' by $\psi_1^{(2)}$, then the energy separation $E_2' - E_1'$ contains a large contribution from the solvent interaction, namely, the difference in energy between a large dipole stabilized by solvent polarization (energy state E_1') and a large dipole destabilized by solvent polarization (energy state E_2'). By letting R in equation (35) be 6 Å, one obtains 0.7 e.v. as the contribution of solvation to the energy separation $E_2' - E_1'$. For this case, however, no "optical interaction absorption" is expected. That is, the probability of an electronic transition between E_1' and E_2' for completely non-equivalent copper atoms is very small.

In general, if $\frac{\mu_1^2(K-1)}{R^3(2K+1)}$ is of the order of magnitude of $2\alpha^2/(H^{33}-H^{11}_{11})$, then the copper atoms will be only "partially equivalent". That is, the ground electronic state will be represented by

$$\Psi = a\psi_1^{(1)} + b\psi_1^{(2)} + c\psi^{(3)},$$

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* This stabilization refers to the contributions of exchange integrals between $\psi_1^{(1)}$ and $\psi^{(3)}$ alone.

where $|c|$ is small and $|a|$ and $|b|$ are not equal. In this case a large transition probability is still predicted. Furthermore, both electronic resonance energy and solvent dipole interaction contribute to the separation, $E_2' - E_1'$. It is clear then that the requirement, $E_2' - E_1' = 2\text{-}3$ e.v., does not imply that the resonance stabilization of the ground electronic state of $Cu_2Cl_3 \cdot 4H_2O$ is 2-3 e.v.

These qualitative considerations may represent some indication of the actual character of the ground and first excited electronic states of Cu_2Cl_3 in aqueous solution. The effect of solvation has probably been severely underestimated. Actually differences in the bonding of chlorine atoms and water molecules to the two copper atoms may serve to increase the separation of E_2' and E_1'. <u>This interpretation still requires an interaction of structures (1), (2) and (3) so that each copper atom is copper (II) part of the time in the ground electronic state</u>. In this case a large transition probability between the two electronic states is easily understandable.

<u>The Electronic Resonance Stabilization of the Ground State of Cu_2Cl_3 in Aqueous Solution</u>

As emphasized in the preceeding section, the 400-600 mμ spectral absorption need bear no simple relationship to an electronic resonance stabilization of the ground state of Cu_2Cl_3 in aqueous solution. Only if this resonance stabilization is great enough to produce effectively equivalent copper atoms can one say that the ground state of Cu_2Cl_3 is stabilized by 2-3 e.v. (It may be noted that the resonance between structures (1'), (2') and (3') strongly stabilizes the ground state of the cyanine dyes.) Even if the copper atoms were completely equivalent, a resonance stabilization of 2-3 e.v. cannot be said to be obviously incompatible with the observed instability* of Cu_2Cl_3 in aqueous solutions. This is true since the heat (ΔH) of the gaseous reaction,**

$$CuCl(H_2O)_3^+ + CuCl_2(H_2O)_2^- \rightarrow Cu_2Cl_3(H_2O)_4 + H_2O,$$

may well have positive contributions from, for instance, the loss of a copper-water molecule bond. Furthermore, the heat of solvation (in the spherical cavity approximation) of $Cu_2Cl_3 \cdot 4H_2O$ with equivalent copper atoms is certainly less than the sum of the heats of solvation of $CuCl(H_2O)_3^+$ and $CuCl_2(H_2O)_2^-$.

Other arguments favor a smaller (than 2-3 e.v.) electronic resonance stabilization. For instance, the chloro-interaction complexes of other elements (Sn, Sb, Fe) in aqueous solutions are quite similar to Cu_2Cl_3 in that they are easily detected spectrophotometrically but are so unstable that they have not been detected by chemical methods. It would be unexpected to find that the hydration destabilizations of the ground states of all of these complexes

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* See in particular pages 33 and 42 concerning the instability of Cu_2Cl_3 in aqueous solutions.

** The complex species $CuCl^+$ and $CuCl_2^-$ were the predominate chloro-complexes of copper (I) and copper (II) present in the solutions found (Part III-A) to contain much smaller concentrations of Cu_2Cl_3.

(corresponding to their formation in aqueous solution from the simpler and predominant chemical species) were delicately balanced against large electronic resonance stabilizations so as to yield small but detectable concentrations of the interaction complexes. Also, crystalline solids containing a metallic element in two oxidation states and exhibiting intense absorption spectra usually show no marked stability.

The conclusion is that it is unlikely that the resonance stabilization of the ground electronic state of Cu_2Cl_3, corresponding to the interaction of structures (1), (2) and (3), is as great as 2-3 e.v.; thus solvation effects (in part) do contribute to the separation of E_2' and E_1' according to Interpretation I.

Interpretation I and a General Theory of "Optical Interaction Absorption"*

Interpretation I predicts a gaseous system of Cu_2Cl_3 molecules (with equivalent, or partially equivalent** copper atoms in each molecule) to exhibit a relatively sharp and intense absorption band. This absorption band is predicted to be absent in gaseous systems containing $CuCl^+$ or $CuCl_2^-$ and is thought of as giving rise to the 400-600 mμ

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* The definition of "optical interaction absorption" is given on page 24 for the copper (I)-copper (II) chloro-complex system. For references to publications describing the many examples of optical interaction absorption, see references (3) and (4) to Part III.

** Partially equivalent is taken to mean that each copper atom has some copper (I) and some copper (II) character in the ground electronic state.

spectral absorption of Cu_2Cl_3 in aqueous solution. There appears to be little possibility of testing this prediction experimentally. Nevertheless, the absorption spectra of isolated interaction complexes (complexes containing two atoms of a metallic element in different oxidation states) is of great importance for any adequate theory of optical interaction absorption. In particular, it is necessary to know whether the electronic states responsible for the optical interaction absorption are discrete or essentially continuous.* The extension of Interpretation I to other interaction complexes requires these electronic states to be discrete and, in fact, well separated from the other electronic states of the interaction complex. At present the possibility of observing the absorption spectra of isolated interaction complexes appears remote. However, Dr. Norman Davidson has suggested an experiment which might prove to be of considerable value in connection with this problem: Crystals of Cs_2SbCl_6, which are known to contain atoms of Sb(III) and Sb(V) and which exhibit optical interaction absorption, are isomorphous with crystals of $Cs_2Sn(IV)Cl_6$. If the optical density of interaction absorption in crystals of Cs_2SnCl_6 containing small concentrations of Sb(III) and Sb(V) could be shown experimentally to depend upon the product of the concentrations of Sb(III) and Sb(V),

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* Needless to say, it is important to know the wavelength of the absorption maximum, if the interaction spectrum is represented by a sharp band.

then this dependence would indicate that the crystals of Cs_2SnCl_6 contained small concentrations of some dimeric complex of Sb(III) and Sb(V), probably $Sb(III)Cl_6^{\equiv}\cdot Sb(V)Cl_6^-$. The absorption spectra of such crystalline solutions at low temperatures might then give some indication as to the discrete or continuous character of the electronic states responsible for the interaction absorption.*

In principle, Interpretation I could be extended to include the absorption spectrum of Cs_2SbCl_6 itself. The large number of valence bond structures (corresponding to (1), (2) and (3) for Cu_2Cl_3) appropriate to a crystal of Cs_2SbCl_6 would suggest an extremely intense and practically continuous absorption spectrum covering a large wavelength range. Visual observation indicates that this is the case. Any application of Interpretation I to the absorption spectrum of Cs_2SbCl_6 would require a consideration of the effect of resonance between a large number of valence bond structures on the stability of this substance.

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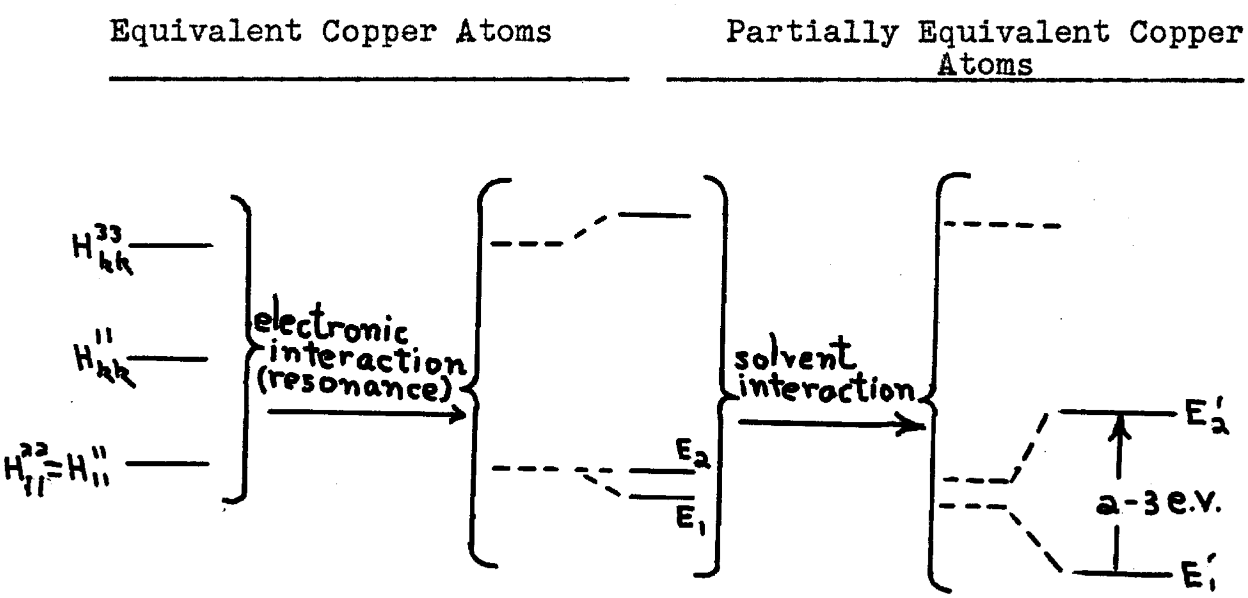
* The unstable molecule N_2O_3 exhibits a sharp and intense absorption band which is not observed in either NO or NO_2. The similarity between N_2O_3 and Cu_2Cl_3 (intense absorption bands, low stabilities and possible structures) led Dr. Oliver Wulf to suggest that this molecule might be considered in connection with the general problem of interaction absorption. Actually simple valence bond charge resonance structures for N_2O_3 bear little formal resemblance to those used in Interpretation I to account for the 400-600 mμ spectral absorption of Cu_2Cl_3. Also, it may be noted that the formal oxidation number of nitrogen in N_2O_3 is normal whereas in Cu_2Cl_3 the formal oxidation number of copper is 1.5. In general unusual oxidation numbers are associated with the appearance of optical interaction absorption.

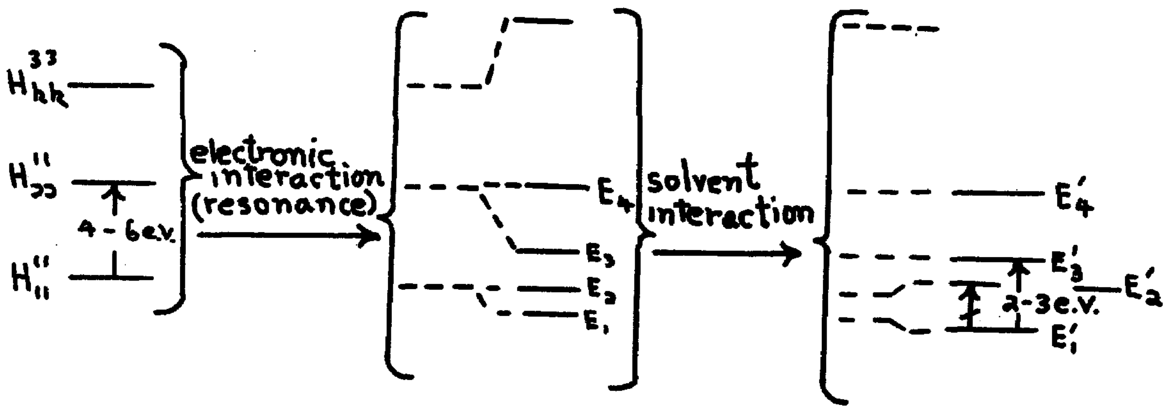
Interpretation II

This interpretation of the 400-600 mμ spectral absorption of Cu_2Cl_3 amounts to a consideration of alternate assumptions regarding the inequalities (11), (12) and (13). Although it is possible to reformulate these inequalities to correspond to the assumptions of Interpretation II, it will be much more convenient to illustrate the differences between these two interpretations by means of energy level diagrams. The following energy level diagram will be recognized as schematically representing the energy states of Cu_2Cl_3 considered in Interpretation I.



Interpretation II assumes little or no electronic resonance stabilization of the ground electronic state of Cu_2Cl_3 but does assume a strong resonance stabilization of the first excited electronic state. The electronic states of Cu_2Cl_3 considered in this case are indicated in the diagram:

Equivalent Copper Atoms   Non-equivalent Copper Atoms



This excited state stabilization, which is indicated in the energy level diagram (39) by a large lowering of E_3 relative to H_{22}^{11} (the energy of some excited state in the absence of this stabilization), is assumed to account for the fact that Cu_2Cl_3 exhibits a spectral absorption at longer wavelengths than do $CuCl_2$ or $CuCl_2^-$. In the approximation that the wave function corresponding to the excited state E_3' of Cu_2Cl_3 may be obtained by taking a linear combination of wave functions corresponding to the excited states of $CuCl_2$ and $CuCl_2^-$ in the 200-300 mμ wavelength range*, this interpretation postulates that the separation of H_{11}^{11} and H_{22}^{11} (for equivalent copper atoms) is of the order of magnitude of 4-6 e.v. At present there is no satisfactory quantum mechanical description of these excited electronic states of $CuCl_2$ and $CuCl_2^-$ and it is therefore difficult to decide

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* Of course more highly excited electronic states of $CuCl_2^-$ and $CuCl_2$ might be more important.

whether the interaction of these excited electronic states may reasonably be expected to lead to a large resonance stabilization of E_3. Nevertheless, in view of the uncertainties of Interpretation I, it is at least necessary to consider this excited state stabilization as an _a priori_ possibility*.

An examination of the assumptions made in Interpretation I indicates (a) the covalent character of the copper chlorine bonds is essentially the same in the electronic states E_1' and E_2', and (b) the contribution of structures (3'') to the states E_1' and E_2' is small. In Interpretation II the covalent character of the copper chlorine bonds may indeed be different in the states E_1' and E_3'. Also, the contribution of structures (3'') to the electronic state E_3' may be large. The assumed resonance stabilization of state E_3' may then arise from strong resonance among structures (1''), (2''), and (3'').

It is also possible that the excited state E_3 cannot be accurately represented by a linear combination of wave functions for (1''), (2'') and (3''). If this were the case, another type of electronic structure might give rise to a stabilization of E_3. For example, if E_3 were represented by a linear combination of wave functions representing

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* Recently R. S. Mulliken has indicated the possibility of attributing the _visible_ absorption of the _weak_ benzene-iodine complex to a transition to an excited state in which the benzene and iodine components of the molecule interact much more strongly than these components do in the ground electronic state. This interaction stabilizes the excited state relative to the corresponding more highly excited states of benzene and iodine molecules.

electrons(s) in <u>excited</u> atomic orbitals, then a strong overlap of the excited atomic orbitals might account for a stabilization of E_3. A very simple hypothetical model, the hydrogen molecule ion with an interatomic separation of 4.6 Å, may be used to illustrate this possibility.

Fig. 11 exhibits the potential energy vs. interatomic separation (r) curves* for three electronic states of H_2^+. It is seen that at an interatomic separation of 4.6 Å ($r = 8.5$, in units of 0.54 Å) the ground electronic state of H_2^- has practically the same energy as the $2p\sigma$ electronic state. Thus, there is essentially no resonance stabilization of the $1s\sigma$ ground state relative to a hydrogen atom (1s) and a proton at infinite separation. On the other hand, the first excited electronic state ($3d\sigma, r = 8.5$) is stabilized by 1.3 e.v. relative to the first excited state of the hydrogen atom (2p), which is 10.14 e.v. above the ground state.

In some respects the systems, H^+, $H\cdot$ and H_2^+ ($r = 8.5$) are analogous to $CuCl^+$, $CuCl_2^-$ and Cu_2Cl_3. The ground electronic states of Cu_2Cl_3 and H_2^+ are not strongly stabilized by resonance, but Cu_2Cl_3 and H_2^+ ($r = 8.5$) exhibit intense absorption spectra** at wavelengths were $CuCl^+$,

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* Calculations of E. Teller(12).

** Since the energy of the $1s\sigma$ and $2p\sigma$ states are essentially identical, one may consider the $2p\sigma \rightarrow 3d\sigma$ transition here. A simple calculation indicates the strength of this transition ($r = 8.5$) to be about one-third the intensity of the $1s$-$2p$ transition for the hydrogen atom.

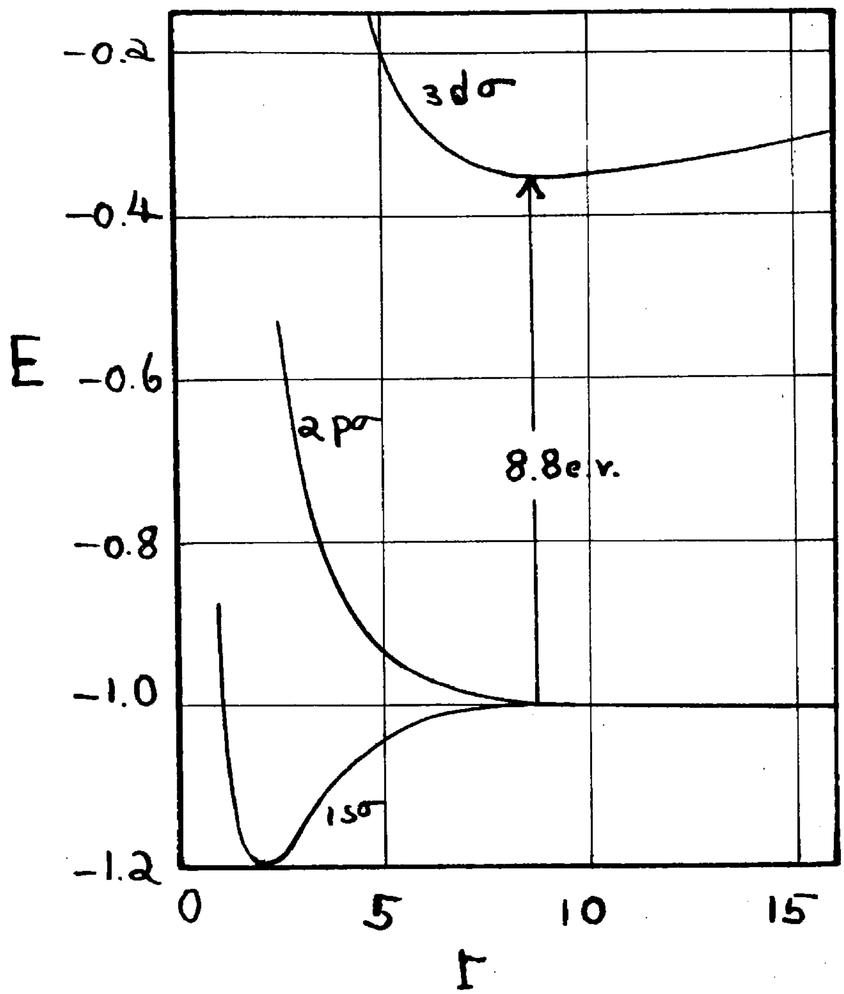

Fig. 11 Electronic states of the hydrogen molecule ion. The energy, E, is given in units of 13.54 e.v. and the interatomic separation, r, is given in units of 0.54 Å.

$CuCl_2^-$ and H^+, H• are transparent. It may be noted that a reasonable value for the copper-copper separation in Cu_2Cl_3 is also 4.6 Å. Of course this analogy cannot be carried too far. Although the stabilization of the $3d\sigma$ state of H_2^+, 1.3 e.v., is of the same order of magnitude as the apparent stabilization of the first electronic state of Cu_2Cl_3 relative to the first excited electronic states of $CuCl_2^-$ or $CuCl_2$, 1-4 e.v., the total energy required for the 1s - 2p transition in the hydrogen atom is much greater than that required for the corresponding electronic transitions in $CuCl^+$ or $CuCl_2^-$.

One description of a stabilized excited state of Cu_2Cl_3 which bears some analogy to the hydrogen molecule ion picture may be indicated. If one assumed the 200-250 mμ absorption spectrum of $CuCl_2^-$ to correspond to the excitation of one of the two p_{1z} electrons (see page 53) of copper (I) into a large Rydberg-like molecular orbital, then the 400-600 mμ spectral absorption of Cu_2Cl_3 might be attributed to a similar excitation involving a large Rydberg-like orbital encompassing both copper atoms. The resonance of this electron between the two copper atoms might then account for the stabilization of $E_3^{\prime}$ relative to the corresponding Rydberg state in $CuCl_2^-$.

In simple molecules in the gaseous state, Rydberg transitions generally require high energies ($>\sim 5$e.v.). Although the effect of solvent on Rydberg states has not been thoroughly investigated, this particular mechanism for the stabilization of E_3 does not appear probable since a very large stabilization of E_3 might be required to lower the energy of the Rydberg state, E_3, to 2-3 e.v. above the ground state. (In the case of Cs_2SbCl_6 the Sb(III) and Sb(V) atoms are separated by two chlorine atoms and an excited state stabilization of this type appears even less probable.)

If a strongly stabilized excited state is responsible for the 400-600 mμ spectral absorption of Cu_2Cl_3, then this spectral absorption gives no indication whatever of the contribution of resonance to the stability of the ground electronic state of Cu_2Cl_3.

CONCLUSIONS

The two preceding interpretations of the origin of a low electronic excited state of the complex Cu_2Cl_3 are indeed different from one another in that different assumptions have been made in describing the ground and first excited electronic state. Since each of these qualitative interpretations appears to be consistent with the experimental data, no conclusion can be reached at present as to which interpretation is to be preferred. As stated in the introduction, it is possible that the best description of the ground and first excited electronic states of Cu_2Cl_3 in the 400-600 mμ range is intermediate to the two different descriptions.

The interpretations do have certain points in common which are likely to be important for the appearance of optical interaction between other halogen complexes (in aqueous solutions and in crystalline solids) containing a metallic element in two oxidation states. First, each interpretation makes use of the fact that in Cu_2Cl_3 there are two electronic structures which differ greatly in charge distribution but not in energy. This consideration immediately reduces the probability of observing optical interaction between different elements* in two oxidation states. Interpretation I and the preferred mechanism in Interpretation II require for the transfer of charge from one metallic atom to the other the transfer of charge from and to a chlorine

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* For instance, copper (II) and Ag (I).

ion. It is expected that anions with high ionization potentials in aqueous solutions (e.g., ClO_4^-, F^-) will not serve in this capacity. On the other hand, Br^- and I^- are satisfactory in this respect and it is possible that a study of the spectral absorption of, say, Cu_2Br_3, might permit some decision to be reached as to which of the above interpretations is to be preferred.

It may be mentioned in conclusion that studies should be made of the interaction absorption between non-metallic elements in two oxidation states. It is possible that such studies might shed light on the nature of the interaction between metallic elements in two oxidation states and at the same time lead to interesting semiquantitative results. The I_3^- ion is a case in point.

REFERENCES

Part III

(1) E. Doehlemann and H. Fromherz, Z. physik. Chem. A 171, 371 (1934).

(2) M. v.Stackelberg, Z. Electrochem., 46, 125 (1940).

(3) C. I. Browne, Master's Thesis, California Institute of Technology, 1948.

(4) J. Whitney and N. Davidson, J. Am. Chem. Soc., 69, 2076 (1947); 71, 3809 (1949).

(5) A. A. Noyes and M. Chow, ibid, 40, 746 (1918).

(6) K. Chang and Y. Cha, J. Chinese Chem. Soc., 2, 293 (1934).

(7) G. Bodlander and O. Storbeck, Z. anorg, Chem., 31, 1, 456 (1902).

(8) Náráy-Szábo and Z. Szábo, Z. physik. Chem. A 166, 230 (1933).

(9) N. Birnbaum and S. Edmonds, Ind. Eng. Chem., Anal. Ed., 12, 155 (1940).

(10) L. Pauling-Gilman, Organic Chemistry, Vol. 2, P. 888; K. F. Herzfeld and A. L. Sklar, Rev. Mod. Phys., 14, 294 (1942).

(11) E. R. Rabinowitch, Rev. Mod. Phys., 14, 112 (1942).

(12) E. Teller, Z. physik, 61, 458 (1930).

(13) R. S. Mulliken, J. Am. Chem. Soc., 72, 600 (1950).

PART IV

Spectrophotometric Investigation of the Interaction Between Iron (II) and Iron (III) in Hydrochloric Acid Solutions

Introduction

Optical interaction absorption is observed in hydrochloric acid solutions containing iron in two oxidation states, iron (II) and iron (III). That is, a 5-12 F hydrochloric acid solution containing both iron (II) and (III) exhibits a total light absorption in the 550-800 mμ wavelength range which is markedly greater than the sum of the light absorptions of (a) the complexes containing only iron (II) and (b) the complexes containing only iron (III) present in the solution.

The results of previous investigations[(1),(2)] of optical interaction absorption in hydrochloric acid solutions containing an element (antimony, tin or copper) in two oxidation states suggest that the total light absorption (in the above wavelength range) by a hydrochloric acid solution containing iron (II) and iron (III) is the sum of the light absorption of the complexes containing only iron (II), the light absorption of the complexes containing only iron (III) and the light absorption of certain "interaction complexes", each interaction complex containing one atom of iron (II), one atom of iron (III) and a number of coordinating chloride ligands.

The absorption spectra of the iron (III) chlorocomplexes and the complex $Fe(OH)^{++}$ present in dilute hydrochloric acid solutions containing iron (III) (and no iron (II)) have been determined by Rabinowitch and Stockmayer[3]. The complexes studied by these investigators correspond to the values i = 1,2,3 in the following equilibria:

$$Fe^{+++} + iCl^{-} = FeCl_i^{3-i}$$

$$[FeCl_i^{3-i}]/[Fe^{+++}][Cl^{-}] = K_i \qquad (1)$$

The equilibrium constants K_i of eq. (1), as well as all other equilibrium constants discussed in Part IV, are to be considered as including the activity coefficients of the individual complexes appearing in the thermodynamic equilibrium equations. The square brackets denote concentrations in moles per liter.

The results of the above mentioned investigation[3] may be used to show that in more concentrated hydrochloric acid solutions, 5-12 F, the concentration and light absorption of $Fe(OH)^{++}$ is negligible in comparison to the concentrations and light absorptions of the predominant iron (III) chloro-complexes. It is probable that higher chloro-complexes of iron (III) are present in appreciable concentrations in these 5-12 F hydrochloric acid solutions, corresponding to i = 4,5,6 in eq. (1). Metzler and Myers[4] have suggested that the predominant complex species of iron (III) in 12 F hydrochloric acid is $FeCl_4^{-}$.

There is no information in the literature on the stability or light absorption of iron (II) chloro-complexes. Evidence will be presented later indicating that such chloro-complexes do exist in spectrophotometrically detectable concentrations in 5-12 F hydrochloric acid solutions. The formation equilibria of the probable iron (II) chloro-complexes present in these solutions are represented below:

$$Fe^{++} + iCl^- = FeCl_i^{2-i}$$

$$[FeCl_i^{2-i}]/[Fe^{++}][Cl^-]^i = M_i \qquad (2)$$

The following equations are used to represent the formation of the interaction complexes described above:

$$Fe^{+++} + Fe^{++} + iCl^- = Fe_2Cl_i^{5-i}$$

$$\frac{[Fe_2Cl_i^{5-i}]}{[Fe^{+++}][Fe^{++}][Cl^-]^i} = L_i \qquad (3)$$

The purpose of Part IV is to show that, in so far as the validity of eqs. (1), (2) and (3) may be tested spectrophotometrically in concentrated solutions, the complexes formed in these reactions are sufficient to account for the total light absorption of hydrochloric acid solutions containing both iron (II) and (III).

It is readily shown that the optical density, D(II,III), of a solution containing only the complexes formed in the equilibria of eqs. (1), (2) and (3) is given by eq. (4):

$$D(II,III) = (a-c)\,\epsilon_{III} + (b-c)\,\epsilon_{II} + (a-c)(b-c)\,k \qquad (4)$$

In this equation, a is the formal concentration of iron (III), b is the formal concentration of iron (II) and c is the <u>total</u> concentration of the interaction complexes of eq. (3). The quantities ϵ_{II} and ϵ_{III} are the formal extinction coefficients of iron (II) and (III) respectively, and are concentration averages (for a particular solution) of the extinction coefficients of the individual complexes of eqs. (1) and (2); k is a function of the equilibrium constants of eqs. (1), (2) and (3), the extinction coefficients of the interaction complexes, and the free chloride ion concentration.

Previous investigations of optical interaction absorption have always shown that the total concentration of the interaction complexes is negligible in comparison to the formal concentration of either of the oxidation states of the element. With this approximation, eq. (4) simplifies to eq. (5).

$$D(II,III) = a\epsilon_{III} + b\epsilon_{II} + a\ b\ k \qquad (5)$$

In eq. (5) $a\epsilon_{III}$, $b\epsilon_{II}$, and abk are the contributions to the total optical density by the iron (III) chloro-complexes and Fe^{+++}, the iron (II) chloro-complexes and Fe^{++}, and the interaction complexes, respectively. The term abk will be called the optical density of interaction absorption, or briefly, the optical interaction absorption.

Materials and Proceedures

Hydrochloric acid solutions containing iron (III) were prepared by slowly dissolving anhydrous ferric chloride in hydrochloric acid of the desired formality. It was assumed that the change of the hydrochloric acid formality was negligible. The iron (III) concentration was determined by reduction to the ferrous state with amalgamated zinc and titration with standard potassium permanganate solution, using the Zimmerman Reinhardt procedure. Hydrochloric acid solutions containing both iron (II) and (III) were prepared by washing crystals of $FeCl_2 \cdot 4H_2O$ with hydrochloric acid and then dissolving the crystals in hydrochloric acid solutions containing iron (III). The iron (II) concentration was determined with standard potassium permanganate solution and the total iron concentration was determined as above. Solutions containing manganese (II) and iron (III) were prepared by dissolving weighed samples of crystalline $MnCl_2 \cdot 4H_2O$ in 12 F hydrochloric acid solutions containing iron (III). The crystals of $MnCl_2 \cdot 4H_2O$ were analyzed by the method of Lingane and Karplus(5) to insure that the water of hydration corresponded to this formula. Weighed crystalline samples of $MgCl_2 \cdot 6\ H_2O$ were dried at 85° (decomp. temp. 117°) for a period of thirty minutes. Zinc chloride solutions were prepared from fused zinc chloride. Hydrochloric acid solutions containing only iron (II) were prepared by dissolving powdered iron metal in hydrochloric acid of known formality, and then filtering the solution through a fine sintered glass funnel. The operations of dissolving the iron, filtering the solution and measuring volumetric samples were all performed in the same closed air-free apparatus, which was completely flushed with carbon dioxide. Titrations of iron (II) were performed in a carbon dioxide atmosphere. Hydrochloric acid concentrations were determined by titration with standard sodium hydroxide solution to the methyl orange end point.

Absorption spectra were measured with the Model DU Beckmann Spectrophotometer. All the absorption data except those given in Figs. 14, 15, and 18 were obtained with one centimeter light paths. The absorption data of Fig. 13 were determined with 0.10, 0.03 and 0.01 cm. light paths obtained with calibrated quartz spacers placed in a quartz cell of 1.00 $\pm$ 0.002 cm. light path. Some of the data of Figs. 15 and 18 were determined with a 10.0 cm. light path.

Results and Discussion

Fig. 12 illustrates the effect of added ferrous chloride, manganous chloride, and zinc chloride, and magnesium chloride on the absorption spectrum of a solution of ferric chloride in 12 F hydrochloric acid. Since solutions of $FeCl_2$ are essentially colorless in this wavelength range, there is clearly a marked specific effect of this substance on the absorption spectrum of the iron (III). The much smaller effect (7% changes in the optical density) of $ZnCl_2$, $MnCl_2$, and $MgCl_2$ on the absorption spectrum of iron (III) may be due to the chloride ions furnished by these salts, and may also be due to changes of activity coefficients and other effects. The effect of these three salts in depressing the absorption of iron (III) in 12 F hydrochloric

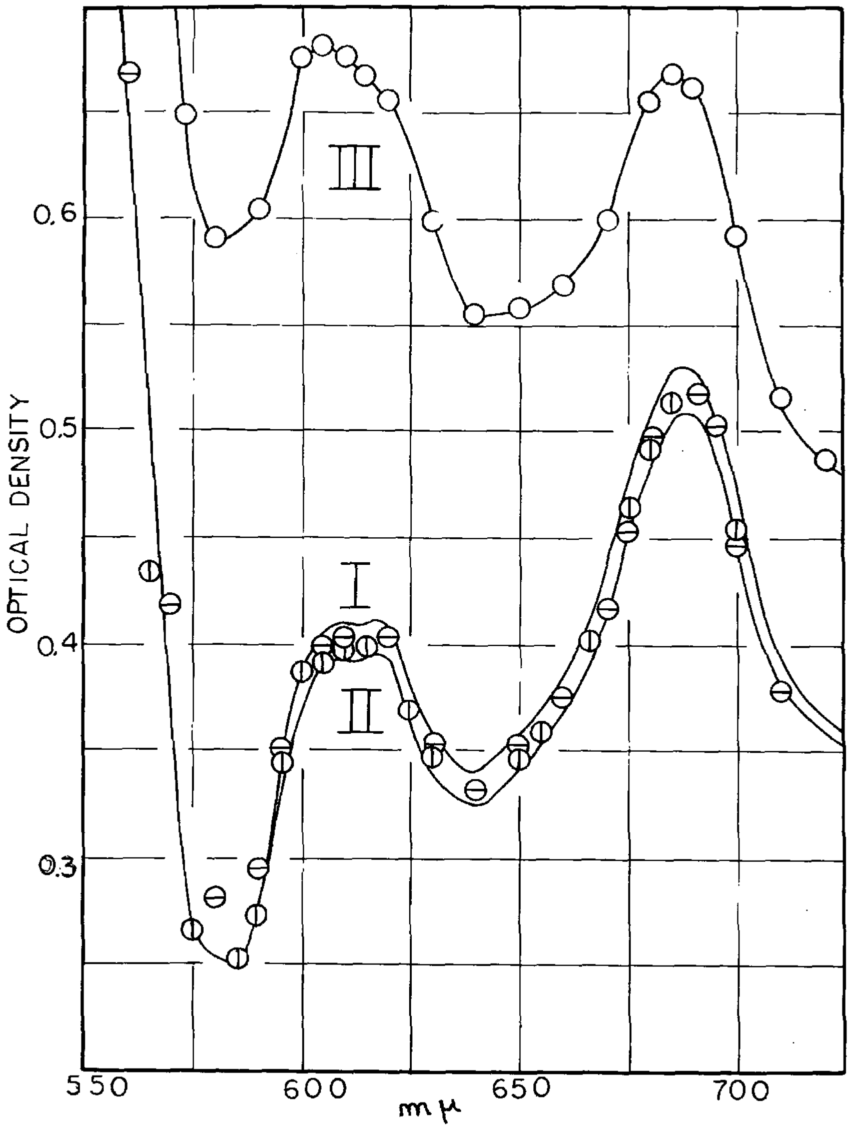

Fig. 12 Effects of several salts on the absorption spectrum of iron (III) in 12 F hydrochloric acid; curve I, 0.88 F $FeCl_3$, no added salt; curve II, 0.88 F $FeCl_3$, 0.13 F $MgCl_2$; points , 0.88 F $FeCl_3$, 0.13 F $MnCl_2$; points , 0.88 F $FeCl_3$, 0.13 F $ZnCl_2$; curve III, 0.88 F $FeCl_3$, 0.13 F $FeCl_2$.

acid is similar to the effect of increasing hydrochloric acid concentration in depressing the iron (III) absorption for total hydrochloric acid concentrations above 8 F.[3] To evaluate the specific interaction absorption between iron (II) and (III), we assume (a) that there is a non-specific effect of $FeCl_2$ on the $a\epsilon_{III}$ term of eq. (5) and (b) that the magnitude of this non-specific effect may be estimated from the observed effect of $MnCl_2$ or $MgCl_2$ on the $a\epsilon_{III}$ term. This correction is especially important at shorter wavelengths, 450-550 mμ. (It may be remarked that in the concentration and wavelength ranges studied, $MnCl_2$ in hydrochloric acid is effectively colorless.)

Figure 13 is a plot of the values of the interaction function, k, calculated from the data of Fig. 12 using eq. (5). The figure also exhibits values of k obtained from a series of measurements on 12 F hydrochloric acid solutions containing concentrations of iron (III), iron (II), manganese (II) and magnesium (II) which were one-half the values used for Fig. 12. The agreement between these two sets of data demonstrates the validity of eq. (5) for the concentrations and wavelengths employed. The small values of k prevented an experimental confirmation of eq. (5) for lower concentrations of iron (II) and (III). As the solutions were practically saturated with $FeCl_3$ and $FeCl_2$,

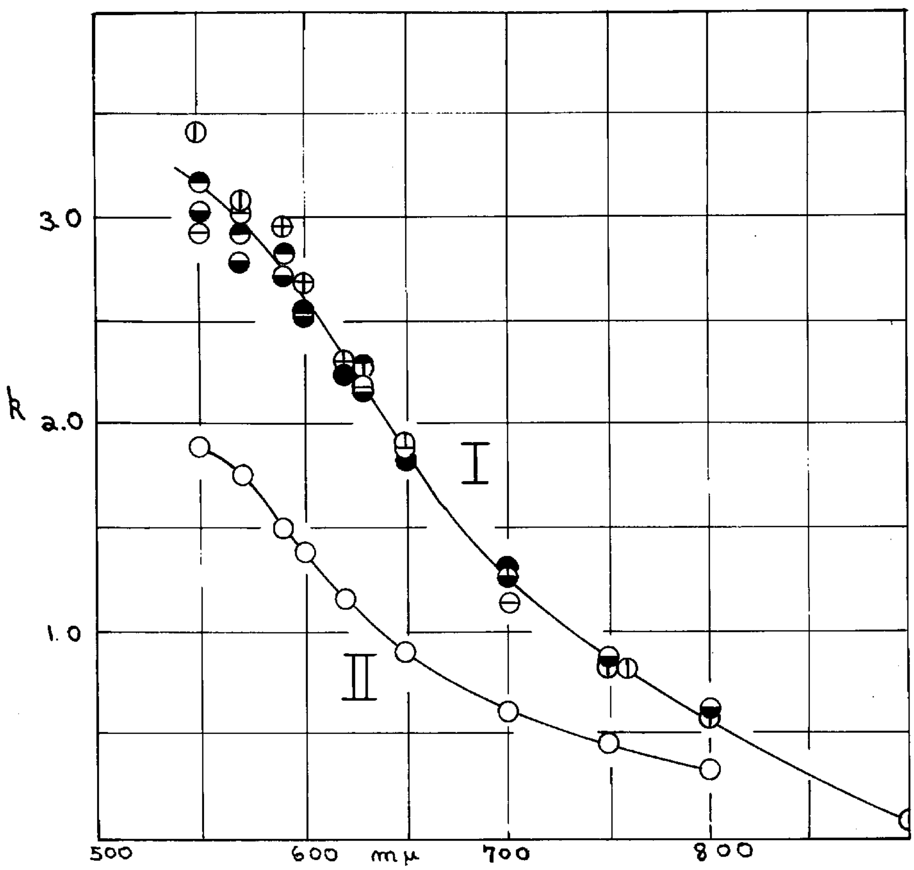

Fig. 13 Dependence of k on wavelength and hydrochloric acid concentration: I, 12 F HCl solutions. Points ◐ and ⊖ of the figure calculated from the data of Fig. 1, using magnesium and manganese corrections, respectively; points ◒ and ◓ , solutions of Fig. 1, diluted by a factor of two, magnesium and manganese corrections, respectively. II, 5.0 F HCl solutions, data of Fig. 5 (ordinates, k x 10).

it was impossible to employ higher concentrations. However it is likely that eq. (5) is generally applicable to solutions containing ferrous and ferric iron as equations of this form have been found to be valid over wide concentration ranges of the two oxidation states of other elements which exhibit optical interaction. The data of Fig. 13 show that the values of k calculated from the optical densities of solutions in which iron (II) was replaced by manganese (II) agree within about 10% with the values of k calculated from the optical densities of solutions in which magnesium (II) replaced iron (II).

An attempt was made to determine the interaction absorption at shorter wavelengths, 450-555 mμ, by employing short light paths. The results are shown in Fig. 14. The optical density of interaction absorption is small compared to the large optical densities due to the iron (III) chloro-complexes in this wavelength range. Furthermore, the difference between the optical densities of an iron (III), magnesium (II) mixture and an iron (III), manganese (II) mixture is of the same order of magnitude as the difference between the optical densities of an iron (III), iron (II) mixture and an iron (III), manganese (II) mixture. The values of the interaction absorption function, k, are therefore quite different depending on whether mixtures of iron (III) with manganese (II) or with magnesium (II) are used to determine the iron (III) absorption; it is

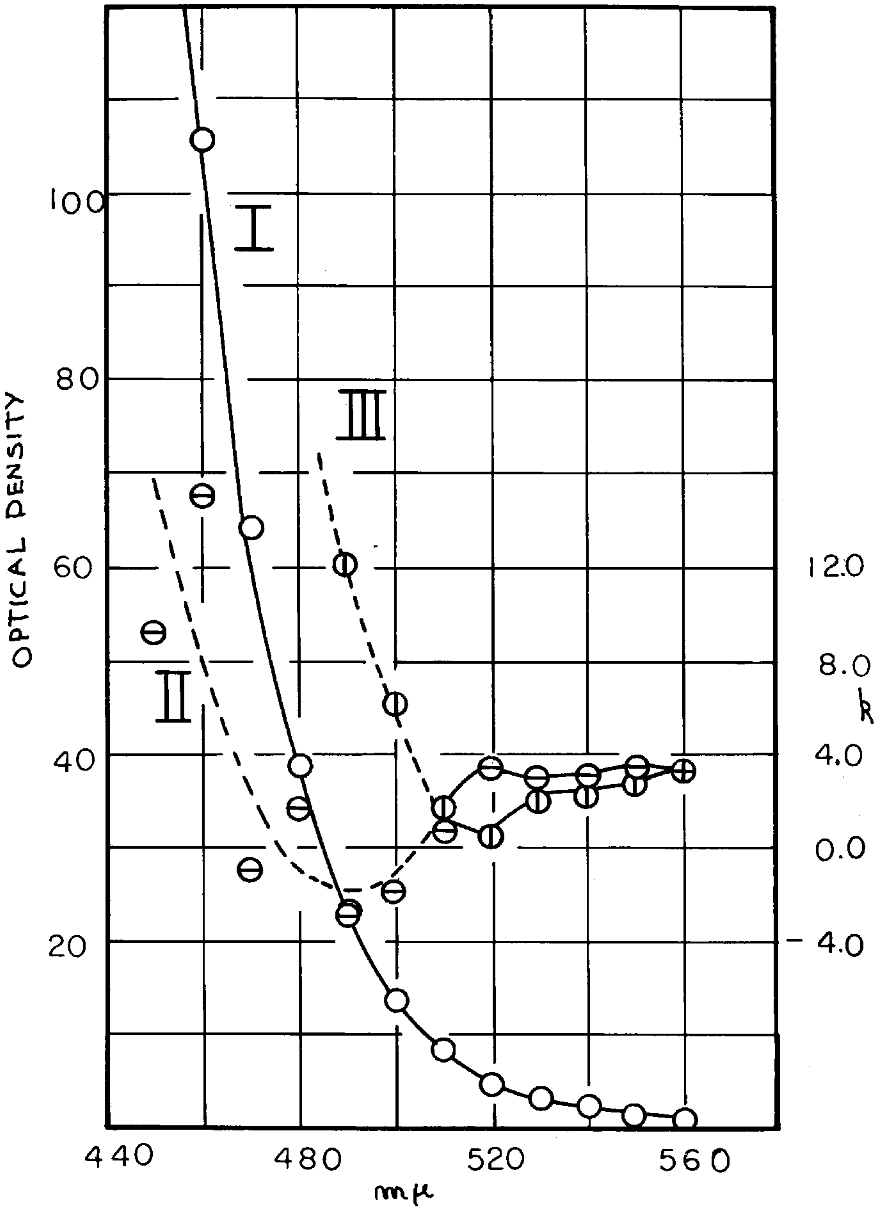

Fig. 14 Optical interaction in the 460-560 mμ range: I, optical density, D (referred to a 1.00 cm. light path), of 0.88 F $FeCl_3$ in 12 F HCl and containing 0.13 F $MgCl_2$. II, III, values of k calculated using magnesium (II) and manganese (II) corrections, respectively. Concentrations identical with those of Fig. 1. (Curves are dashed in regions of large probable error.)

not even possible to say with certainty whether the interaction absorption in this range is greater or less than in the 550-700 mμ range.

Figure 15 gives the optical densities, D(II,III), $a\epsilon_{III}$, and $b\epsilon_{II}$, measured with the Beckmann Spectrophotometer from 720 to 1,000 mμ. As shown in Fig. 13, the interaction absorption is observed to decrease continuously with increasing wavelength. At 920 mμ, the optical interaction absorption is equal to zero within the experimental error of 5%; that is, $k \approx 0$. At wavelengths greater than 920 mμ, k was found to be zero within the experimental error; however, the high intensity of scattered light in the spectrophotometer at these wavelengths makes this conclusion uncertain.

Figure 16 gives the data used in the determination of optical interaction absorption in 5 F hydrochloric acid solutions. The optical interaction absorption in 5 F hydrochloric acid solutions is not sufficiently intense to allow an experimental verification of eq. (5). Assuming eq. (5) to hold for these solutions values of k have been calculated from the data of Fig. 16 and are plotted in Fig. 13. It may be seen from Fig. 13 that k decreases (by a factor of approximately 20) when the hydrochloric acid concentration is decreased from 12 to 5 F.

Figure 17 shows the absorption spectra of solutions containing $Fe(ClO_4)_2$ and $Fe(ClO_4)_3$ in 4 F perchloric

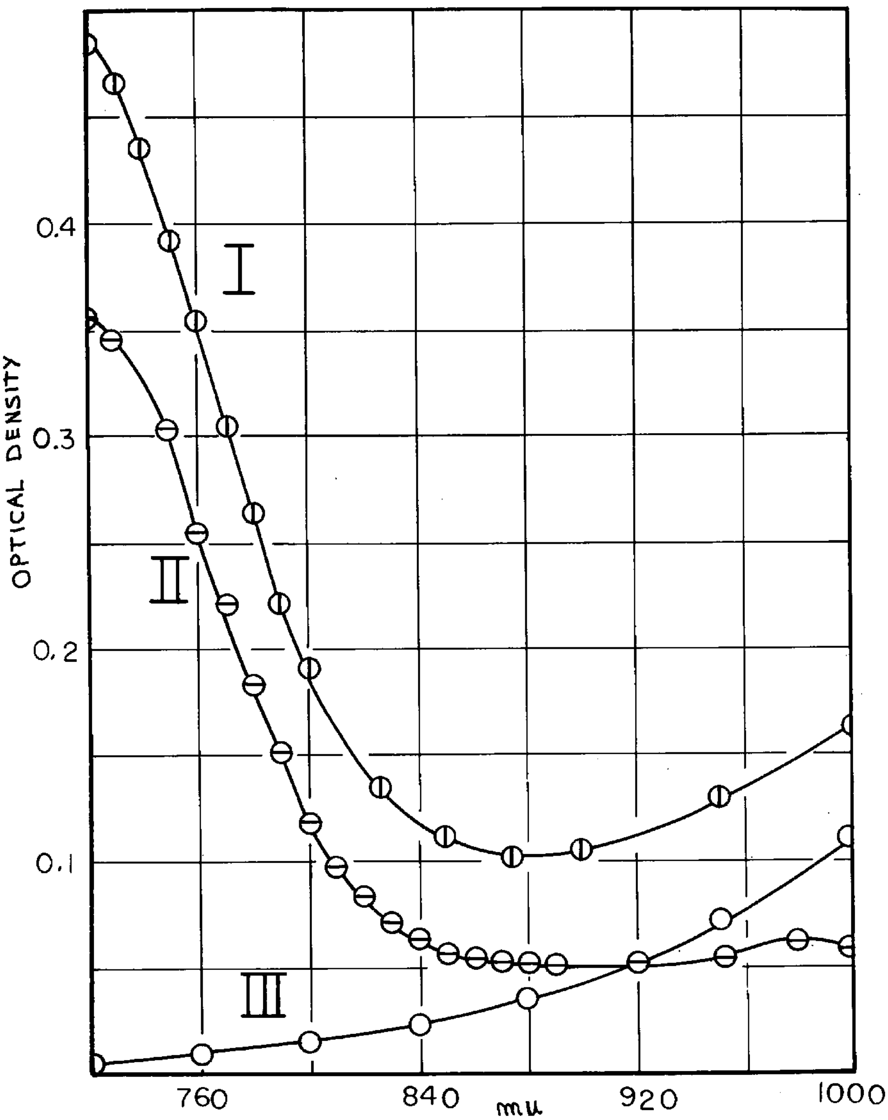

Fig. 15 Optical densities of 12 F hydrochloric solutions containing I, 0.88 F iron (III) and 0.13 F iron (II); II, 0.88 F iron (III) and 0.13 F magnesium (II); III, 0.13 F iron (II).

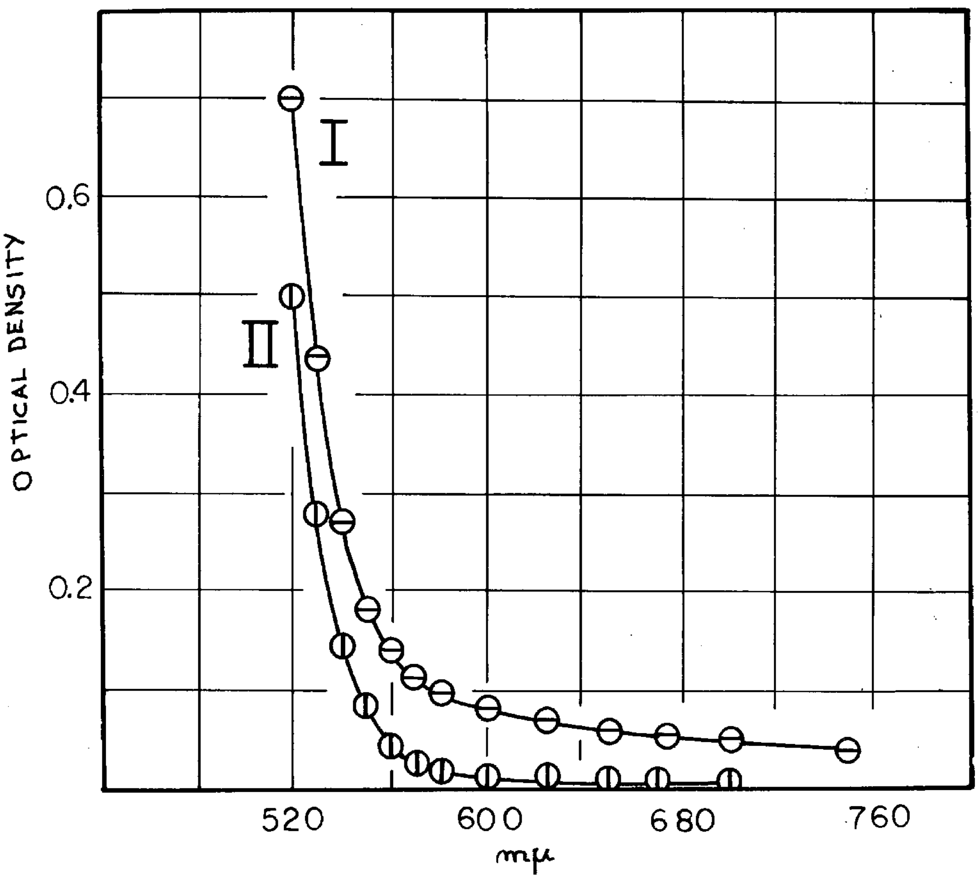

Fig. 16 Optical densities of 5 F hydrochloric acid solutions containing I, 0.68 F iron (III), 0.71 F iron (II); II, 0.68 F iron (II), 0.71 F magnesium (II). (The light absorption by iron (II), not shown in the figure, is important at wavelengths above 625 mμ and has been taken into account in calculating k for these wavelengths.)

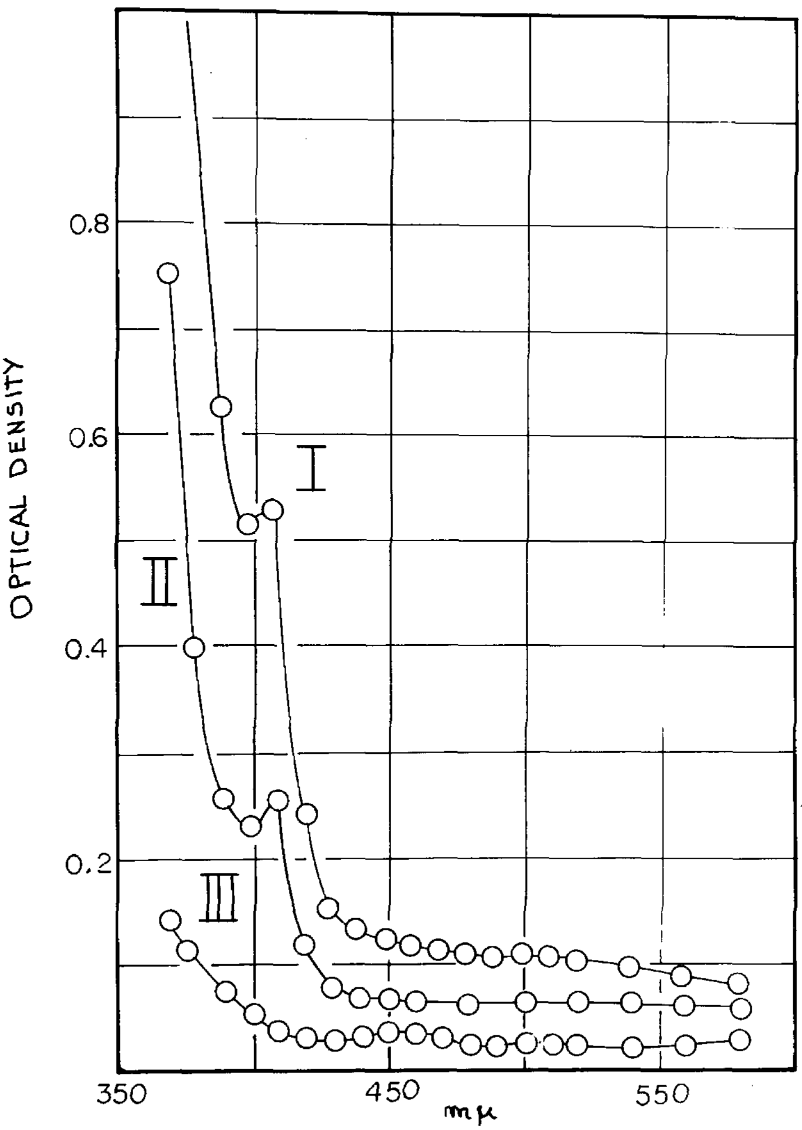

Fig. 17 Optical densities of 4.0 F perchloric acid containing: I, 1.08 F $Fe(ClO_4)_3$, II, 0.54 F $Fe(ClO_4)_3$, 0.54 F $Fe(ClO_4)_2$; III, 1.08 F $Fe(ClO_4)_2$.

acid.* In these solutions the values of k (eq. (5)) are calculated to be 0 $\pm$ 0.05 and we may infer that the interaction absorption between $Fe(H_2O)_6^{++}$ and $Fe(H_2O)_6^{+++}$ is much less than that between the chloro-complexes of these ions.

Before discussing the significance of these results, evidence will be presented for the formation of chloro-complexes of iron (II) in hydrochloric acid solutions. Figure 18 gives the extinction coefficients of iron (II) in the 750-950 mμ range for several hydrochloric acid concentrations. The effect of increasing hydrochloric acid concentration in depressing the formal extinction coefficient of iron (II) might be interpreted as being due either to the formation of chloro-complexes or to a change in the hydrolysis of the Fe^{++} ion. The latter possibility is ruled out because the hydrolysis of the Fe^{++} ion in the strongly acid solutions of Fig. 18 must be extremely small ($Fe(OH)_2$ is precipitated at a relatively high pH, 7-8). Since the extinction coefficients of simple complex ions in the wavelength range of Fig. 18 never reach the large values characteristic of their "electron transfer" spectra at shorter wavelengths,[6] very small concentrations of $Fe(OH)^+$ cannot be responsible for the light absorption. An extension of the curves of Fig. 18 to shorter wavelengths shows that the concentration of iron (III) in these solutions is

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* The data of Fig. 16 were taken by Mr. Wendell Miller.

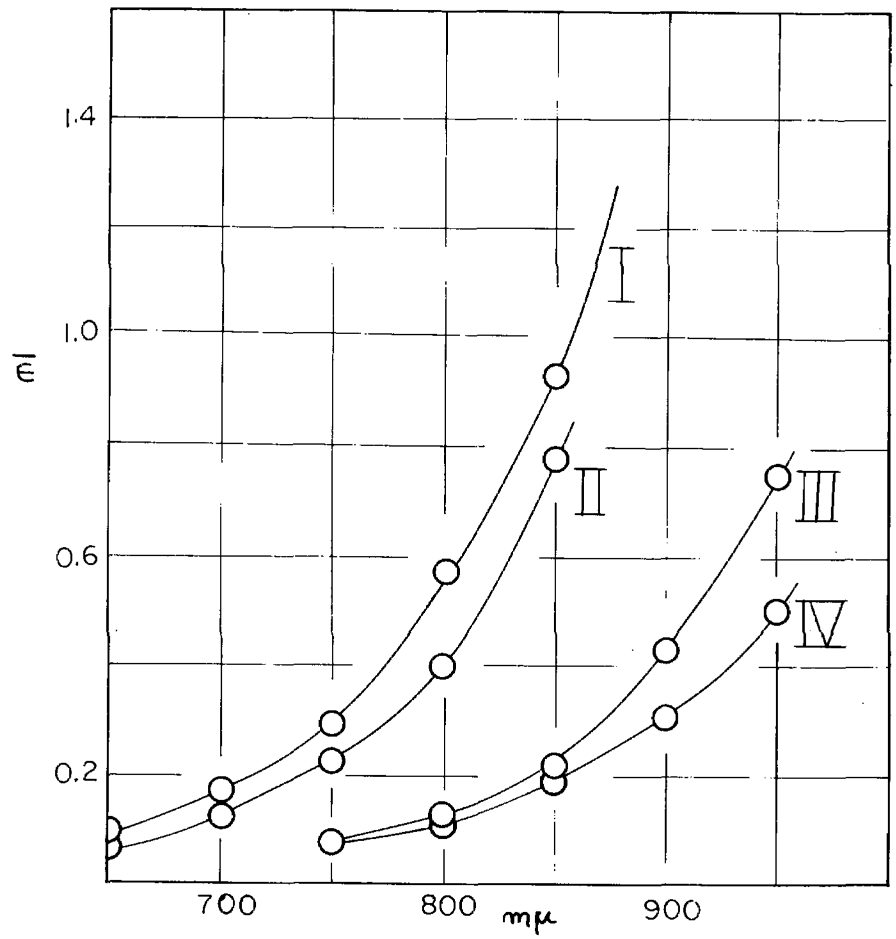


Fig. 18 Dependence of the formal extinction coefficient of iron (II), $\bar{\epsilon}$, in hydrochloric acid concentration: I, 4.1 F HCl, 0.31 F $FeCl_2$; II, 5.0 F HCl, 1.42 F $FeCl_2$; III, 10.4 F HCl, 0.29 F $FeCl_2$; IV, 12 F HCl, 0.08 F $FeCl_2$.

less than 10^{-4} F. As the extinction coefficients of iron (III) in hydrochloric acid solutions are small in the 700-900 mμ range (Fig. 16), there is no appreciable error in these curves due to absorption by iron (III).

The fact that the optical interaction constant, k, of eq. (5), for the interaction between the chloro-complexes of iron (II) and (III) decreases with decreasing hydrochloric acid concentration may be due to one or both of the following factors. Due to both mass action and activity effects, the concentrations of the absorbing interaction complexes may be increased by increasing the hydrochloric acid concentration. Furthermore it is to be expected that of the various interaction complexes formed, those having a larger number of chloride ligands will be the more strongly colored in the long wavelength part of the absorption spectrum. This is similar to the shift of the "electron transfer" spectra of complexes containing a single cation to longer wavelengths as the number of chloride ligands is increased.[6] The effect of hydrochloric acid in increasing the interaction constant, k, has been observed for all the cases of interaction absorption which have been studied to date, viz., Sb(III,V), Sn(II,IV), Cu(I,II) and Fe(II,III).

Finally, we may survey the occurrence of interaction absorption in systems containing iron (II) and (III). Besides the case studied here, there appears to be interaction absorption in the solid ferro-ferricyanides, in

Fe_3O_4, in freshly precipitated mixtures of $Fe(OH)_2$ and $Fe(OH)_3$ and in numerous minerals containing iron (II) and iron (III), e.g., biotite and tourmaline.[7] As mentioned above $Fe(H_2O)_6^{++}$ and $Fe(H_2O)_6^{+++}$ do not interact in perchloric acid solution. Mr. J. A. Ibers of these Laboratories has observed no interaction absorption in mixed solutions of $Fe(CN)_6^{\equiv}$ and $Fe(CN)_6^{\equiv}$. The absence of interaction absorption in these cases may be attributed to an electrostatic factor, namely that the two ions of like charge cannot approach each other closely enough to interact. It is suggested, however, that direct chemical bridging of a ligand between the two iron atoms is important for the occurrence of interaction absorption. The ferri-ferrocyanides contain the bridged structure, Fe-C = N:Fe, in which each iron has some plus 2 and some plus 3 character. In Fe_3O_4 there is an $O^=$ bridge between the two kinds of iron atoms. It is not unreasonable then to suggest that the interaction complexes in hydrochloric acid solution contain a halogen bridge between the iron (II) and iron (III) atoms. In this connection it is of value to have established that iron (II) can be coordinated by chloride. Similarly one might expect interaction absorption to occur in mixed solutions of $Fe(ClO_4)_2$ and $Fe(ClO_4)_3$ which are less acid than those studied here. In solutions in which Fe^{+++} is hydrolyzed to $Fe(OH)^{++}$ there might be a dimer of iron (II) and iron (III) containing hydroxyl bridges. Finally it should be remarked that there is one case of interaction absorption where there is evidence that there is not a direct bridge of the type discussed above. The intensely black salts of the type Cs_2SbCl_6 have been found to have a structure in which each antimony ion is surrounded by an octahedron of chlorides and each chloride ion is coordinated to only one antimony ion.[8]

REFERENCES

Part IV

(1) J. Whitney and N. Davidson, J. Am. Chem. Soc., 71, 3809 (1949).

(2) H. McConnell and N. Davidson, ibid., 72 (1950).

(3) E. Rabinowitch and W. Stockmayer, ibid., 64, 335 (1942).

(4) D. E. Metzler and R. J. Meyers, ibid., 72, (1950).

(5) J. Lingane and R. Karplus, Ind. Eng. Chem., Anal. Ed., 18, 191 (1946).

(6) E. R. Rabinowitch, Rev. Mod. Phys., 14, 112 (1942).

(7) L. Pauling, Chem. Eng. News, 25, 2970 (1947).

(8) L. A. Jensen, Z. anorg. Chem., 252, 317 (1944).

Propositions Submitted by Harden McConnell

Ph.D. Oral Examination, July 7, 1950, 9:00 A.M. Crellin Conference Room
Committee: Professors Davidson(Ch.), Bates, Epstein, Kirkwood, Lucas and Pauling.

1. In discussing the life-time of a triplet electronic state (^3F, 30,000 cm.$^{-1}$) of aliphatic ketones, D.S. McClure has taken the radial spin-orbit-interaction integral of oxygen(I) to approximate the exchange integral between this triplet state (^3F) and a singlet state (^1Z, 51,000 cm.$^{-1}$) of the carbonyl group. It is proposed that: (a) The ^3F state may have the approximate symmetry $A_2(C_{2v})$. (b) The atomic orbital description of the ^1Z state (approximate symmetry, $B_2(C_{2v})$) given by McMurry, together with a reasonable atomic orbital description of the ^3F state, may be used to estimate the angular factors of the spin-orbit exchange integral between the ^3F and ^1Z states. The inclusion of this angular factor may reduce the discrepancy between the calculated and observed life-time of the ^3F state.

D.S. McClure, J.Chem.Phys., 17, 905(1947)
H. McMurry, ibid, 9, 231(1941)

2.(a) It is proposed that the photoconductive Hall-effect in alkali halides containing F centers may be detectable by the use of a pulsed light source and a space charge effect without the use of magnetic fields in excess of 20,000 gauss. The application of conventional techniques in the investigation of the Hall-effect in such crystals appears to be rather unsatisfactory. For example, see J. Evans, Phys. Rev., 57, 47(1940).

(b) It would be interesting to investigate the photoconductive properties of crystals containing a metallic element in two oxidation states.

3.(a) It is proposed that the energy separation of two electronic states of a diatomic molecule may sometimes be estimated by the difference of the valence state energies of the atoms composing the molecule in the two electronic states. Calculations have yielded the following results in the case of the NH molecule.

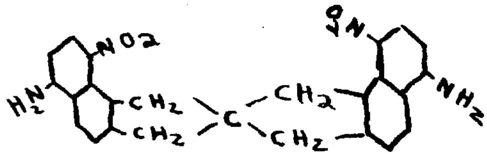
Electronic State	Calculated Separation	Observed Separation
$A^3\Sigma^-, a^1\Delta$	1.19 or 1.59 e.v.	1.09 e.v.
$B^3\Pi, b^1\Pi$	1.73 or 1.91 e.v.	1.21 e.v.

These calculations are based on observed and extrapolated term values for the electronic states of the nitrogen atom.

3.(b) A slight modification of Pauling's calculation of the separation of the $^3\Sigma_g^-$ and $^1\Sigma_g^+$ electronic states of the oxygen molecule is proposed.

L. Pauling, Z. Naturforschg., 3A, 438(1948)

4. It is proposed that the optical rotation of certain organic dye-like substances be examined both experimentally and theoretically. It is possible that the theoretical investigation of the optical rotation of such molecules may lead to unambiguous assignments of absolute configurations. The following compound may be of interest in this connection.



An application of Born's classical theory suggests that the above molecule is dextro-rotatory ($\lambda \approx$ 6,000 Å) when the left hand NH_2-NO_2 group is above the plane of the paper and the right-hand NH_2-NO_2 group lies in the plane of the paper.

5. The conclusions reached by Hume and Kingery as to the stability constants and absorption spectra of bismuth thiocyanate complexes in aqueous solution are open to serious question with respect to two points: (a) The experimental values for the equilibrium constants,

$$K_n = \frac{[Bi(SCN)_n^{3-n}]}{[Bi^{+++}][SCN^-]^n}, \quad n = 1, 2, 4, 6,$$

are not consistant with the data given in their publication. (b) The asserted negligible concentration of $Bi(SCN)_3$ in solutions containing $Bi(SCN)_2^+$ and $Bi(SCN)_4^-$ and the negligible concentration of $Bi(SCN)_5^{=}$ in solutions containing $Bi(SCN)_4^-$ and $Bi(SCN)_6^{\equiv}$ is rather unusual in that investigations of other cation-anion complex systems have generally indicated the existence of all complexes intermediate to the "mono" and "saturated" complexes.

It is proposed that the bismuth-thiocyanate complex equilibria be reinvestigated.

Wm. Kingery and D. Hume, J.Am.Chem.Soc., 71, 2393(1949)

6. The interpretation of the "anomalous" 295 mμ absorption band of α-phenyl ketones given by Alpen, Kumler and Strait appears to be unreasonable. A more reasonable interpretation is proposed.

Alpen, Kumler and Strait, J.Am.Chem.Soc., 72(in press)

7.(a) The structure of the IF_5 molecule is not known. On the basis of an infra-red and Raman investigation, R.C. Lord <u>et al</u>. have concluded that this molecule has the symmetry C_{4v}. On the basis of an electron diffraction investigation, V. Schomaker <u>et al</u>. have concluded that this molecule does not have the symmetry C_{4v}. It is proposed that the micro-wave absorption spectrum of IF_5 be determined so as to test the conclusions of Lord <u>et al</u>.

R.C. Lord <u>et al</u>., J.Am.Chem.Soc., <u>72</u>, 522(1950)
Schomaker <u>et al</u>., Abstracts, Atlantic City meeting, American Chemical Society, April, 1947

(b) It is proposed that under certain conditions the phosphorous - hydrogen interatomic distance in $HPO_3^{=}$ can be determined by nuclear magnetic resonance methods.

8.(a) It is proposed that the effect of solvation on the "charge resonance" spectra of certain molecules be investigated. It is possible that the charge resonance spectra of certain symmetrical ions (e.g., I_3^- , NO_3^-) in aqueous solution are not greatly modified by solvation and that an adequate interpretation of these spectra can be given.

(b) R.S. Mulliken and N. Bayliss have used completely different models in their interpretations of the absorption spectrum of iodine in benzene solution. It is proposed that the model used by Mulliken is superior.

R.S. Mulliken, J.Am.Chem.Soc., <u>72</u>, 600(1950)
N. Bayliss, J.Chem.Phys., <u>18</u>, 292(1950)

9. Two alternative interpretations of the absorption spectrum of Cu_2Cl_3 are proposed. One interpretation is analogous to that used for the cyanine dyes. The second interpretation is based on an analogy with the electronic states of the hydrogen molecule ion.

This Thesis, Part III-B

10. It is possible that an interesting chemical reaction occurs when solid sulfur, carbon disulfide and liquid nitrogen dioxide are mixed.